ASSESSMENT OF BIOCHAR NUTRIENT COMPOSITION PYROLYZED AT DIFFERENT TEMPERATURES FOR IMPROVEMENT OF PADDY SOIL AVAILABLE SILICON

（水田土壌中可給性ケイ素の改善に向けた異なる温度で炭化されたバイオ炭の養分組成の評価）

NWAJIAKU IFEOMA MONICA

2019

THE UNITED GRADUATE SCHOOL OF AGRICULTURAL SCIENCES,
TOTTORI UNIVERSITY

THE UNITED GRADUATE SCHOOL OF AGRICULTURAL SCIENCES
TOTTORI UNIVERSITY

ASSESSMENT OF BIOCHAR NUTRIENT COMPOSITION PYROLYZED AT DIFFERENT TEMPERATURES FOR IMPROVEMENT OF PADDY SOIL AVAILABLE SILICON

DOCTORAL THESIS

BY

NWAJIAKU IFEOMA MONICA

(D16A4004H)

In Partial Fulfillment of the Requirement for the Award of the Degree of

DOCTOR OF PHILOSOPHY

COURSE OF GLOBAL ARID LAND SCIENCE
THE UNITED GRADUATE SCHOOL OF AGRICULTURAL SCIENCES,
TOTTORI UNIVERSITY

2019

THE UNITED GRADUATE SCHOOL OF AGRICULTURAL SCIENCES,
TOTTORI UNIVERSITY

ASSESSMENT OF BIOCHAR NUTRIENT COMPOSITION PYROLYZED AT DIFFERENT TEMPERATURES FOR IMPROVEMENT OF PADDY SOIL AVAILABLE SILICON

（水田土壌中可給性ケイ素の改善に向けた異なる温度で炭化されたバイオ炭の養分組成の評価）

NWAJIAKU IFEOMA MONICA

MARCH

2019

Approval Sheet

This thesis enclosed herewith, "ASSESSMENT OF BIOCHAR NUTRIENT COMPOSITION PYROLYZED AT DIFFERENT TEMPERATURES FOR IMPROVEMENT OF PADDY SOIL AVAILABLE SILICON" prepared and submitted by NWAJIAKU Ifeoma Monica in partial fulfillment of the requirement for the award of Doctor of Philosophy is hereby approved as to style and contents.

By

Professor Tsugiyuki MASUNAGA

(Academic Supervisor and Chairman of Examination Committee)

FACULTY OF LIFE AND ENVIRONMENTAL SCIENCE,
SHIMANE UNIVERSITY,
JAPAN

Acknowledgement

I express my gratitude to my supervisor Prof. Tsugiyuki MASUNAGA for his guidance and patience during this process. His encouragement and support made me achieve more than I thought possible and I immensely appreciate him. I also wish to extend my appreciation to my co-supervisor Dr. Kuniaki SATO who provided great assistance in the experimentation and useful suggestions and advice on this thesis and manuscripts as well.

I am grateful to the financial support from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and for funding this project. My thanks also to the Meiwa Co. Company, Kanazawa, Japan for providing and processing the material for this research. I am indeed grateful for their contribution.

I extend my heartfelt gratitude to Dr. Sunday Obalum for his recommendation and his great support for my study.

My gratitude to all my colleagues in laboratory of Soil and Ecological Engineering, Shimane University, Japan for providing a good atmosphere for learning and useful discussion during the period of my study.

Most importantly, I thank my beloved husband, Nnawugwu Nwawuike and my son Chidiuto Akachukwudinandum Nwawuike, who have been my source of joy throughout the duration of this study. Your understanding and intellectual contributions were instrumental to the completion of this project. I appreciate my parent late Francis Ezenwa Nwajiaku and Anastasia Iheakanwa Nwajiaku and to my siblings for their support, prayers and encouragement throughout my academics life in Japan.

Above all, I thank God, the most benevolent for making this accomplishment possible.

Nwa jiaku Ifeoma Monica

Abstract

Increasing production in agriculture and management of waste generated from agriculture are two interrelated problems facing the agricultural sector. To manage these problems, conversion of agricultural waste into biochar for soil fertility improvement is a practical solution. In this work, chemical composition of biochar produced from rice husk and sugarcane bagasse, two predominant waste commonly generated from agriculture were studied. These wastes were pyrolyzed at 300 – 700°C and 350 – 700°C for rice husk biochar (RHB) and sugarcane bagasse biochar (SBB) respectively. A pot experiment was conducted in an experimental glasshouse to investigate how change in nutrient composition of rice husk (pyrolyzed at 300°C – 700°C) one of the agricultural wastes with high soil amendment potential could influence rice plant agronomic parameters, soil available silicon and plant silicon uptake. Also, another pot experiment was conducted to investigate the effect rice husk biochar (RHB) and sugarcane bagasse biochar (SBB) on improving the soil fertility status as well as rice plant nutrient uptake. The experimental units were replicated three times and arranged in a complete randomized design. The result of the biochar pyrolysis showed that biochar yield and total nitrogen decreased with increasing pyrolysis temperature while ash content, pH, EC, total carbon, extractable Ca, Mg, Na, available phosphorus and silica were increased. In RHB, extractable K showed increase with increasing pyrolysis temperature, while in SBB it decreased with its maximum observed in RHB at 700°C. The pot experiment indicated that the RHB and SBB treatments did not have much influence on the plant agronomic parameters evaluated in this experiment. The result obtained from post harvest soil available silicon analysis with RHB treatments revealed that the soil available silicon could be improved or at least be maintained with RHB treatments. RHB at 400°C significantly ($p < 0.05$) increased the soil available silicon by 61% compared to the original content (93.8 mg SiO_2 pot^{-1}) of the used soil. The RHB treatments increased soil Si availability for rice growth through the increment of plant Si uptake and soil available Si against the control. The highest increment against the control during the cropping season was found on pot amended with RHB at 500ºC (455.9 mg SiO_2 pot^{-1}). Subsequently from the pot experiment, it was observed that the addition of RHB and SBB can improve nutrient uptake but in relation to pyrolysis temperature no specific trend was observed. Finally, in this study it could be concluded that RHB pyrolyzed at high temperature may produce nutrient rich biochar with high nutrient content which can ameliorate acidic soils. In relation to available silicon, this study supports the application of RHB as Si releasing agent to increase plant available Si in the soil and thus, improve rice plant health.

TABLE OF CONTENTS

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

CHAPTER 6

LIST OF TABLES

CHAPTER 2

CHAPTER 3

CHAPTER 4

CHAPTER 5

LIST OF FIGURES

CHAPTER 1

CHAPTER 2

CHAPTER 3

CHAPTER 4

Chapter 1

General Introduction

1.1 Current situation of rice production in Sub-Saharan African

Rice is the most important staple food because it supports more than half of the world's population (Muthayya et al. 2014). In Sub Saharan Africa (SSA), it constitutes a major part of the diet (FAO, 1996). In the past three decades, rice demand in SSA has consistently increased due to population growth (4% per annum), rising income and a shift in consumer preferences in favor of rice, especially in urban areas (Sohl, 2005; Balasubramanian et al., 2007). Rice production in SSA between the years 2001 – 2005 expanded at the rate of 6% per annum. However, 70% of the production increase was mainly due to land expansion while only 30% of the increment was attributed to increase in productivity (Conteh et al. 2012; AfricaRice, 2013). Recently, rough rice production increased by 55% from 17.03 metric tonnes in 2008 to 26.31 metric tonnes in 2018 (AfricaRice, 2018). The increase was also mainly due to rice area expansion. Despite the recent increase, the rate of expansion is still minimal to cope with the rate of consumption. Global trend has shown that there is a growing import demand for rice in Africa. In 2006, Africa's rice imports accounted for 32% of global imports (Somado et al 2008) which continues to increase. Recently, according to AfricaRice 2018, rice import has increased to 45% from 7.3 metric tonnes to 16 metric tonnes with a 2018 estimated import bill of US$ 6.4 billion.

1.2 Challenges facing rice production in Sub-Saharan Africa and possible solutions

The potential arable land in Africa is 637 million hectares (Okigbo, 1982) and about 68% of the total area is in reserves. Africa therefore has great potential for expanding its agricultural production in general and rice in particular. Despite the existing area expansion, SSA rice yields have been the lowest in the world. For example, during 2014-2016, the average yield for SSA was around 2.1 tons per hectare, compared to the global average of around 4.4 tons per hectare (O'Donoghue and Hansen 2017). However, a number of constraints have been identified as limiting rice production efforts by farmers in Africa. These include unavailability of simple and cheap farm implements, pest and disease management, research, soil fertility management and many others. Pest and disease are important natural factors limiting the production of rice and in severe cases, they account for 100 percent of crop loss (Singh et al. 1997). Again, with regards to soil fertility management, improper and long-term use of inorganic fertilizers is detrimental to soil (Imolehin and Wada 2000). However, rice plant has a critical need for fertilizer especially silicate fertilizer to increase production and sustainability. Rice farmers in Sub-Saharan Africa with Nigeria inclusive are unaware of the importance of this type of fertilizer in terms of the types and the rate of application. Research therefore, should focus on the use of alternative source which is also environmental friendly to stand in gap for the inorganic fertilizers that are not readily available or affordable to the resource poor rice farmers in SSA.

1.3 Silicon as a beneficial element for rice production

Undoubtedly, silicon is an indispensable element for sustainable rice production. However, the processes which control Si availability in soil remain rather understudied. Aside from understanding the processes involved in its availability, the most noticeable beneficial effect of Si is on enhanced resistance to both biotic and abiotic stress. High Si accumulation, according to Datnoff and Rodrigues (2005) enhances resistance of rice plants to biotic stress such as disease caused by both fungi and bacteria (rice blast, sheath blight and gray leaf spot). Also high Si accumulation enhances rice plant resistance to insect pest such as stem borers, brown plant hoppers and rice green leafhoppers (Sakamoto 1958; Savant et al 1997). High Si accumulation also increases rice plant resistance to abiotic stresses such as chemical stress (salt, metal toxicity, nutrient imbalance) and physical stress (lodging, drought, radiation, high temperature, freezing, UV) (Epstein 1994; Savant et al 1997; Ma and Takahashi 2002; Ma 2004; Ma and Yamaji 2006). In addition, high Si accumulation increases the canopy photosynthesis by keeping the leaf blade erect and thereby improving light interception characteristics (Takahashi, 1961).

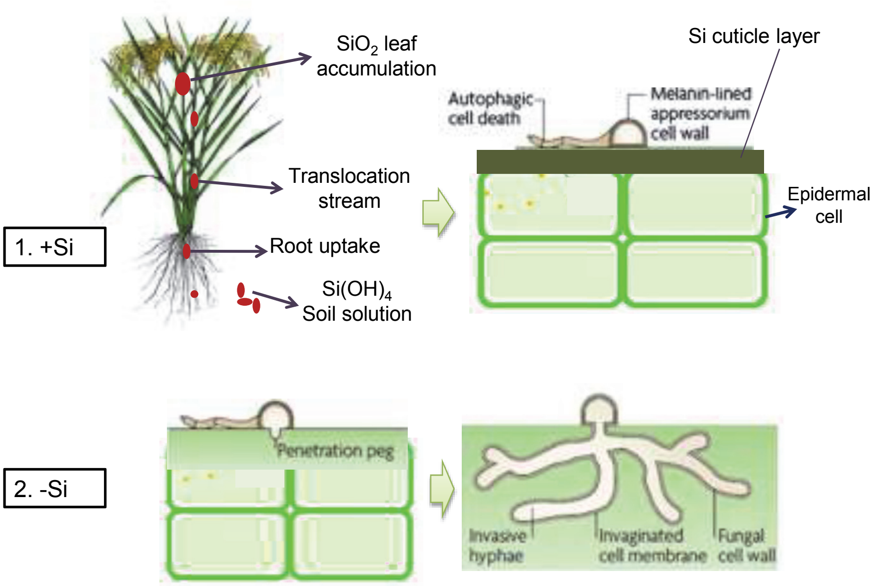

Figure 1.1: Beneficial effect of silicon on plant resistance to blast disease (biotic stress) (Modified from Yan et al 2017)

1.4 Biochar: A solution to waste management challenges in Sub-Saharan Africa

The current population of Africa is 1,300,205,252 as of Monday, November 26, 2018, based on the latest United Nations estimates. Africa's population is equivalent to 16.64% of the total world population and rank second among regions of the world by population. The population of sub-Sahara Africa on the other hand has grown from 186 million to 856 million people from 1950-2010. This implies about 11 million people a year for the past 60 years or approximately 670 million people in 60 years. By 2060, the population of Sub-Sahara Africa could be as large as 2.7 billion people. Compare this demographic shift to Europe's projection of a declining population from 738 million people in 2010 to 702 million in 2060. Nigeria, Ethiopia, Tanzania, Democratic Republic of Congo, Niger, Zambia, and Uganda are projected to contribute millions of people to the world total. Along with China and India, these countries will have the largest populations in the world. In order to sustain the food requirement for the present and projected population, there is a direct need for increase in food production. Increased food production increase means enhanced agricultural practices. As food production increases, waste generated from food production increases (Walsh et al. 2000). It has been reported that about 140 billion metric tonnes of waste biomass are solely generated globally from agricultural activities every year (UNEP 2009). Rice husk is one of the most widely available agricultural wastes in many rice producing countries of the world and has about 20 - 23% by weight of the entire paddy processed (Kumar et al. 2013; Giddel and Jivan 2007). In Nigeria, for example, an estimated amount of about 1.03 metric tonnes of rice husk are generated annually (NAERLS/PCU 2004).

Sugarcane bagasse, a fibrous residual material derived from sugarcane after extracting its juice, is also a common agricultural waste. Traditionally, the sugar mill bagasse is used as fuel in steam production for the milling process and electricity generation. For instance, in Nigeria, recent records indicate that an estimated 1.06 million tonnes of sugarcane were produced out of which about 30% of bagasse residue was generated by sugarcane processed in the mill (FAOSTAT 2014). Not all bagasse produced are used, a substantial amount are left unused for the remainder of the year. The conversion of these wastes into biochar and returning it to fields is a potentially valuable agricultural practice that positively affects the physical and chemical properties of the soil as well as reduce greenhouse gas (CO_2,$CH_4$and N_2O) emissions (Lehmann and Joseph, 2009; Spokas et al., 2009).It will also improve the microbial health of soil. It is an approach that will benefit agriculture, the economy and the environment (Meng et al., 2010) hence, a trilogy of benefits.

1.5 Objective of study

The impact of biochar incorporation on soil properties is the object of numerous publications in Sub Saharan Africa (SSA) but its potential ability to enrich the soil available silicon has not been subjected to enough scientific research. This is quite surprising given that there is strong evidence on risk of Si deficiency, a threat posed by the highly weathered soil scattered all over the Sub-Saharan Africa (Tsujimoto et al., 2014). Farmers in SSA have difficulty in accessing fertilizer especially the silicate fertilizer. The use of organic waste could be an alternate way to source for Silicon. In SSA many organic waste are left unused. This waste can be returned to the soil; it can be converted to mulches or biochar and applied to the soil. In all biochar is the best alternative. This is because biochar is stable; it poses less danger to the environment and the process of its formation concentrate plant nutrient. Also it is a known fact that application of mulches, composts, and manures have positive effect in enhancing soil fertility, but organic matter is usually mineralized very rapidly under tropical conditions (Tiessen et al., 1994). Thus, only a small portion of the applied organic compounds will be stabilized in the soil in the long term given that most will be released back to the atmosphere as CO_2 (Bol et al., 2000; Fearnside, 2000). An alternative to organic amendments is the use of a more stable carbon compounds such as carbonized materials (biochar) or their extracts. Based on these, this study was conducted to:

1. Evaluate the changes in nutrient composition of biochar from rice husk and sugarcane bagasse at varying pyrolytic temperatures.
2. Evaluate the potential effect of pyrolyzed rice husk residue on improving soil available silicon, plant silicon uptake, rice growth and yield parameters.
3. Evaluate the roles of rice husk and sugarcane bagasse biochar on improving the fertility status of the soil.

Chapter 2

Change in nutrient composition of biochar from rice husk and sugarcane bagasse at varying pyrolytic temperatures

2.1 Introduction

Biochar a carbon rich and porous substance produced by thermal decomposition of biomass under oxygen-limited and relatively low temperature (< 700°C) conditions, is receiving great research attention (Lehmann and Joseph 2009). This is due to its potential importance in agronomy and environment. Application of biochar on soil has been shown to have a clear effect on improving soil fertility, crop production and on decontamination of pollutants such as pesticides, heavy metals and hydrocarbon (Beesley et al. 2011; Cabrera et al. 2011). According to Lehmann et al. (2011), physico-chemical properties of biochar can cause changes in the soil nutrient and C availability, and also provide physical protection to microorganisms against predators and desiccation. The type of biomass from which biochar is produced is another important factor. This is because its properties are affected by the nature of the original material. For instance, biochar from manure source posses higher soil cation exchange capacity than that from wood source (Singh et al. 2010). Again, treating soil with woodchip biochar results in higher saturated hydraulic conductivities than with manure based biochar (Lei and Zhang 2013).

There has been a growing interest in the creation of recycling society in which waste are steadily reduced. The technology that is used to produce biochar from waste started in antiquity but recently there is a growing interest on pyrolysis. This is because it is seen as an effective process for converting biomass into resources. The process of pyrolysis concentrates plant nutrients such as phosphorus, potassium, calcium, magnesium and sodium as heating temperature increases (Camps-Arbestain et al. 2015). Consequently, research has proven that even with the concentration of nutrients, percentage retention of alkaline earth metals is higher as opposed to the alkali metals. However, the release and retention of divalent alkaline earth metals are of great importance when biochar acts as a soil amendment (Okuno et al. 2005). Nitrogen is among the most important nutrient required for plant growth. During pyrolysis some forms of nitrogen are lost. This is because N containing organic materials when exposed to high temperature, lead to the enrichment of the heterocyclic form of N such as pyrrole – type N with a decrease in amide N (Kincker and Hatcher 1997). According to Almendros et al. (2003), the microbial decomposition of the enriched N compounds is relatively recalcitrant which limit the conversion of these compounds to plant available form of N. Hongguang et al. (2017), also explained the importance of these enriched heterocyclic N compounds when he observed significant decrease on nitrogen loss from 109.6 mg kg^{-1} (0.01%) to 53.3 mg kg^{-1} (0.005%) in relation to increase in temperature on soils amended with biochar pyrolyzed at different temperatures (250°C, 350°C, 450°C and 550°C).

However, there is limited information on how different sources of biomass as well as pyrolysis temperature could influence the efficiency of applied biochar on improving soil sustainability and crop productivity. Since the use of biochar to ameliorate the soil physical properties for instance porosity (Van Zwieten et al. 2009) and chemical properties for instance chelating nutrients (Kudeyarova 2007) is a function of biomass and pyrolysis conditions as well as quantity (Kammann et al. 2011). Therefore, there is need to study the changes in chemical composition of biochar in relation to pyrolysis temperature. In this study, we tend to control the chemical composition of biochar by investigating different pyrolysis temperatures and agricultural wastes used as biomass. To achieve this aim, the chemical properties of biochar of rice husk at different temperature (300°C - 700°C) using continuous and plant-size carbonizer and sugarcane bagasse at different temperature (350°C-700°C) using batch-type carbonizer were evaluated.

2.2 Materials and Methods

2.2.1 Biochar production

The biochar used in this work were obtained from two agricultural waste residue; rice husk (*Oryza sativa L.*) and sugarcane bagasse (*Saccharum officinarum L.*). All the materials were first air dried and the sugarcane bagasse was cut into smaller pieces (less than 4 – 5cm). Then 10 kg of samples were inserted into experimental electric furnace and pilot batch type carbonizer (Meiwa Co. Ltd. Kanazawa) for 10 min after the inside chamber reached the target temperature.

Sugarcane bagasse Rice husk

Figure 2.1: Agricultural waste biomass used for biochar production

Rice husk biochar

Sugarcane bagasse biochar

Figure 2.2: Image of crushed sample of biochar

2.2.2 Biochar chemical composition characterization

Prior to pyrolysis, the original biomass were analyzed for its chemical composition (Table 2.1). All samples were ground to 0.5 mm in diameter using manual agate mortar and pestle after the pyrolysis process. The biochar yield was calculated as the proportion of the weight of product to the original material. Ash content determination was conducted according to the American Society for Testing and Materials D1752-84. The ash content was thus determined by measuring the weight loss that follows the combustion of about 1g of biochar in a crucible at 750^{o}C after 3 hours. The pH and EC of biochar were measured in 1:20 w/v biochar – water extracts using pH and EC meters (Models D-15 and D-24 Horiba, Kyoto Japan, respectively) (modification in ratio from Ahmedna et al. 1997). Total carbon and nitrogen were determined by dry combustion method using automatic high sensitive NC analyzer (Model Sumigraph NC – 22 Analyzer, Tokyo Japan). Total base cations: Ca, K, Mg and Na were determined after digestion of 0.05 g of biochar with HNO_3 at 160^{o}C for 5 hours using Teflon vessel and measured by Inductively Coupled Plasma Spectroscopy (Model

ICPE – 9000, Shimadzu Kyoto Japan). Available P was extracted by $NaHCO_3$ and was determined by molybdenum blue method according to Olsen and Sommer (1982).

Extractable Ca, K, Mg and Na, which consists of water soluble and ionically exchangeable fractions, were extracted by shaking for 1 hour 0.2 g of biochar in 20 mls of neutral CH_3COONH_4 and quantified on Inductively Coupled Plasma Spectroscopy (Model ICPE – 9000, Shimadzu Kyoto Japan). Available silica from the biochar was extracted using 0.01M $CaCl_2$ (1:30 ratio, continuous shaking for 16 hours, filter) (modification in ratio from Haysom and Chapman 1975), 0.5M HCl (1:50 ratio, shake for 1 hour, filter) (modification in ratio from Savent et al. 1999) and 0.1M Citric acid (1:50 ratio, shake for 2 hours, allow to stay overnight then shake for 1 hour, filter) (Acquaye and Tinsley 1964). Silicon concentrations from the supernatant were determined by molybdenum blue method and measured with spectrophotometer (Model UV 1800, Shimadzu Kyoto Japan) at wavelength of 810 nm.

2.2.3 Statistical analysis

The data was subjected to analysis of variance (ANOVA) using IBM package SPSS 20 while significant differences among the means were tested using Duncan's multiple range test ($P < 0.05$).The available P graphs were plotted using Microsoft excel 2007

Table 2.1: Selected chemical properties of the original biomass prior to pyrolysis

Analyzed Parameters	Biomass	
	Rice Husk	Sugarcane Bagasse
pH	6.5	5.1
EC	0.33	0.32
Ash Content (%)	11.5	4.0
Available Phosphorus (P_2O_5 mg kg^{-1})	605	1167
Available Silica (SiO_2 mg kg^{-1})		
0.1M Citric acid	295	398
0.5M HCl	109	145
0.1M $CaCl_2$	1004	753
Total Carbon (g kg^{-1})	410.9	460.5
Total Nitrogen (g kg^{-1})	2.7	2.7
Total Calcium (mg kg^{-1})	509	1300
Total Magnesium (mg kg^{-1})	222	518
Total Potassium (mg kg^{-1})	2397	1939
Total Sodium (mg kg^{-1})	636	512

EC: Electrical Conductivity (dS m^{-1})

2.3 Results and Discussion

2.3.1 Yield, chemical and elemental properties

Table 2.2 summarized the chemical and elemental properties of RHB and SBB. As pyrolysis temperature increases, the yield of biochar from both rice husk and sugarcane bagasse decreased from 55% to 35% and from 27% to 22% respectively. This was as a result of further disintegration of pyrolytic volatiles into low molecular weight organics and gases as heat passes through the biomass (Thangalazhy- Gapakumar et al. 2010). The relative ash content derived from different temperature ranges in the two biomass; increases significantly ($p < 0.05$) as the pyrolysis temperature increased from 21.8 – 35.6% and 11.0 – 12.8% in RHB and SBB, respectively. The ash content was higher in RHB. This was as a result of rich silica content found in rice plants, which relates strongly with the ash content in the biochar (Mukome et al. 2013). The increase could also be attributed to the progressive concentration of minerals and destructive volatilization of lingo-cellulosic matters as heat passes through the biomass (Tsai et al. 2012; Cao and Harris 2010).

The pH values of RHB and SBB ranged from 6.8 to 10.7 and 7.8 to 9.7 respectively (Table 2.2). The pH of the two biochars increased significantly ($p< 0.05$) with increasing pyrolysis temperature and the maximum (10.7) was observed in RHB at 700°C. This could be attributed to higher ash content at higher temperature and also due to hydrolysis of salts of Ca, K and Mg as the pyrolysis temperature increases (Gaskin et al. 2008). The electrical conductivity (EC) which estimates the amount of total dissolved salts or the total amount of dissolved ions in the biochar varied from 0.09 to 0.40 dS m^{-1} and 0.11 to 0.21 dS m^{-1} in RHB and SBB respectively (Table 2.2). The EC of the RHB and SBB increased significantly ($p< 0.05$) with increasing pyrolysis temperature and the highest EC (0.40 dS m^{-1}) was observed in RHB at 700°C. The increase was likely due to loss of volatile materials as temperature increases while promoting the relative concentrations of salts in the ash fraction (Gai et al. 2014; Ding et al. 2010).

The elemental composition of the RHB and SBB was also presented on Table 2.2. The carbon content ranged from 512.9 to 560.6 g kg^{-1} and from 693.4 to 729.5 g kg^{-1} in RHB and SBB respectively. The maximum (729.5 g kg^{-1}) was observed in SBB at 500°C. The increased biochars' carbon content with increasing pyrolysis temperature indicates that pyrolysis temperature promotes carbonization (Chun et al. 2004; Chen et al. 2012). This promotion was due to high degree of polymerization leading to more condensed carbon structure in the biochar (Lehmann and Joseph 2009). The increase in carbon content could also be associated with H and O loss from biochar as the pyrolysis temperature increases (Antal and Gronli 2003). Total nitrogen content was found to decrease with increased pyrolysis temperature from 4.9 to 3.6 g kg^{-1} and from 6.0 to 3.8 g kg^{-1} in RHB and SBB respectively (Table 2.2). This is because when plant biomass are subjected to pyrolysis, tend to loss some of its nitrogen content and also some N containing structures, ie. amino sugars, amino acids and amines, which are part of nitrogen transformed into heterocyclic N aromatic structures (Cao and Harris 2010; Koutcheiko et al. 2006). This implies that nitrogen will not be available to plants on the immediate but will be released with passage of time.

Table 2.2:The chemical and elemental properties of the biomass at different pyrolysis temperature

Biomass	Temperature	Biochar Yield	Ash Content	pH	EC	Total C	Total N
	(ºC)	(%)		(H_2O)	(dS m^{-1})	(g kg^{-1})	
Rice husk	300	55	21.8 ± 0.2e	6.8 ± 0.4c	0.09 ± 0e	512.9	4.5
	400	44	27.5 ± 0.3d	8.6± 0.2b	0.13± 0d	541.1	4.9
	500	36	32.8 ± 0.2c	10.4± 0.4a	0.23 ± 0c	546.7	4.7
	600	35	33.9 ± 0b	10.6± 0.1a	0.31±0b	560.6	4.3
	700	35	35.6 ± 0a	10.7 ± 0.1a	0.40. ± 0a	545.0	3.6
Sugarcane	350	27	11.0 ± 0.6c	7.8 ± 0.6bc	0.11 ± 0e	693.4	6.0
bagasse	400	24	11.0 ± 0.4bc	8.3 ± 0.1b	0.12 ± 0d	707.3	5.7
	500	24	11.5 ± 0.5bc	9.2 ± 0.7a	0.16 ± 0c	729.5	5.3
	600	22	12.4± 0.1ab	9.6± 0.2a	0.17± 0b	702.2	4.7
	700	22	12.8± 0.2a	9.7± 0a	0.21 ± 0a	696.3	3.8

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p< 0.05$).

2.3.2 Base nutrient composition

Though there was an increase in the total concentration of base elements, there was no specific trend with increase in pyrolysis temperature (Table 2.3). They ranged from K (3105 to 4211 mg kg^{-1} and 3753 to 4711 mg kg^{-1}), Ca (1012 to 1619 mg kg^{-1} and 1922 to 3844 mg kg^{-1}), Mg (522 to 864 mg kg^{-1} and 905 to 1711 mg kg^{-1}) and Na (509 to 1629 mg kg^{-1} and 1203 to 2660 mg kg^{-1}) in RHB and SBB, respectively. The overall maximum K (4711 mg kg^{-1} at 350°C), Ca (3844 mg kg^{-1} at 400°C), Mg (1711 mg kg^{-1} at 350°C) and Na (2660 mg kg^{-1}at 350°C) were all observed in SBB. The increase found in total base elements after pyrolysis of the original biomass is an indication that the relevant chemical components were concentrated in biochar as heat passed through the crop residues (Yuan et al. 2011). The loss of volatile compounds of the original materials after thermal degradation yielded the remaining nutrient content in the biochars (Amonette and Joseph 2009; Chan and Xu 2009).

Pyrolysis significantly altered the extractable nutrient elements in both RHB and SBB at $p < 0.05$. Although, the extractable Na in SBB showed no significant difference, a change in its composition was observed with increasing pyrolysis temperature (Table 2.3). The extractable K and Mg of RHB increased with increasing pyrolysis temperature while extractable Ca and Na showed no specific trend. They ranged from K (165 to 684 mg kg^{-1}), Ca (67 to 103 mg kg^{-1}), Mg (16 to 29 mg kg^{-1}) and Na (21 to 38 mg kg^{-1}). In SBB, the extractable K (Table 2.3) decreased significantly with increasing pyrolysis temperature from 396 to 251 mg kg^{-1} while extractable Mg, Ca and Na decreased from 350°C (18 mg kg^{-1}, 170 mg kg^{-1} and 26 mg kg^{-1}) to 600°C (13 mg kg^{-1}, 137 mg kg^{-1} and 22 mg kg^{-1}) and afterward an increase was observed at 700°C (16 mg kg^{-1}, 180 mg $kg^{-1}$and 24 mg kg^{-1}). The overall maximum Ca (180 mg kg^{-1}) was observed in SBB at 700°C while maximum K (684 mg kg^{-1}), Mg (29.0 mg kg^{-1}) and Na (38 mg kg^{-1}) were observed in RHB at 700°C. Extractable K data obtained indicate that for K release, higher temperature is required. This is because as heat passes through the biomass during combustion, they tend to induce higher effective reaction temperature. This leads to increase in vapor pressure and the convective flux of KCl (Johansen et al. 2011). At higher temperature in RHB, sublimated KCl was not volatilized but rather combines with silicate to form potassium silicate (Muthadhi et al. 2007). In SBB, a decrease in extractable K was observed with increasing pyrolysis temperature, which could be as a result of higher diffusional resistance during devolatilization due to still intact organic matrix as heat passes through the biomass. (Van Lith et al. 2008).

Table 2.3: The base nutrient composition of the biomass at different pyrolysis temperature

Biomass	Temperature	CH_3COONH_4 extractable element				Total elements			
		K	Ca	Mg	Na	K	Ca	Mg	Na
	(°C)	mg kg^{-1}				mg kg^{-1}			
Rice husk	300	165 ± 2e	67± 7d	16 ± 4c	21±1c	3357	1411	716	1596
	400	380 ± 4d	103± 6a	19± 3bc	32± 8a	4211	1619	864	1629
	500	537 ± 3c	90± 7bc	21± 1bc	26± 0bc	3628	1240	631	700
	600	608 ± 7b	84 ± 4c	23± 1b	29± 5ab	3122	1012	522	603
	700	684 ± 6a	101± 1ab	29± 0a	38± 1a	3105	1027	585	509
Sugarcane bagasse	350	396 ± 3a	170 ± 2b	18± 2a	26± 4a	4711	3721	1711	2660
	400	378 ± 4b	167± 2b	16± 2a	25± 5a	4417	3844	1656	2028
	500	332 ± 6c	153± 5c	13± 0b	23± 2a	3753	1922	905	1368
	600	304 ± 9d	137± 4d	13± 0b	22± 2a	4287	2053	986	1590
	700	251± 1e	180 ± 7a	16± 1a	24± 3a	3951	2253	949	1203

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p< 0.05$).

2.3.3 Available phosphorous

In RHB, phosphorous availability significantly increased (225 mg kg^{-1} to 1842 mg kg^{-1}) with increasing pyrolysis temperature at $p < 0.05$, (Figure 2.3). Though SBB is statistically significant at $P < 0.05$, it was found to have irregular trend with increasing pyrolysis temperature (Figure 2. 4). In biochar, its P content is a function of the type of biomass and pyrolysis condition (Downie et al. 2009). Generally, charring enhances P availability from plant tissue. This is because with combustion, there is disproportionate volatilization of carbon which leads to cleavage of organic phosphorus bonds and hence yields biochar with high soluble phosphorus salts (Knoepp et al. 2005). This was in line with the continuous increase of available P observed in RHB with increasing pyrolysis temperature. In sugarcane bagasse biochar the trend of the phosphorus bioavailability was not specific. Part of the reason might be because cation-phosphate complexes which exist in biochar strongly influence phosphorus reactivity and bioavailability (Hunger et al. 2008; Güngör et al. 2007). In this study, data obtained suggest that there is every possibility that Ca/Mg-P complexes dominated P availability. Again, the change might be because diverse forms of organic phosphorus (OP) have diverse levels of mobility. For instance, the OP bond to organic matter containing abundance of O-alkyl groups (e.g., phytic acid) is more labile than those containing ample refractory alkyl and aromatic carbon groups (e.g., nucleic acid and phospholipid) (Hamdan et al. 2012). Hence, the production of biochar can alter the fate of P by changing the form of P in agricultural residues.

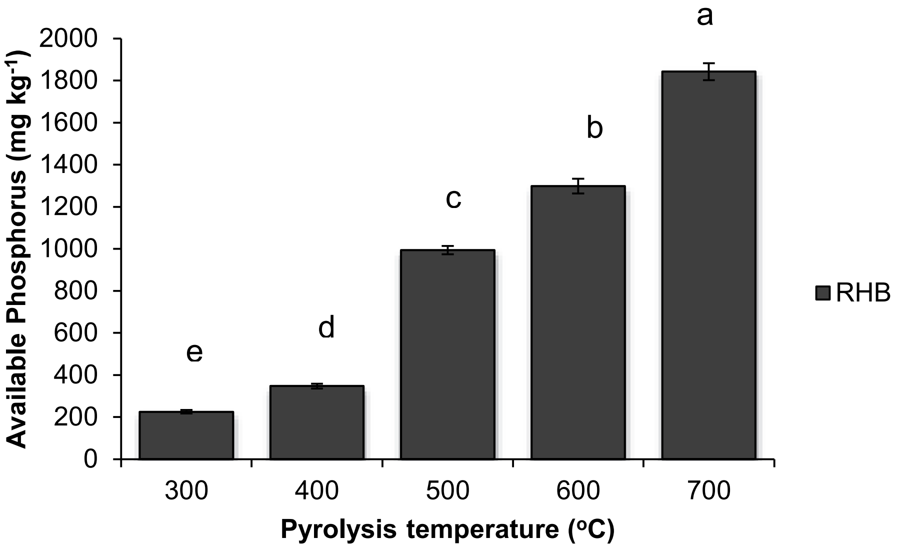

Figure 2.3: Available phosphorus (Olsen P) concentration of rice husk biochar (RHB)

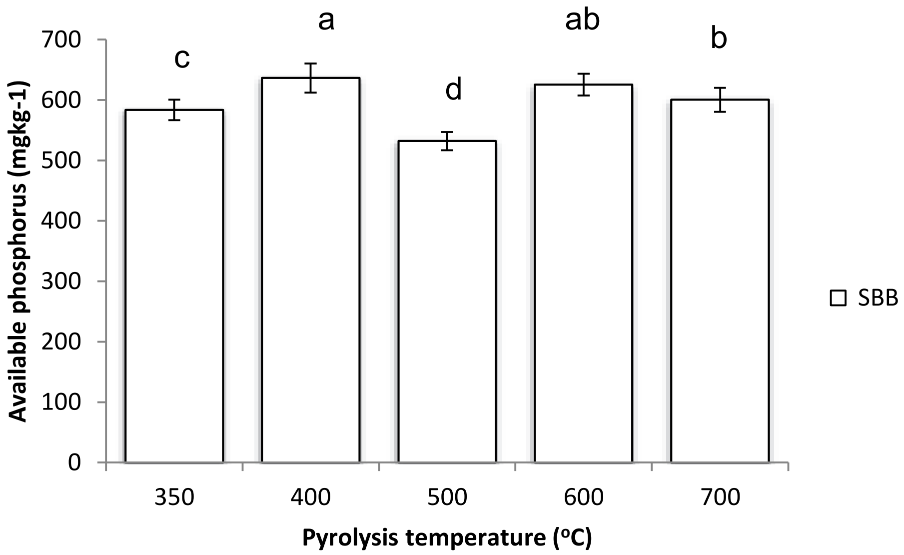

Figure 2.4: Available phosphorus (Olsen P) concentration of sugarcane bagasse biochar (SBB)

Note: For each material (RHB and SBB), the different alphabet in a bar showed statistical difference ($p< 0.05$).

2.3.4 Available silicon

Available silicon of the biomass at $P < 0.05$ significantly increased with increasing pyrolysis temperature in both RHB and SBB respectively (Table 2.4). In RHB, 0.01M $CaCl_2$ extracted silicon ranged from 61 to 3124 mg kg^{-1} with its maximum (3124 mg kg^{-1}) at 700^oC. In SBB the trend of increase continued from 350^oC to 500^oC (266 to 343 mg kg^{-1}) afterwards there was a decrease at 600^oC (275 mg kg^{-1}). In 0.5M HCl and 0.1M citric acid extracted silicon, the range found in RHB was (86 to 475 mg $kg^{-1}$and 16 to 418 mg kg^{-1}) and SBB was (236 to 7262 mg kg^{-1} and 207 to 9313 mg kg^{-1}) respectively. The maximum of 0.5M HCl and 0.1M citric acid were observed in SBB (7262 mg kg^{-1} and 9313 mg kg^{-1}) respectively at 700^oC. The increase obtained with increasing pyrolysis temperature was as a result of change in the form of silica upon heating. It is reported that the amorphous form silica changes into crystalline form when heat is applied (Todkar et al. 2016; Parry and Smithson 1964). This form change generally reduces the availability of silicon. However, our results showed reverse trend. It is probably due to the short heating time, i.e. 10 min. The differences observed with the different extraction methods might be a function of the chemical composition of the biomass. The amount of available silicon extracted from RHB with acidic extraction method was low when compared with SBB. Part of the reason might be because rice husk upon charring produces about 70 – 80% reactive SiO_2 while sugarcane is about 40 – 50% (Ganesan et al. 2007). According to Patcharin et al. (2009), introduction of acid can increase the amount of silica extracted from bagasse by the removal of its alkali and alkaline metals. It is viewed that $CaCl_2$ extraction method extract only the soluble fraction of silica (Berthelsen et al. 2001) while that with citric acid or diluted acid (example H_2SO_4) extract a combination of both soluble and adsorbed silica fractions (Beckwith and Reeve 1964). This is because acidic ions compete not only with silicic acid in the sorption sites but also formed complexes with metallic ions that are known to bind silicic acid. In the present study, we could not find out the reason why available silicon in RHB was not extracted by acid solutions (HCl and citric acid).

Table 2.4: The available silicon of the biomass at different pyrolysis temperature under different extraction methods

Biomass	Temperature (°C)	0.1M $CaCl_2$	0.5M HCl	0.1M Citric acid
			(SiO_2mg kg^{-1})	
Rice husk	300	61± 3e	86± 4e	16± 2e
	400	1306± 12d	117± 3d	55± 4d
	500	2952 ±51c	190± 10c	157± 6c
	600	2800± 12b	263± 11b	214± 5b
	700	3124± 77a	475± 30a	418± 21a
Sugarcane bagasse	350	266± 10b	236± 4d	207± 7d
	400	333± 8a	259± 7d	306± 5d
	500	343± 5a	2074± 20c	2946± 40c
	600	275± 3b	4686± 117b	5391± 145b
	700	279± 4b	7262± 135a	9313± 137a

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p < 0.05$).

2.3.5 The relationship between pyrolysis temperature and biochar chemical compositions

A regression analysis was calculated in order to determine the relationship between pyrolysis temperature and the biochar chemical composition. The results showed that pyrolysis temperature quantitatively influenced some of the biochar chemical properties. Correlation analysis was also conducted to determine the relationship between Pyrolysis temperatures and biochar chemical compositions. The result gave strong significant correlation on ash content ($r = 0.95$), EC ($r = 0.99$), pH ($r = 0.95$), Ext. K ($r = 0.99$), Ext. Mg ($r = 0.97$) and available P ($r = 0.99$) in RHB while ash content ($r = 0.96$), EC ($r = 0.98$), pH ($r = 0.97$) and Ext. K ($r = 0.99$) showed strong influence in SBB (Figure 2.5 and 2.6). The other biochar chemical compositions in both RHB and SBB though related but were not significant. The result implies that the biochar chemical compositions are possibly designed by changing pyrolysis temperature.

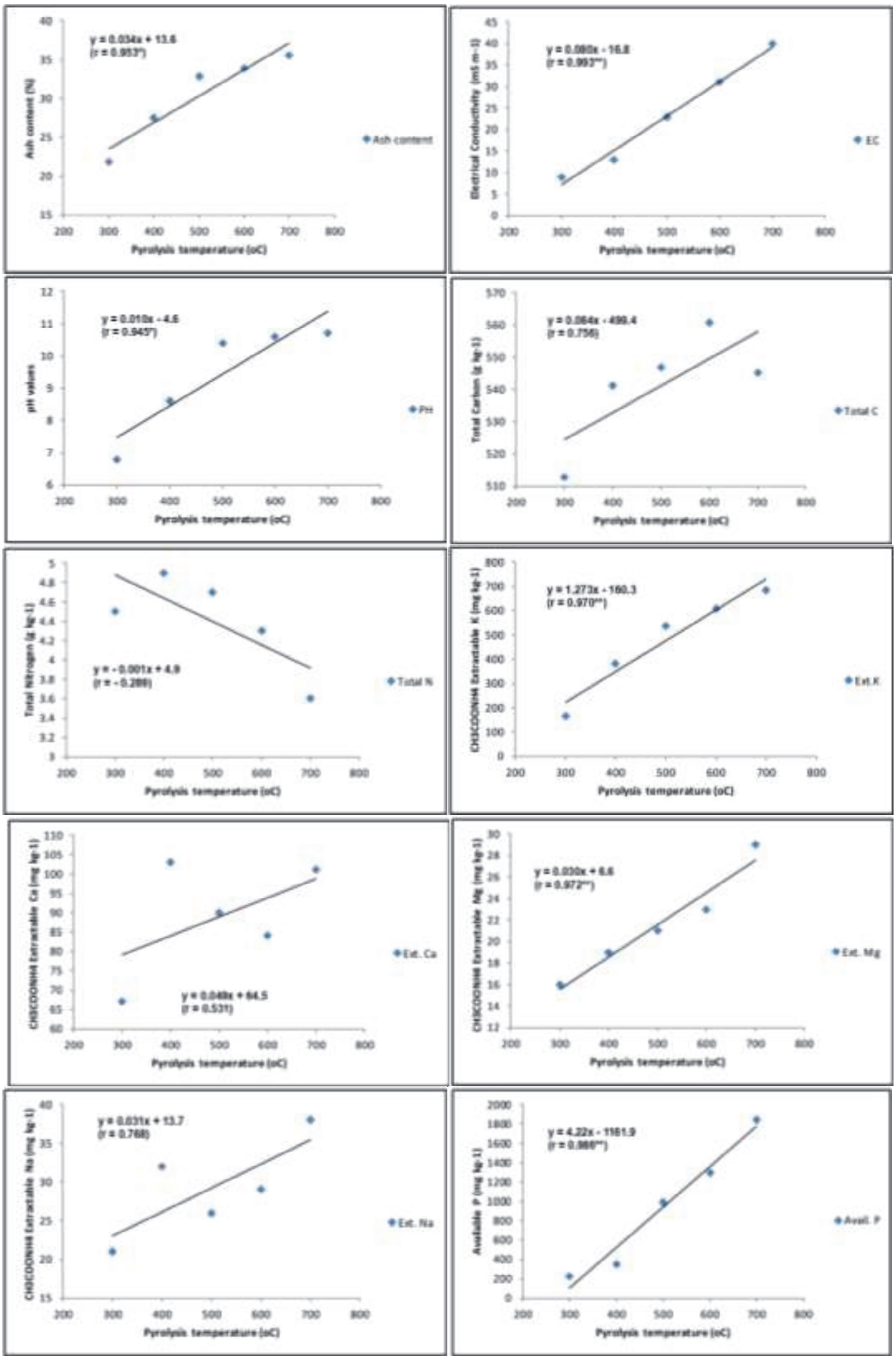

Figure 2.5: The relationship between pyrolysis temperature and rice husk biochar chemical composition (probability level =* for 5%, ** for 1%)

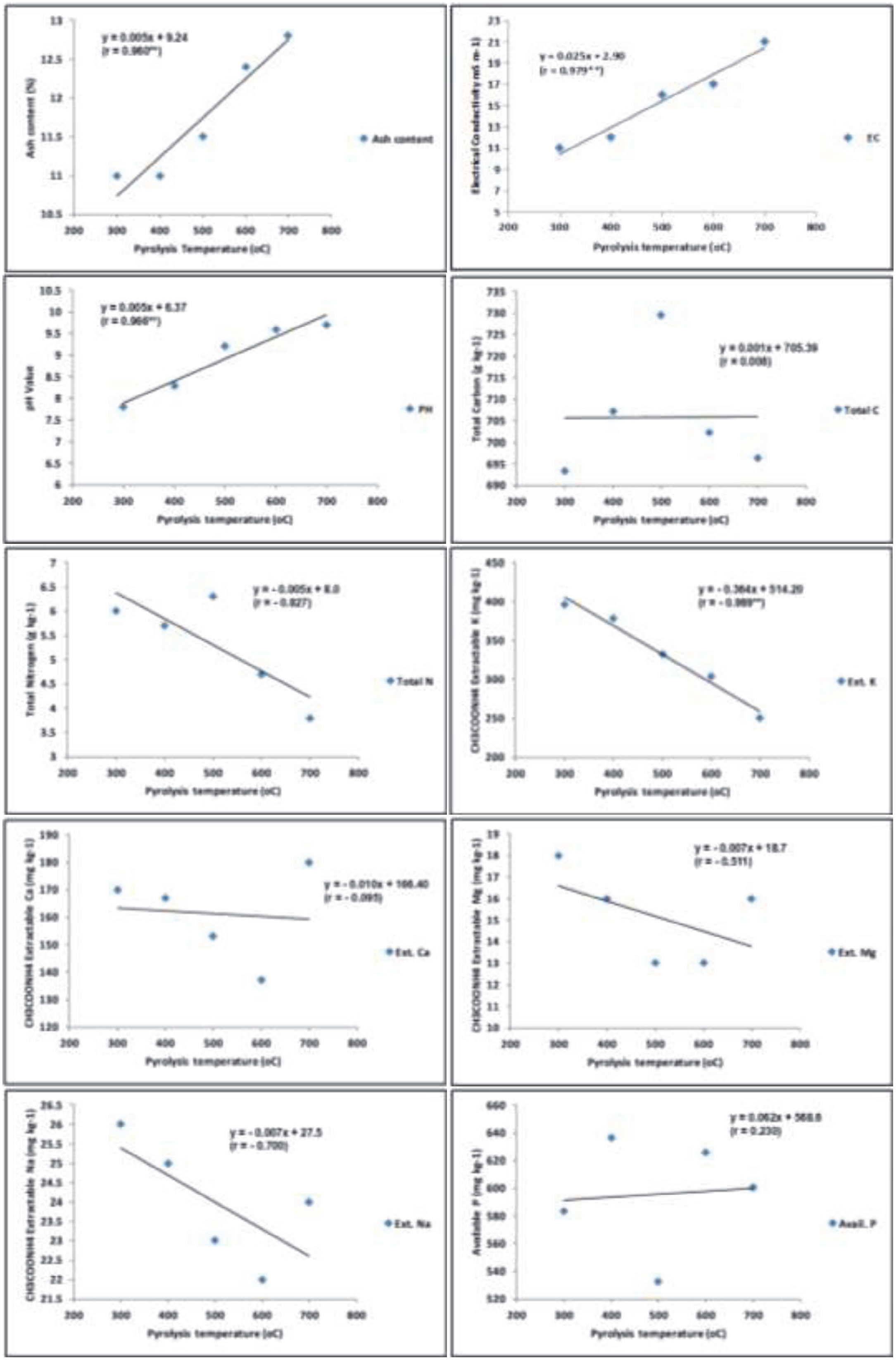

Figure 2.6: The relationship between pyrolysis temperature and sugarcane bagasse biochar chemical composition (probability level =* for 5%, ** for 1%)

2.4 Conclusion

The data indicated that both the pyrolysis temperature and biomass significantly affect the chemical compositions of the biochar. In all, an increase in temperature leads to generation of biochar with high nutrient content. Developing an innovative process, which can generate high temperature, would be a key priority for the local communities to improve the productivity and quality of the produced biochar. RHB at high temperature may produce nutrient-rich biochar, with high pH, EC, ash content, available silicon, phosphorus, extractable base cations for acidic soil amendment. Finally, SBB could give high available silicon with acid pre-treatment.

Chapter 3

Improvement of silicon availability of rice husk residue for replenishment of available silicon in paddy soil

3.1 Introduction

Silicon (Si) the second most abundant element of the earth's crust and is commonly found as silica (SiO_2) or as silicates (Lutgens et al. 2000). Despite silicon's long-standing history on plant growth, it has long been neglected by ecologists. This is because it was not considered an essential nutrient for plants (Yoshida, 1965). However, in recent years, researchers have shown its beneficial effect on the growth of many plants especially rice, wheat and barley (Klotzbucher et al 2015). Plants vary in their ability to accumulate silicic acid. Rice stands as the greatest accumulator of silicic acid and can accumulate SiO_2 in the stem and leaves up to 10% in its dry weight with the application of a large quantity of silicon fertilizer (Takahashi, 1961). Silicon plays a crucial role in maintaining stable rice production by increasing the resistance of rice plant to fungal diseases (e.g., rice blast, brown spot and sheath blight), insect attacks and abiotic stresses including drought and lodging (Savant et al. 1997; Ma, 2004).

Rice is a staple food for more than half of the world's population (Muthayya et al. 2014). More than 3.5 billion people depend on rice for their 20% daily calories (GRiSP, 2013). Apart from the Asians whose, global rice consumption rate is about 90%, Africa's rice demand especially in the Sub-Saharan region recently has been on a continuous increase (GRiSP, 2013). To meet up with the booming demand for rice in Sub-Saharan Africa (SSA), there is a need for urgent intervention in the area of fertilization. To maintain a sustainable rice production system, a large silicon supply is needed from soil, irrigation and external inputs such as fertilizer (Tsujimoto et al. 2014; Ning et al. 2014). In Japan, silicate materials such as calcium silicate slag are being applied widely to the paddy fields (Takahashi and Okuda, 1966). Silicate material was first recognized as a fertilizer in 1955 and since then 1.5 to 2 t ha^{-1} has been applied to silicate deficient paddy soils till date. An increase of about 5 to 15 % in rice yield has been reported as a result of this application (Takahashi et al. 1990). Nowadays, countries like South Korea, Taiwan, Thailand, China and the USA also use silicate fertilizer in their paddy fields (Liang et al. 1994; Kornodorfer and Lepsch, 2001). But in other regions especially in SSA, the use of silicate fertilizer has never been a concern even with the potential risk of Si deficiency found in the highly weathered soil widely distributed in the SSA (Juo and Sanchez, 1986). This could be attributed to the unawareness about the importance of silicate fertilizer in rice production. Besides this, the cost of silicate fertilizers makes them unaffordable for farmers. To maintain sustainable rice production in this region, there is a need to research on alternative silicon sources which are locally available and affordable.

The use of plant residue through recycling could be a possible alternative. According to Tuck et al. (2012), rice husk is one of the agriculturally processed high-volume residues. For every five tonnes of harvested rice, one tonne of husk is produced, amounting to 1.2×10^8 tonnes of rice husk per year across the globe. This huge amount of waste, if not well managed could lead to environmental nuisance. Hence, developing uses for this waste resource will enhance the global sustainable development. Rice husk and straw are considered as good organic sources of silicon (Sahebi et al. 2015; Liang et al. 2007). They are considered as valuable silicon resources because they have the capacity to partly replenish silicon in the paddy fields. However, decomposition of these materials in the flooded field is always related to the emission of methane which is a greenhouse gas. Globally rice base system contributes an estimate of 9 – 19 % of this gas (Denman et al. 2007; Haefele et al. 2011). Therefore, converting the rice residue (rice straw and husk) into biochar could be a way to address this environmental issue while maintaining the nutrient efficacy of the soil. According to Kajiura et al. (2015), the use of biochar charred at a high pyrolysis temperature (>500°C) on agricultural fields causes a greater reduction in a cumulative CO_2 release. In humid tropics, high stability of biochar in soil plays an active role in improving the soil fertility of poor soils (Lehmann et al. 2006).

Presently, researchers working in this area have found that applying biochar to soil may be beneficial to rice production. This is because of biochar's potential to increase soil organic carbon (SOC), nutrient supply, plant growth and other soil properties (Glaser et al. 2002; Lehmann et al. 2003). However, little attention has been given to the effectiveness of biochar in relation to increasing silicon availability in the rice field. Based on this, the study intends to (1) give an overview of the chemical composition of rice husk residue pyrolyzed at different temperature; (2) test the agronomical effect of the pyrolyzed rice husk residue on rice plant; (3) evaluate the potentials of the pyrolyzed rice husk residue on improving soil available silicon and plant silicon uptake.

3.2 Materials and Methods

3.2.1 Soil and biochar

The soil used for the experiment was collected from a paddy field in Matsue, Shimane Prefecture, Japan (35°30´29.67N and 133°06´42.46E). The soil had its available silicon above the critical level (86 mg SiO_2 kg^{-1}) (Dobermann and Fairhurst, 2000). The bulk soil was air-dried, homogenized, crushed and passed through 2 mm sieve prior to pot experiment. The selected soil properties are presented in Table 3.1. Rice husk residue (RH) was used for the experiment. Prior to the pyrolysis, RH was first characterized for its chemical compositions (Table 3.1). The RH was air-dried and 10 kg of it was inserted into an experimental electric furnace (Meiwa Co. Ltd Kanazawa, Japan) and pyrolyzed for 10 minutes after the inside chamber reached the targeted temperatures. The unpyrolyzed RH and the pyrolyzed RH (RHB) were ground to less than 0.5 mm in diameter using a stainless steel ball grinder and a manual agate mortar and pestle respectively.

3.2.2 Pot experiment

The pot experiment was set up in the Experimental Glasshouse, Shimane University, Japan (35°29′14.30N and 133°04′07.92E) during the summer season (June to September 2017). Plastic pots (12 cm in diameter and 14 cm in height) were filled with 680 g of air dried soil and amended with biochar at 10 g pot^{-1} (at the rate of 15 t ha^{-1}). The pots were fertilized with a basal dose of 1.42 g pot^{-1} of $(NH_4)_2SO_4$ as the source of nitrogen (N) fertilizer (at transplant and at panicle initiation) and 1.32 g pot^{-1} of KH_2PO_4 as potassium (K) and phosphorus (P) fertilizer sources (at transplant only). Each treatment was replicated three times and arranged in a complete randomized design. All the experimental pots were irrigated with deionized water up to 5 cm above the soil level. The pots were allowed to stay overnight after which one *Koshihikari* rice seedling per pot was planted. The average temperature during the period of the experiment was 26°C with the minimum of 20°C and maximum of 38°C during the experimental period. Regular watering was done daily to maintain the waterlogged condition required for lowland rice production.

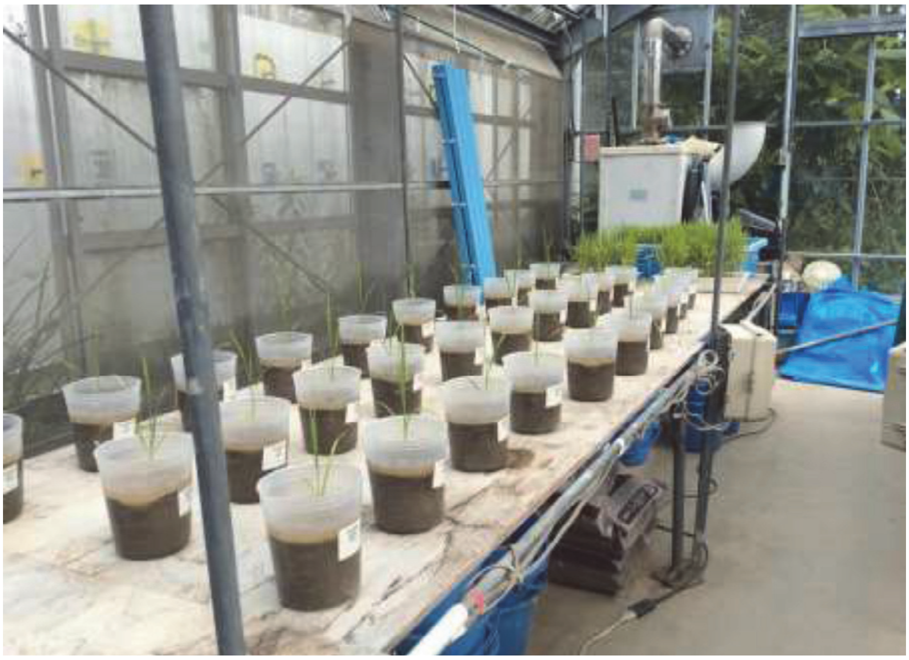

Figure 3.1: Initial set-up of the pot experiment in the glasshouse

On the 56th day after transplantation, the plant height was measured and tiller numbers were counted. Three months after the transplanting date, the above-ground biomass (shoot) of the plants was harvested and air-dried in the greenhouse. Two weeks after, the grains were separated from the shoot and the shoot was oven dried at 60°C in a paper bag until a constant weight was reached. The root was also harvested, washed thoroughly with deionized water and oven dried at 60°C in paper bags until a constant weight was gained. The dried samples were ground with a stainless steel ball mill grinder and stored in zip lock bags at room temperature prior to plant-silica analysis. The soil from each pot was air-dried and thoroughly mixed. The air-dried soil was passed through a 2 mm sieve to remove any visible roots in the soil.

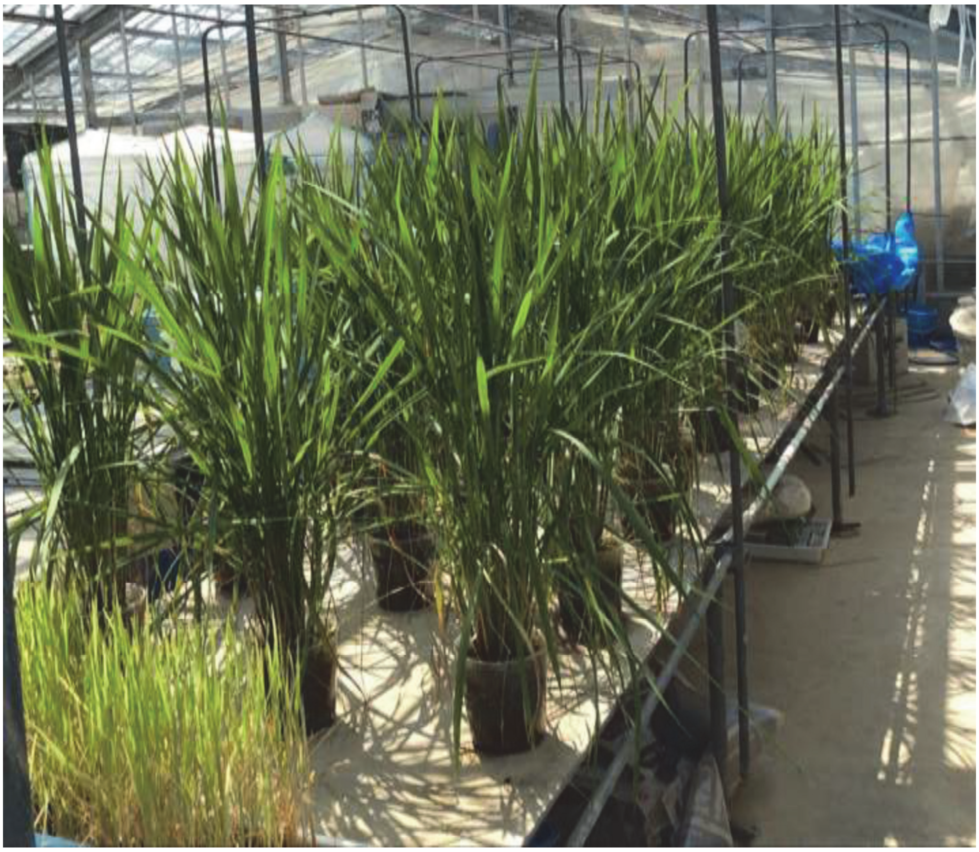

Figure 3.2: Rice plant at pinnacle stage in the pot experiment

Figure 3.3: Harvesting of rice plant in the pot experiment

3.2.3 Chemical analysis

The pH and EC of biochar were measured in 1:20 w/v biochar - water extracts (modification in ratio) (Ahmedna et al. 1997) using pH and EC meters (Models D-15 and D-24 Horiba, Kyoto Japan, respectively). Total carbon and nitrogen were determined by dry combustion method using NC analyzer (Model Sumigraph NC-22 Analyzer, Tokyo Japan). Available P was extracted by $NaHCO_3$ and was determined by the molybdenum blue method (Olsen and Sommers, 1982). Available silicon from the biochar was extracted using 0.5M HCl at 1:50 ratio, shake for 1 hour and filter (modification in ratio, Savant et al. 1999). This extraction method was used because biochar in this context was considered as a silica fertilizer. According to Ma and Takahashi, 2002 and NIAES, 1987, the official method for gauging Si availability in slag which is the most common silica fertilizer is by extracting its silica with 0.5 M HCl. The silicon concentrations from the supernatant were determined by the molybdenum blue method and measured with a spectrophotometer (Model UV 1800, Shimadzu Kyoto Japan) at a wavelength of 810 nm. For the total Si concentration, 0.1 g of biochar was extracted using diluted hydrogen fluoride solution (Saito et al. 2005) and the Si supernatant was determined with molybdenum yellow method at a wavelength of 400 nm (Weaver et al. 1968).

Table 3.1: The physio-chemical properties of the soil used for the pot experiment and the rice husk residue

Properties	Soil	Rice Husk residue (RH)
Clay (%)	35.05	-
Silt (%)	19.56	-
Sand (%)	45.39	-
Olsen-P_2O_5 ($mgkg^{-1}$)	248.3	605.0
EC (mSm^{-1})	6.8	33.1
pH (H_2O)	4.7	6.5
Total C (gkg^{-1})	15.0	410.9
Total N(gkg^{-1})	1.0	2.7
Ash (%)	-	11.5
Available Si (mg SiO_2kg^{-1})	138.1	109
Exchangeable Ca ($cmol_ckg^{-1}$)	3.49	-
Exchangeable Na($cmol_ckg^{-1}$)	0.15	-
Exchangeable K($cmol_ckg^{-1}$)	0.25	-
Exchangeable Mg($cmol_ckg^{-1}$)	1.07	-
Total Si (g SiO_2 kg^{-1})	-	20.7

For soil analysis, the pH and electrical conductivity were measured in 1:2.5 w/v and 1:5 w/v of soil – water using pH and EC meters (Model D-15 and D-24 Horiba, Kyoto Japan respectively). Soil total carbon and nitrogen were determined using dry combustion methods (Sumigraph NC-22 analyzer). Available phosphorus was determined using Bray 2 extraction method (Bray and Kurtz 1945). Total exchangeable bases were extracted with 1M ammonium acetate (pH 7.0) and measured by Inductively Coupled Plasma Spectroscopy (ICPE-9000 Shimadzu Kyoto, Japan). Available silicon was extracted by acetate buffer (pH 4.0) (ratio of 1:10), with intermittent shaking for 5 hours at 40°C. The Si supernatant was determined using the molybdenum blue method (Imaizumi and Yoshida 1958). For the plant analysis, the total silica from the rice plant parts was extracted using a diluted hydrogen fluoride solution (Saito et al. 2005). The Si supernatant was determined with molybdenum yellow method at a wavelength of 400 nm (Weaver et al. 1968). The uptake of Si by the rice plant from each pot was calculated as follows:

Uptake (g pot^{-1}) = Si concentration in plant x the plant dry weight in each pot

3.2.4 Statistical analysis

Analysis of Variance (ANOVA) and Duncan's multiple range tests were done to determine the statistical significance of the RH and RHB treatments effect on rice plant growth performance, soil available Si and plant silica uptake using SPSS IBM 20.0 and 5% probability ($p < 0.05$) was considered to be statistically significant.

3.3 Results and Discussion

3.3.1 Characteristics of biochar

As shown in Table 3.2, the nutrient content of the produced biochar increased with increasing pyrolysis temperature. The biochar had high pH values attributed to high ash content (Table 3.2) (Gaskin et al. 2008). Biochar with high ash content can provide more mineral nutrients such as K, Ca, Na and Mg which increase pH values (Wu et al. 2012). The EC of the biochar produced from RH showed an increasing trend with an increase in pyrolysis temperature. This trend is due to the loss of volatile materials at higher temperature while promoting the relative concentration of salts in the ash fraction (Amonette and Joseph, 2009). Available phosphorus and silicon increased with increase in pyrolysis temperature. The increase obtained in available P is because, during pyrolysis, there is disproportionate volatilization of carbon. This leads to the splitting of organic P bonds and hence results in biochar with high soluble P salts (Knoepp et al. 2005). The increase obtained from silicon with increasing pyrolysis temperature (Table 3.2) might be as a result of a change in the form of silica relative to the time of charring.

3.3.2 Effect of biochar on rice plant growth, yield and yield components

Table 3.3 shows the effect of RH and RHB on rice growth, yield and yield components. The tiller number, shoot and root biomass showed significant differences ($p < 0.05$) among the treatments while the plant height and grain yield did not. It is evident from the result that plants treated with RH gave the lowest root biomass (7.7 g pot^{-1}), shoot biomass (27.3 g pot^{-1}), root/shoot ratio (0.268), tiller numbers (19.3) and grain yield (16.3 g pot^{-1}). This is because the incorporation of plant residue with high C/N ratio might cause N immobilization in the soil, resulting to low yield. Application of residue with low C: N ratio encourages mineralization but applying residue with a high C: N ratio advances N immobilization (Vigil and Kissel 1991).

Comparison between control (no biochar amendment) and the RHB treated pots showed that control has higher root biomass (16.3 g pot^{-1}) than RHB treatments while the tiller numbers and the shoot biomass showed no significant difference. This implies that smaller root biomass in RHB treatments did not limit the shoot growth. This is because biochar has the ability to retain nutrients to improve productivity (Abebe et al. 2012). Thus, RHB treatment reduces the need for root elongation in search of the nutrients. Although no statistical difference was observed in tiller number and shoot biomass, pots amended with RHB at 700°C gave the highest tiller number (25.3) and shoot biomass (33.3 g pot^{-1}) against control. The grain yield also showed no significant difference in this experiment. Neglecting the significance level of the statistical analysis, lowest grain yield was observed from the pot amended with RH. This supports the findings of Li et al. (2016), which states that applying amendments with high C: N ratio reduces annual rice yield. In general, RHB application did not significantly influence plant growth in this experiment. This was because the soil had enough level of available Si for plant growth and the plant was grown under stress - free condition such as pest, disease, drought and so on.

Table 3.2: The chemical and elemental properties of the rice husk biochar at different pyrolysis temperatures

Rice Husk Biochar	pH (H_2O)	EC	Biochar yield	Ash content	Available P	Available Si (SiO_2)	Total SiO_2
		mS m^{-1}	%		mg kg^{-1}		g kg^{-1}
RHB 300°C	6.8	9.04	55	21.8	225	86	13.9
RHB400°C	8.6	13.36	44	27.5	347	117	15.5
RHB500°C	10.4	22.9	36	32.8	994	190	13.6
RHB600°C	10.6	31.1	35	33.9	1298	263	13.2
RHB700°C	10.7	40.05	35	35.6	1842	475	14.5

Table 3.3: Effect of rice husk (RH) and rice husk biochar (RHB) applications on rice growth, yield and yield components

Treatments	Plant height (cm pot^{-1})	Tiller number	Shoot weight	Root weight	Root/ shoot	Grain weight
			g pot^{-1}			
Control	87.7a	24.0ab	30.7ab	16.3a	0.52a	19.8a
RH	90.3 a	19.0 b	27.3 b	7.7 c	0.268 c	16.3 a
RHB 300°C	89.0 a	24.0 ab	31.3 ab	10.0 bc	0.324 bc	19.7 a
RHB400°C	83.6 a	23.0 ab	31.3 ab	14.3 ab	0.450 ab	18.0 a
RHB500°C	84.8 a	25.0 ab	31.0 ab	12.0 abc	0.380 bc	18.7 a
RHB600°C	83.5 a	23.0 ab	30.3 ab	10.7 bc	0.353 bc	20.0 a
RHB700°C	85.2 a	25.0 a	33.3 a	14.0 ab	0.419 ab	20.0 a

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p< 0.05$).

3.3.3 Effect of biochar on soil available Si

Fig. 3.1 shows the effect of RH and RHB on soil available Si after harvest. The soil available Si after harvest ranged from 87 to 151 mg pot^{-1} with an increment from 0.2 to 56 mg pot^{-1}compared with the initial soil Si status (calculated from Fig. 3.1). Soil amended with RHB at 400°C gave the highest soil available Si ($p < 0.05$) after harvest compared to RH and other RHB treatments. Although the RH and RHB had an increase in soil available Si after harvest compared with the control, the increase is not statistically significant. This result implies that RH and RHB could serve as a Si source as its effect on soil available Si remained after harvest. In this study, a trend of increase was observed in soil available Si with increasing pyrolysis temperature from RH (112 mg pot^{-1}) to RHB at 400°C (151 mg pot^{-1}). However, at higher pyrolysis temperature (RHB > 400°C), the soil available Si fluctuated (Fig. 3.1). This result contradicts the trend found in the available Si of the used biochar amendment, which shows continuous increase with increasing pyrolysis temperature (Table 3.2). This might be because Si release behaviour of the biochar is strongly controlled by Si speciation and content as well as the interaction between Si and carbon structure of the biochar (Xiao et al. 2014). According to Wang et al. (2018), the amount of Si release from a pure Si-rich biochar increase with increasing pyrolysis temperature but the degree of the increase slightly decrease. This might be related to the balance between the re-adsorption of silicic acid by the pores of the biochar carbon structure and the release of Si from the Si component of the biochar. This implies that from the results obtained in this study (Fig. 3.1), part of the reason for the observed fluctuation in soil available Si among RHBs might be due to re-adsorption of the silicic acid by the pore of the RHB carbon structure at higher pyrolysis temperature (RHB > 400°C). Another possible reason which could cause the variation in soil Si concentration might be the uniqueness of the RHB at 500°C and 700°C. This is due to the dissolution of Si and sorption reactions between soluble Si and soil components as well as the biochar surface (Wickramasinghe and Rowell 2006). Biochar performance in relation to the extractable Si release rate might have led to high plant Si uptake obtained in RHB at 500°C. Also, it led to less soil Si availability after harvest. Haynes et al. (2013) found that a negligible quantity of the very high total Si content (29.1%) of fly ash was in extractable form compared with steel slag and processing mud, which had the lowest total Si contents but relatively high extractable Si.

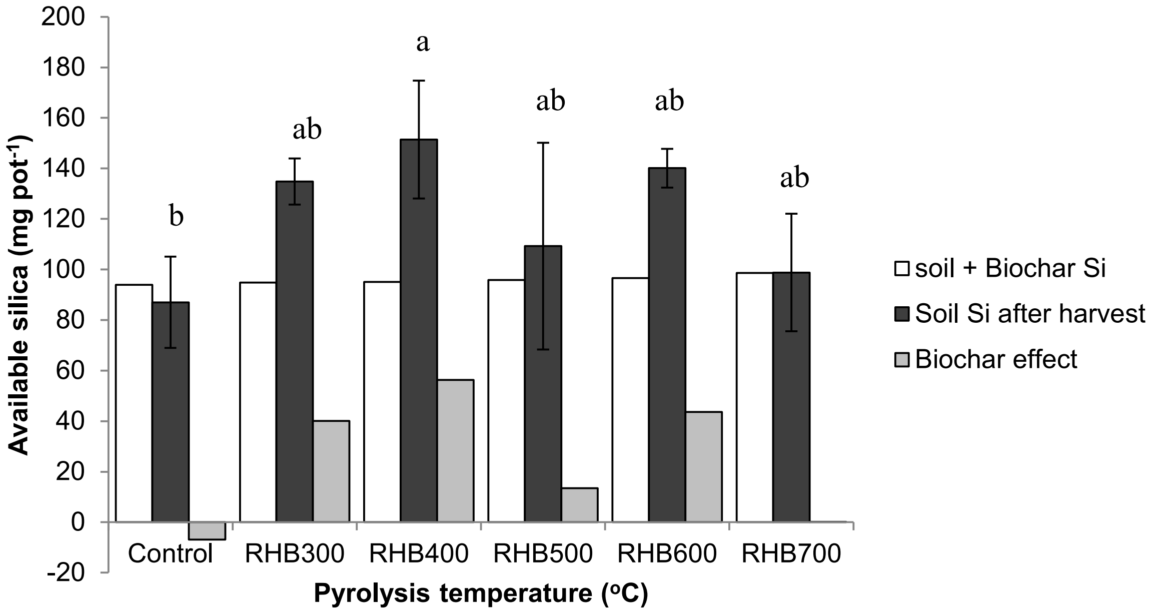

Figure 3.4: The biochar effect of the rice husk biochar at different pyrolysis temperature on soil available Si

Note: For each material (RHB and SBB), the different alphabet in a bar showed statistical difference ($p< 0.05$).

3.3.4 Effect of RH and RHB on plant Si concentration and uptake

The Si concentration of the matured rice straw differed significantly ($p < 0.05$) among the treatments (Table 3.4). They ranged from 56.5 g SiO_2 kg^{-1} to 72 g SiO_2 kg^{-1}. The highest straw Si concentration was from pot amended with RHB at 500°C (72 g SiO_2 kg^{-1}). The Si concentration of the matured rice husk also showed a significant difference at $p < 0.05$ among the treatments (Table 3.4). They ranged from 18.5 g SiO_2 kg^{-1} to 20.0 g SiO_2 kg^{-1}. The highest rice husk Si concentration was reported from pot amended with RHB at 500°C (20.0 g SiO_2 kg^{-1}). The lowest Si concentration from both straw and husk were from the control pots (56.6 g SiO_2 kg^{-1} and 18.5 g SiO_2 kg^{-1} respectively). This also reflects the potentiality of RH and RHB as Si source. Among the treatments, the rice husk Si uptake differed significantly at $p < 0.05$ while the rice straw Si uptake did not (Table 3.4). The rice husk Si uptake ranged from 98 to 133.5 mg SiO_2 pot^{-1}. The highest was from pot amended with RHB at 700°C (133.5mg SiO_2 pot^{-1}) while the lowest was from pot amended with RHB at 400°C (98 mg SiO_2 pot^{-1}). In all experimental pots, the amount of Si taken up by plants was much higher than the available Si in the initial soil, RH and RHB. They ranged from 1971.7 to 2478.8 mg SiO_2 pot^{-1} (calculated from Table 3.4 and Figure3.4) as opposed to the cumulative available Si supply from the initial soil and biochar which ranged from 94.8 to 98.7 mg SiO_2 pot^{-1} (calculated from Table 3.2 and Figure 3.4). The result implies that the effect of RH and RHB application on plant Si uptake was not only through the initial available Si supply but also through the continuous release of Si from the materials (biochar) and other mechanisms such as silicon dissolution in soil minerals. It is known that Si dynamics is also regulated by adsorption of silicic acid (soluble Si) by biochar (Wang et al. 2018) and reaction with other elements in the soil like Ca, Mg, Fe, Zn etc (Rodrigues and Datnof 2015) which may accelerate or retard Si release. According to Marxen et al. (2016) plant-silicon-uptake accelerates the release of the dissolved Si in soil by weathering of phytoliths in the biochar and soil minerals.

Table 3.4: Effect of rice husk (RH) and rice husk biochar (RHB) pyrolyzed at different temperatures on silicon concentration and uptake in rice

Treatments	Silicon Concentration ($g\ SiO_2\ kg^{-1}$)		Silicon uptake ($mg\ SiO_2\ pot^{-1}$)	
	Straw	Husk	Straw	Husk
Control	56.5b	18.5b	1794.5a	132.5a
RH	61.0ab	19.0b	1749.5a	111.0bc
RHB300ºC	70.0a	20.0a	2216.0a	118.5ab
RHB400ºC	63.5ab	19.0b	1951.0a	98.0c
RHB500ºC	72.0a	20.0a	2237.5a	132.0a
RHB600ºC	61.5ab	19.0b	1772.5a	131.5a
RHB700ºC	59.0ab	18.5b	1852.5a	133.5a

Note: Silicon content in rice husk seemed to be under estimated. We discussed on this issue in Chapter 5; For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p < 0.05$).

3.3.5 Effect of RHB on soil Si dynamics and its Si release rate

Figure 3.5 shows the effect of RHB application on soil Si availability for rice growth, the increment of plant Si uptake and soil available Si at harvest. The increment in RHB treatments ranged from 30.6 to 455.9 mg SiO_2 pot^{-1} against control. This improvement was at least partly due to the available Si release from RHB (Ma and Takahashi 2002). The improvement also might be due to the biochar cumulative Si release rate during the cropping season (Haynes et al. 2013). Another possible mechanism for the increment of Si uptake in plant and availability in soil might be due to the enhancement of available Si release from the soil through the effect of RHB on soil physiochemical properties (Ponamperuma 1982; Tavakkoli et al. 2011). In this study, the trend of Si release as a function of soil available Si after harvest and plant Si uptake differ with the available Si from RHB at a different pyrolysis temperature (Table 3.2). This is because Si availability in the soil is dependent on many controlling factors such as pH, soil redox potential and the type of existing metals in the soil (Rodrigues and Datnof 2015). Among all the factors listed, soil redox potential is the principal factor in flooding condition like lowland paddy field. It reported that with an increased submerged time of soil, a corresponding reduction in soil redox potential is accompanied by an increase in the solubility of soil Si (Ponnamperuma 1965). This is because sufficient reduction of soil redox potential permits Fe-reducing bacteria to be activated. Thereby causing increased dissolution of Fe oxide especially those attached to Si, hence the release of Si (Mihara et al. 2017). This supports the finding in this study since RHB application had higher soil available Fe compared to control (Figure 3.6), which indicates that RHB possibly enhances the reduction of soil redox. However, the concentration of soil available Fe did not differ significantly among the RHB treatments and thus, does not explain the difference on cumulative SiO_2 of plant Si uptake and soil available Si. This indicates that Fe dissolution is not the main mechanism but Si release from the RHB and other factors could likely be the major controlling factor of the increment of Si availability in the present study condition. Another possible mechanism could be the adsorption of silicic acid (soluble Si) by the pores of the biochar. According to Wang et al. (2018), pores on the surface of the biochar may be effective sites for silicic acid adsorption. This is because the surface of the Si-rich biochars was found to be porous after Si release. The open pores on the surface of biochar are then occupied by silica or phytolith because of similarity in size (Wang et al. 2018). Porosity is a function of temperature increase in biochar. This supports the reduced cumulative available Si obtained from the study in RHB at 600°C and 700°C. Brewer et al. (2014) also found that biochar produced from grass using slow pyrolysis process had its porosity increased with increasing temperature with the highest recorded at 700°C.

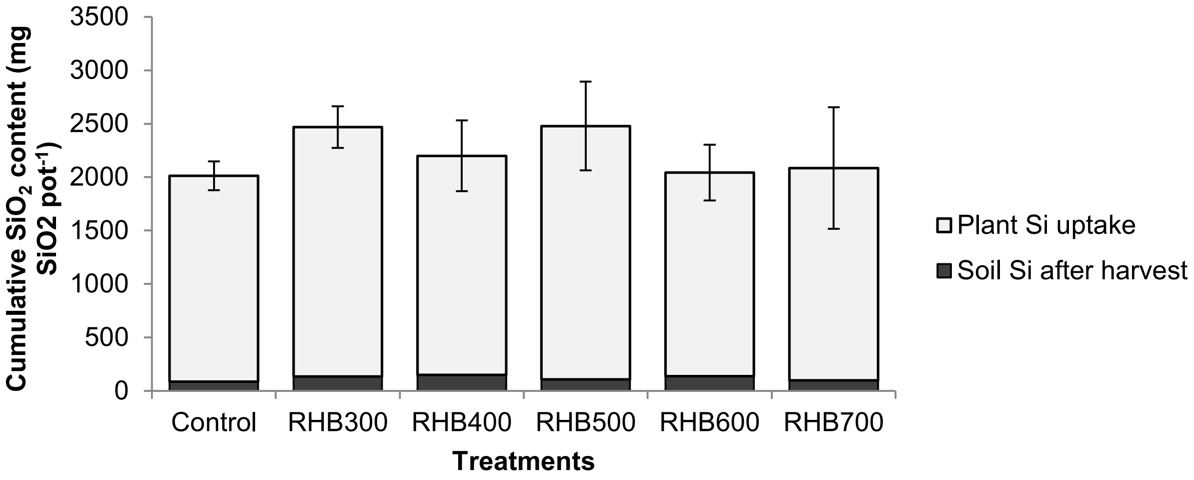

Figure 3.5: The effect of RHB at different pyrolysis temperatures on cumulative Si content during rice growth

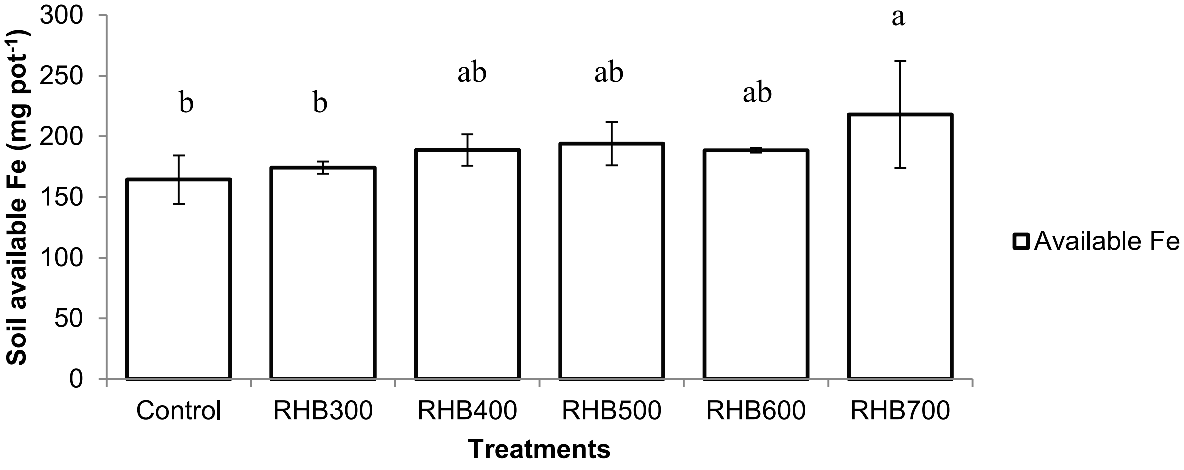

Figure 3.6: The effect of RHB at different pyrolysis temperatures on soil available Fe

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p < 0.05$).

3.4 Conclusion

This study suggests that pyrolysis increases the Si availability in RH. The degree of the Si increment differs at different pyrolysis temperatures. Application of RHB increases plant Si uptake but had insignificant influence on plant growth and yield in this experiment. The enhancement of soil available Si was also observed through the post-harvest effect on soil available Si. The percentage Si release was much higher in RHB treatments than RH during the cropping season. Finally, this study supports the application of RHB as Si releasing agent to increase plant-available Si in the soils that will improve rice plant health.

Chapter 4

Roles of biochar on soil fertility improvement andrice growth performance

4.1 Introduction

Rice (Oryza sativa L.) is the world most important staple food. This is because according to Muthayya et al. 2014, rice supports more than half of the world population. Globally in 2016, rice production amount 759.6 million tonnes (FAO. 2018) with Asia countries accounting for 90% of the world total rice production (Muthayya et al. 2012). Other non-Asia countries including Brazil, the United States, Egypt, Madagascar and Nigeria, which together account for 5% of the rice produced globally (FAO, 2013). In Africa, rice is the fastest growing staple food with its total cereal production raised steadily from 9.3% in 1961 to 15.2% in 2007 (IRRI, 2013). However, only 54% of the rice consumption is supplied locally and the region still imports over 40% of its rice need (FAO, 2018). Although the potential for local rice production in Africa is enormous which include favourable production cost, the rice section still suffers from inefficiencies related to low productivity, a factor strongly controlled by soil related issues.

Maintaining the organic matter threshold level is crucial for soil to uphold its integrity in performing agricultural functions (Izaurralde et al. 2001). In the tropics depletion in soil organic matter, soil nutrients, agricultural productivity and changes in climates due to human activities are posing great threat to agricultural sustainability (Pender, 2009). The use of chemical fertilizers has undoubtly played a vital role toward increasing the agricultural productivity over the past half century. However, the use of chemical or inorganic fertilizer is not a sustainable approach for improving the agricultural yield and soil fertility.

This is because excess use of inorganic fertilizer has the ability to deteriorate not only the soil environment but also lead to the mineralization of organic matter (Palm et al. 2001; Liu et al. 2010). The use of biochar has been considered as a key input for rising and sustaining production and reduces dependence on fertilizer (Barrow 2012).

Since the discovery of black high soil fertility in Amazon River Basin, biochar has attracted the attention of many scientists (Sombroek, 1966; Lehmann and Joseph, 2009). In Japan, biochar has been employed at least since 1697. It was applied in agriculture and horticulture inclusive for improving the vigor of ancient pine trees near shrine (Ogawa and Okimori, 2010). In Spain, biochar was used to improve soil fertility (Olarieta et al. 2010). In SSA, despite the soil fertility challenges facing this region, research on the use of biochar a byproduct of pyrolysis on improving its highly weathered soil and crop performance have received little attention. Based on this, the objective of this work were to evaluate the influence of biochar produced from two agricultural residues rice husk and sugarcane bagasse on improving rice productivity, soil nutrient availability and plant nutrient uptake.

4.2Materials and method

4.2.1 Pot experiment

The soil for the pot experiment was collected from Matsue, Japan. The two agricultural biomass (rice husk and sugarcane bagasse) used for the biochar was produced by the Meiwa Co. Ltd, Kanazawa, Japan following the method described in chapter 2. Prior to the pot experiment, the biochar together with the uncharred biomass was analyzed (Described in chapter 2). The data collection in the pot experiment was the same with that described in chapter 3.

4.2.2 Soil and plant Analysis

The soil analytical method was the same with that described in chapter 3. For plant analysis, the total plant nutrient were determined after digestion of 0.05g of plant part with HNO_3 at 160°C for 5 hours using Teflon vessel and washed into 25 ml conical flask. The supernatant was measured by Inductively Coupled Plasma Spectroscopy (Model ICPE-900, Shimadzu Kyoto Japan). The uptake of nutrient by rice plant from each pot was calculated as follows:

$$\text{Uptake (g pot}^{-1}\text{)} = \text{Nutrient concentration in plant x the plant dry weight in each pot}$$

4.2.3Statistical analysis

Analysis of variance (ANOVA) and Duncan's multiple range tests were used to determine the statistical significance of the RHB and SBB treatments effect on rice plant growth performance, soil chemical properties and plant nutrient uptake using SPSS IBM 20.0. 5% probability ($P < 0.05$) was considered to be statistically significant.

Figure 4.1: Plant growth observation

4.3 Results and Discussion

4.3.1 Chemical properties of used soil and biochar

The soil used is low in soil nutrient with the exception of available P (248.3 mg P_2O_5 kg^{-1}) and Si (138.1 mg SiO_2 kg^{-1}) (See chapter 3). The biochar used content high plant nutrient compared to that present in the used soil (see chapter 2).

4.3.2Effect of biochar on rice plant growth, yield and yield components

Table 4.1 shows the effect of RH, RHB, SB and SBB on rice growth, yield and yield components. From the result obtained, the addition of biochar produced from both plant residue (RHB and SBB) significantly ($p < 0.05$) increased shoot biomass, root biomass and tiller numbers with no significant increase in plant height and yield. The lowest values of shoot biomass (27.3g pot^{-1} and 24.8g pot^{-1}), root biomass (7.5g pot^{-1} and 6.3g pot^{-1}) and tiller number (19.3 and 18.7) were recorded on the pots amended with the uncharred residues of rice husk and sugarcane bagasse respectively. This might be due to N immobilization caused by incorporating plant residue with high C/N ratio, hence low yield. According to Vigil and Kissel 1991, application of residue with low C: N ratio encourages mineralization but applying residue with a high C: N ratio advances N immobilization.

Comparison between control (no biochar amendment) and the biochar treated pots (RHB and SBB); the result showed that control pots have higher root biomass (16.3 g pot^{-1}) than the amended pots. This is because biochar has the ability to retain nutrients that will improve productivity (Abebe et al 2012). Although we used pots without drainage holes, which prohibited nutrient from leaching out of the pot, biochar may accumulate nutrient and allow plant root to effectively uptake nutrients. Thus, RHB and SBB treatments might reduce the need for root elongation in search of the nutrients. The control pots (no biochar amendment) tiller numbers and the shoot biomass showed no significant difference with RHB and SBB treatments. This implies that smaller root biomass in RHB and SBB treatments did not limit the shoot growth. Although no statistical difference was observed in tiller number and shoot biomass, the highest tiller number (25.3 and 24.0) and shoot biomass (33.3 g pot^{-1} and32.2 g pot^{-1}) against control were from pots amended with RHB at 700^{o}C and SBB at 400^{o}C respectively. The grain yield also showed no significant difference in this experiment. This was because the plant was grown under stress - free condition such as pest, disease, drought and so on.

Table 4.1: Effect of Biochar on Rice Plant Growth, Yield and Yield Components

Treatments	Plant Height	Tiller number	Root weight	Shoot weight	Root – Shoot ratio	Yield
	cm		g pot-1			
Control	87.7a	24.0ab	16.3a	30.7ab	0.52a	19.8a
RH	90.3a	19.3b	7.5b	27.3b	0.268c	16.3a
RHB300	89.0a	24.7ab	10.2ab	31.6ab	0.324bc	19.9a
RHB400	83.6a	23.0ab	14.1a	31.2ab	0.450a	17.7a
RHB500	84.8a	25.0ab	11.8a	31.2ab	0.380ab	18.6a
RHB600	83.5a	22.7ab	10.7ab	30.1ab	0.353abc	20.0a
RHB700	85.2a	25.3a	13.9a	33.3a	0.419ab	20.0a
Control	87.7a	24.0ab	16.3a	30.7ab	0.52a	19.8a
SB	82.8a	18.7b	6.3b	24.8b	0.254b	18.3a
SBB350	86.7a	22.7a	12.2a	31.7a	0.384a	16.5a
SBB400	86.3a	24.0a	10.7ab	32.2a	0.332ab	19.2a
SBB500	84.2a	21.7ab	9.1ab	28.6a	0.318ab	16.1a
SBB600	89.9a	22.0ab	8.9ab	30.1a	0.293ab	19.7a
SBB700	86.3a	23.0a	10.9a	31.3a	0.343ab	18.4a

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p< 0.05$).

4.3.3 Effect of biochar on selected soil chemical properties

Table 4.2 showed the effect of RH, RHB, SB and SBB treatments on some selected soil chemical properties. The addition ofbiochar gave a significant ($p < 0.05$) decreased on soil pH compared to the unamended pots (control).This might be attributed to uptake of nutrient by the crop (Gaskin et al. 2010). Soil exchangeable K showed significant effect while soil available P, Fe, Zn, Mn and exchangeable Ca, Mg and Na gave no significant effect with the addition of biochar. The soil exchangeable K ranged from 0.126 to 0.159 cmol$_c$ pot^{-1} and 0.129 to 0.173 cmol$_c$ pot^{-1} in RHB and SBB treatments respectively with its maximum on RH (0.159 cmol$_c$ pot^{-1}) and SBB at 500°C (0.173 cmol$_c$ pot^{-1}). Charring of biochar increases the available K in RHB while SBB gave a decrease. The reason was due to the different chemical processes posed by the different biomass (Muthadhi et al. 2007; Van Lith et al. 2008- See chapter 2). In relation to soil exchangeable K, its response also differs. The low exchangeable K found on RHB treated pots when compared with its uncharred counterpart (Table 4.2), could be liken to the chemistry of K in flooded condition. According to Fageria et al 2011, in reduced condition, large fraction of K ion are being exchanged from the exchangeable complex (both biochar and soil exchangeable complex) into the soil solution by relative large amount of Fe ions. Thus, leading to greater available K for plant uptake and hence a reduction in the exchangeable site (Patrick and Mikkelsen 1971).Although SBB treated pots showed significant effect ($p < 0.05$) in soil exchangeable K, no specific trend was observed (Table 4.2). Sugarcane bagasse contains lignocelluloses which enhanced microbial growth and might vary widely irrespective of the pyrolysis temperature. Lignocelluloses might influence Fe dissolution by increasing the number Fe reducing bacteria in an anaerobic condition. According to Fageria et al 2011, the release of relatively large amount of Fe will also enhance the displacement of some K ions from the exchangeable complex to the soil solution.

Application of biochar did not significantly influence soil available Zn and Mn but showed significant effect on soil available Fe in both RHB and SBB (Table 4.2). The soil available Fe ranged from 164.1 to 218.2 mg pot^{-1} and from 164.1 to 199.1 mg pot^{-1} in RHB and SBB respectively. The overall maximum was from pot treated with RHB at 700°C (218.2 mg pot^{-1}).Sufficient reduction of soil redox potential which is obtainable in a reduced condition permits Fe-reducing bacteria to be activated, hence, increase dissolution of Fe oxide (Mihara et al 2017). From the result an increasing trend was observed with RHB while SBB showed no specific trend. This indicates that RHB application could have a great impact on soil redox potential (Nwajiaku et al. 2018). The trend found in SBB could also be related to the activities of Fe- reducing bacteria in the present of lignocelluloses (Tejirian and Xu, 2010).

Table 4.2:Effect of biochar on soil chemical properties

Treatments	Soil pH	Available P	Exchangeable cations				Available micronutrients		
			Ca	Mg	K	Na	Fe	Zn	Mn
			cmolc/ pot				mg/pot		
Control	6.38a	225.7	5.9	1.8	0.129b	3.8	164.1b	1.41	109.4
RH	5.79c	223.0	5.1	1.6	0.159a	3.5	170.0b	1.28	126.4
RHB300	5.90bc	239.3	5.4	1.7	0.134b	3.7	174.3b	1.16	115.2
RHB400	5.99b	240.3	5.4	1.7	0.126b	3.5	188.9ab	1.28	110.1
RHB500	5.98b	262.3	5.1	1.6	0.131b	3.6	193.4ab	1.30	121.2
RHB600	5.94bc	252.0	5.2	1.6	0.132b	3.5	188.6ab	1.31	112.7
RHB700	5.93bc	248.7	5.5	1.6	0.130b	3.7	218.2a	1.50	113.6
Control	6.38a	225.7	5.9	1.8	0.129b	3.8	164.1b	1.41	109.4
SB	5.83c	227.7	4.9	1.5	0.155ab	3.1	199.1a	1.34	123.5
SBB350	5.86c	267.7	5.1	1.5	0.132b	3.8	187.1ab	1.25	117.9
SBB400	5.98bc	261.0	5.3	1.6	0.135b	3.8	189.1ab	1.35	114.3
SBB500	5.84c	261.3	5.0	1.6	0.173a	3.6	188.8ab	1.32	113.1
SBB600	6.03b	257.0	5.1	1.6	0.132b	3.4	181.7ab	1.19	115.2
SBB700	6.03b	263.7	5.3	1.6	0.138b	3.7	188.0ab	1.35	112.5

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p < 0.05$).

4.3.4 Effect of biochar on rice shoot nutrient uptake

4.3.4.1 Effect of biochar on rice shoot macronutrient uptake

Table 4.3 showed the effect of RH, RHB, SB and SBB on rice shoot macronutrient uptake. Ca, Mg, K and P shoot uptake showed significant ($p < 0.05$) effect among the RHB treatments while SBB treatments was significant only on P shoot uptake. In relation to pyrolysis temperature, no specific trend was observed among the RHB and SBB treatments. They ranged from 71.3 to 262.1mg pot^{-1} and 94.2 to 118.8mg pot^{-1}(Ca), 80.3 to 197.2mg pot^{-1} and 98.2 to 135.3mg pot^{-1} (Mg), 110.3 to 167.8 and 91.6 to 156.7mg pot^{-1}(P) and 117.2 to 336.3mg pot^{-1} and 195.3 to 439.6mg pot^{-1} (K) in RHB and SBB treatments respectively. The highest Ca, Mg, P and K were 262.1mg pot^{-1} and 118.8mg pot^{-1} (RHB500 and SBB400), 197.2mg pot^{-1} and 135.3mg pot^{-1} (RHB500 and SBB600), 167.8mg pot^{-1} and 156.7mg pot^{-1} (RHB700 and control) and 336.3mg pot^{-1} and 439.6mg pot^{-1} (RHB600 and SBB600) in RHB and SBB treatments respectively.

Neglecting the significant level, the result obtained reveals that biochar amendments could improve nutrient uptake. This is because pyrolyzed biochar possess greater negative surfaces, charge density and higher surface area than other organic amendments (Somebroek, 1993).

P shoot uptake was significantly influence by the addition of both RHB and SBB but in a decreasing trend except RHB at 700°C which showed an increased trend (Table 4.3). Some biochar can be a potential P source and some can adsorb P efficiently from solution (Peng et al. 2012, Yao et al. 2013). From the result obtained, it suggested that the RHB and SBB biochars used in this experiment could play a role in retaining P from the solution. The high P uptake found in RHB at 700°C could be a reflection of surface characteristics (Han et al. 2016).

Although, no specific trend was observed in relation to pyrolysis temperature of the biochar, SBB treated pots possess higher K shoot uptake. In Ca and Mg, RHB treated pots possess high Ca and Mg shoot uptake compare to SBB treated pots. This could be due to the high antagonistic properties between K and other base elements like Ca, Mg and Na. According to Gunarathne et al. 2017 rice biochar cations especially K and Na may directly or indirectly depress Ca uptake particularly at low Ca concentration. In relation to Mg content in plant tissues, Ohno and Grune, 1985 stated that high K content in plant tissues could lead to the depression of Mg content through the antagonistic interaction mechanism.

4.3.4.2 Effect of biochar on rice shoot micronutrient uptake

The effect of biochar on shoot micronutrients (Fe, Zn and Mn) uptake showed significant ($p < 0.05$) effect with RHB treatments while SBB treatments were not significantly influence (Table 4.3). They ranged from 9.8 to 19.2mg pot^{-1}, 0.86 to 1.61mg pot^{-1} and 23.0 to 97.9mg pot^{-1} in Fe, Zn and Mn respectively. The highest Fe (19.2 mg pot^{-1}), Zn (1.61 mg pot^{-1}) and Mn (97.9 mg pot^{-1}) were from pots treated with RHB at 500^{o}C.Although no specific trend was observed among RHB and SBB treatments in shoot micronutrient uptake in relation to pyrolysis temperature, RHB treated plants gave higher shoot uptake of Fe and Mn while Zn was higher in SBB treated plants. The low uptake of Fe found on SBB treated plants could be a reflection of the Fe-K displacement on the exchangeable site (Fageria et al. 2011).Like the activity of Fe ion in a flooded condition, the release of relative large amount of Mn ion could also lead to the displacement of K in the exchangeable site, hence low content of Mn for plant uptake by the SBB treated plants. In the Zn shoot uptake though significant with RHB treatments, both treatments were generally low. This because there is an established knowledge that Zn concentration is highly controlled by soil pH. According to Fegeria et al. 2011, Zn concentration decreases with increasing soil pH due to flooding. The wide variation found among the treatments is because though the mobility and the bioavailability of elements is a function of biochar type, it remains unknown to what extent biochar can influence translocation and accumulation of these nutrients (Kasozi et al. 2010).

Table 4.3:Effect of biochar on rice shoot nutrient uptake

Treatments	Macronutrients				Micronutrients			
	P	Ca	Mg	K	Fe	Zn	Cu	Mn
	mg/pot				mg/pot			
Control	156.7ab	116.6bc	134.6abc	223.5bc	11.6b	1.22abc	0.77	45.7b
RH	118.9ab	71.3c	80.3c	127.2bc	9.8b	0.89bc	0.53	23.0b
RHB300	137.9ab	183.9ab	165.9ab	195.0bc	11.4b	0.86c	0.58	63.3ab
RHB400	139.3ab	136.2bc	120.4bc	117.2c	9.9b	1.38abc	0.66	32.6b
RHB500	110.3b	262.1a	197.2a	243.7ab	19.2a	1.61a	0.77	97.9a
RHB600	123.1ab	141.0bc	147.7abc	336.3a	12.3ab	1.47ab	0.71	65.6ab
RHB700	167.8a	193.3ab	168.4ab	147.1bc	14.8ab	1.52a	0.78	50.7ab
Control	156.7a	116.6	134.6	223.5	11.6	1.22	0.77	45.7
SB	110.3b	98.5	102.2	196.1	11.3	1.41	0.68	36.3
SBB350	126.8ab	102.9	111.7	195.3	8.3	1.54	0.74	31.6
SBB400	123.5ab	118.8	127.4	243.8	8.4	1.55	0.75	38.4
SBB500	116.3ab	94.2	98.2	216.1	8.2	1.14	0.69	36.3
SBB600	91.6b	113.3	135.3	439.6	8.3	1.36	0.78	50.5
SBB700	120.4ab	117.4	132.3	254.0	8.3	1.79	0.66	47.6

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p< 0.05$).

4.3.5 Effect of biochar on rice grain nutrient uptake

Table 4.4 showed the effect of biochar on rice grain macronutrient (Ca, K, Mg and P) uptake. Ca, K, Mg and P rice grain uptake was significantly ($p < 0.05$) influenced by the addition of SBB treatments while RHB treatments was not significant ($p < 0.05$). In relation to the pyrolysis temperature no specific trend was observed. The SBB macronutrient grain uptake ranged from 3.4 to 4.4mg pot^{-1}, 29.4 to 43.7mg pot^{-1}, 16.7 to 24.9mg pot^{-1}and 94.6 to 135.5 mg pot^{-1} in Ca, K, Mg and P respectively. The highest Ca (4.4mg pot^{-1}), K (43.7mg pot^{-1}), Mg (24.9 mg pot^{-1}) and P (135.5 mg pot^{-1}) were from pot treated with SBB600 (Table 4.4). RHB treatments though not significant, possess a no consistence trend of uptake in the shoot Ca uptake(Table 4.4). The Ca grain uptake was also not consistent as low Ca was observed in the grain uptake as pose to that found on the shoot. The low Ca uptake on some RHB treatments is as a result of immobile nature of Ca ion (Sharma et al. 2017). According to White 2001, Ca concentration found in leaves/straw depends greatly upon the phyto-availability of Ca in the rhizosphere and the transpirational water flux but are restrained in the straw due to its immobility in the phloem. Unlike Ca, the trend possessed by K uptake in the shoot is maintained in the grain K uptake. This is because K ion is very mobile in plant and as such its uptake in the grain is expected (Karley and White, 2009). The micronutrient grain uptake showed no significant effect with biochar amendments with the expectation of Cu in RHB treatments and Mn in SBB treatments (Table 4.4). They ranged from 0.38 to 0.59 mg pot^{-1} (Cu) and 0.09 to 0.34 mg pot^{-1} (Mn) in RHB and SBB treatments respectively.

Table 4.4: Effect of biochar on rice grain nutrient uptake

Treatments	Macronutrients				Micronutrients			
	P	Ca	Mg	K	Fe	Zn	Mn	Cu
	mg/pot				mg/pot			
Control	116.8	4.2	20.7	30.6	0.38	0.81	0.26	0.51ab
RH	99.0	3.6	18.0	29.0	0.33	0.72	0.26	0.38b
RHB300	107.4	4.3	19.2	28.2	0.50	0.82	0.16	0.43ab
RHB400	105.4	3.5	18.8	36.8	0.41	0.61	0.19	0.41b
RHB500	113.1	4.0	20.5	32.4	0.39	0.84	0.27	0.50ab
RHB600	122.4	4.5	22.6	32.7	0.38	0.85	0.30	0.59a
RHB700	118.7	3.7	21.1	29.0	0.30	0.81	0.17	0.44ab
Control	116.8ab	4.2a	20.7abc	30.6cd	0.38	0.81	0.26ab	0.51
SB	110.4ab	4.1ab	20.1abc	35.2abcd	0.71	0.80	0.30ab	0.44
SBB350	96.7b	3.4b	18.9bc	29.4d	0.34	0.63	0.22ab	0.40
SBB400	118.2ab	3.9ab	22.2ab	39.2abc	0.46	0.66	0.23ab	0.51
SBB500	94.6b	3.7ab	16.7c	33.4bcd	0.34	0.73	0.09b	0.39
SBB600	135.5a	4.4a	24.9a	43.7a	0.40	0.94	0.34a	0.50
SBB700	111.0ab	3.7ab	20.3abc	41.1ab	0.34	0.66	0.09b	0.54

Note: For each material (RHB and SBB), the different alphabet in a column showed statistical difference ($p< 0.05$).

4.5 Conclusion

The results obtained revealed that the biochars in this experiment can be used as soil amendment though its efficacy as soil amendments to improve crop and soil productivity should not be generalized. This is because the chemical and physical characteristics of biochar vary widely and their interactions on improving crop and soil productivity need to be uniquely evaluated. In relation to plant agronomical parameter no significant effect was observed in this experiment. A further study in a field environment is recommended to fully evaluate the in-situ physical and chemical effect of the studied biochar on crop productivity, soil improvement and nutrient uptake.

Chapter 5

Underestimation of Silicon determination in plant samples

5.1 Introduction

The current gravimetric analysis for the measurement of the silicon content of plant required more than 1 g dry matter of plant sample and more than 17 hour for digestion, drying, filtration, dehydration and weighing. The wet digestion method with HNO_3 and dissolution with boric acid, followed by calorimetric determination, can be applied for 50 mg of plant sample, but required 24 hours from extraction to determination. The wet digestion method also cannot be used to actually quantify the total amount of silicon, since some are lost during the boric acid dissolution process through volatilization of silicon as SiF_4 at high concentration. Therefore, in the present study, we tend to avoid silica corrosiveness as well as lost of silicon through vapourization; hence diluted hydrofluoric acid solution method for plant silicon determination according to Saito et al. 2005 was used. The Si values in rice straw were comparable with other studies unlike that in the rice husk. For instance Si content in rice straw presented by Mihara et al. (2017) using Saito et al, 2005 plant Si analytical method ranged from 43.2 to 70.2 g kg^{-1} and was comparable with the rice straw Si content obtained in the present work (See chapter 3, Table 3.4). However, the rice husk Si content in the present study seemed underestimated. Previous researches like Yao et al. (2016), Igwebike-Ossi, (2017) and Guntamukkala and Pusarla (2017) presented the Si contents in the rice husk ranging from 90 to 260 g kg^{-1}, which was more than 7-20 times higher than that of the present study (Table 3.4). This means that some factors might have limited Si dissolution in rice husk in the present study. A possible factor that might hinder dissolution could be crystallization of Si in rice husk, although we could not state categorically what could have hindered dissolution. In order to find out the cause and improve the analysis method, the analysis method was examined with some modification in this chapter.

5.2 Materials and Method

5.2.1 Initial Plant Silicon analysis method

The extraction solution (hydroflouride solution, HF) consisting of 1.5M HF (49%):0.6M HCl was prepared under a ventilated hood by combining 1volume of concentrated hydrofluoric acid (49%), 1 volume of concentrated hydrochloric acid and 18 volume of distilled water. 0.25 g of finely grinded sample was weighed into 50 ml (15 ml) plastic centrifuge tube and 5 ml of extracting solution (HF) was added and shake for 1 hour at 120rpm. It was then allowed to stay overnight for better extraction. 20 ml of distilled water was added after which hand shaking was applied. The tube was allowed to stand for some time for the plant sample to settle down or centrifuge to enhance settlement. The supernatant was determination calorimetrically at 400 nm absorption.

5.2.2 Modified Plant Silicon analysis method

In order to explore any possible solution to overcome underestimated Si in rice husk we implored some modification on the initial plant Si analytical method by Saito et al. 2005.The method was the same with the initial plant silicon analytical method with a little modification on the shaking time (1 hour 10 min) and on speed resolution (150 rpm).

5.2.3 Silicon determination method

See section 3.2.3 in chapter 3 page 35.

5.3 Results and Discussion

Table 5.1 showed the maximum amount of silica measured with both the original HF solution according to Saito et al. 2005 and a modified analytical method. They ranged from 13.2 to 15.5 g kg^{-1} and from 11.8 to 14.6 g kg^{-1}. The result showed that modification of the analytical method did not improve the amount of total silica extracted at all, although the shaking time and the speed were increased.

Table 5.1: The total Si from rice husk biochar with the initial HF solution and the modified HF solution

Biochar	Initial method	Modified method
	g kg^{-1}	
RHB300	13.9	14.6
RHB400	15.5	14.0
RHB500	13.6	13.2
RHB600	13.2	11.8
RHB700	14.5	13.7

We need to further increase the shaking time and the speed in order to examine the effect of modification in the shaking process. Although we could not find out any reason of the underestimation, it is worthy trying to adopt pre-treatment of the rice husk before extraction which could possibly enhance Si dissolution. According to Javed et al. 2008, treating rice husk with potassium permanganate (KMnO4) has not only reduced the cellulose contents of the rice husk but also has acted as an oxidizing agent in thermal degradation process and generated more amorphous silica. A pre-treatment to destruct the carbon structure of rice husk may enhance the dissolution of Si. We need further examination on this issue.

Chapter 6

General Conclusion

The study examined how changes in nutrient and elemental composition of rice husk and sugarcane bagasse at varying pyrolysis temperature can improve rice plant productivity and soil fertility under lowland rice cultivation. It also evaluated how specifically pyrolysis could enhance the silicon content in rice husk for the improvement of soil available silicon. In line with the objectives of this study the major findings are highlighted below.

Pyrolysis temperature impacts a significant change on the nutrient and elemental composition of the produced biochar (RHB and SBB). The result showed that biochar yield and total nitrogen decreased with increasing pyrolysis temperature while ash content, pH, EC, total carbon, extractable Ca, Mg, Na, available phosphorus and silica were increased. Also, RHB extractable K showed increase with increasing pyrolysis temperature, while in SBB it decreased. In all, it was observed that an increase in pyrolysis temperature leads to the generation of biochar with high nutrient content. Among the two biochars, RHB at high pyrolysis temperature produced nutrient rich biochar with high pH, EC, ash content, available silicon, phosphorus, extractable base cations for acidic soil amendment.

Pyrolysis temperature can improve the silicon (Si) availability in the rice husk residue. Its application on soil can improve the soil available Si as was observed in soil available Si post harvest effect. Also it was observed that application of rice husk biochar not only improved soil available Si but also enhanced Si uptake by rice plant. This is achieved through the cumulative Si release by the biochar throughout the cropping season and enhancement of available Si release from the soil through the effect of RHB on soil physicochemical properties. Hence, application of RHB as Si releasing agent to increase plant-available Si in the soils can improve rice plant health.

Pyrolysis temperature influences soil available nutrient as well as nutrient uptake by the rice plant but its effect showed no specific trend. The result also revealed that though RHB and SBB can be used as amendment; its efficacy cannot be generalized. This is because the chemical and the physical characteristics of biochar vary widely in the soil and their interaction on improving crop and soil productivity need to be uniquely evaluated.

Finally, pyrolysis of agricultural waste biomass could be a promising method of improving the nutrient composition of the produced biochar. On aspect of silicon application for the improvement of rice productivity, pyrolysis of rice husk by controlling the heating temperatures is an effective way of improving rice husk as Si amendment. Thus, the use of pyrolyzed rice husk could be an alternative way to locally source Si in the absent of Si fertilizer which is environmental friendly for local farmers in the Sub-Saharan Africa. Therefore this method should be considered as a practical option for not just improving rice production but also a way to manage waste generated in agricultural sector. It is therefore necessary for the government to develop an innovative process, which can generate high temperature. This will be a key priority for the local communities' to improve the productivity and quality of the produced biochar.

References

Abebe N., Endalkachew K., Mastawesha M. and Gebermedhin A.(2012). Effect of biochar application on soil properties and nutrient uptake of lettuces (Lactuca sativa) grown in chromium polluted soils, Jimma, Ethiopia. American-Eurasian J. Agric. and Environ. Sci. 12 (3): 369-376.

Acquaya, D. M. and Tinsley, J. (1964). Soluble silica in soils. Experimental Pedology, Butterworth Co. Ltd., London, England, pp. 127 – 148.

AfricaRice (2018). Rice trend in Sub-Saharan Africa (2008 – 2018) by Dr Harold Roy-Macauley on September 25, 2008. www.africaRice.org

Ahmedna M., Johns M. M., Clarke S. J., Marshall W. E. and Rao R. M. (1997). Potential of agricultural by-product-based activated carbons for use in raw sugar decolorization. J. Sci. Food Agri. 75,117–124.

Amonette J. and Joseph S. (2009). Characteristics of Biochar: Micro Chemical Properties. In: Lehmann, J. and Joseph, S., Eds., Biochar for Environmental Management: Science and Technology, Earthscan, London, pp 33-52.

Antal Jr. M. J. andGrønli, M. (2003). The Art, Science, and Technology of Charcoal Production. Ind. Eng. Chem. Res 42 (8): 1619–1640.

Balasubramanian, V., Sie, M., Hijmans, R.J., Otsuka, K., (2007). Increasing Rice Production in Sub-Saharan Africa: Challenges and Opportunities. Adv. Agron. 94, 55-133.

Barrow C. J. (2012). Biochar: Potential for countering land degradation and for improving agriculture. Applied Geography 34: 21–28.

Beckwith R. S. and Reeve R (1964). Studies on soluble silica in soils II - The release of monosilicic acid from soils. Aust J Soil Sci 2:33-45.

Beesley L., Moreno-Jiménez E., Gomez-Eyles J. L., Harris E, Robinson B. and Sizmur T. (2011) A review of biochars' potential role in the remediation, re-vegetation and restoration of contaminated soils. Environ Pollut159:3269–3282.

Berthelsen S., Hurney A., Noble A. D., Rudd A., Garside A. L. and Henderson A (2001). An assessment of current silicon status of sugar cane production soils from Tully to Mossman. Proceedings of the Austra. Soc. of Sugarcane Techn 23:289–296.

Bol, R., Amelung, W., Friedrich, C., Ostlea, N., (2000). Tracing dung-derived carbon in temperate grassland using 13C natural abundance measurements. Soil Biol. Biochem. 32, 1337–1343.

Bray, R.H. and Kurtz, L.T. (1945). Determination of Total Nitrogen and Available Forms of Phosphorus in Soils. Soil Science, 58, 39-46.

Brewer C. E., Chuang V. J., Masiello C. A., Gonnermann H., Gao X., Dugan B., Driver L.E., Panzacchi P., Zygourakis K. and Davies C. A. (2014). New approaches to measuring biochar density and porosity.Biomass and Bio.energ. 1- 10.

Cabrera A., Cox L., Spokas K. A., Celis R., Hermosin M. C., Cornejo J. and Koskinen, W. C. (2011). Comparative sorption and leaching study of the herbicides fluometuron and 4-Chloro-2-methylphenoxyacetic acid (MCPA) in a soil amended with biochars and other sorbents.J Agric Food Chem 59: 12550-12560.

Camps-Arbestain M., Amonette J. E., Singh B., Wang T. and Schmidt H. P. (2015). A biochar classification system and associated test methods. In Biochar for Environmental Management: Science, Technology and Implementation. 2nd edn. (eds J Lehmann, S Joseph) pp 165-193. Rutledge, London.

Cao X. D. and Harris W. (2010). Properties of dairy-manure-derived biochar pertinent to its potential use in remediation. Bioresour Technol 101: 5222–5228.

Chan K. and Xu Z. (2009). Biochar: Nutrient Properties and Their Enhancement. In: Lehmann, J. and Joseph, S., Eds., Biochar for Environmental Management: Science and Technology, Earthscan, London, UK, pp 67-84.

Chen Y., Yang H., Wang X., Zhang S. and Chen H. (2012). Biomass-based pyrolytic polygeneration system on cotton stalk pyrolysis: influence of temperature. Bioresour Technol, 107: 411– 418.https://doi.org/10.1016/j.biortech.2011.10.074

Chun Y., Sheng Chiou C. T. and Xing B. (2004). Compositions and Sorptive Properties of Crop Residue-Derived Chars. Environ Sci Technol 38 (17) 4649–4655.

Conteh A.M.H., Yan X. and Sankoh F.P. (2012). The influence of price on rice production in Sierra Leone. Agricultural Sciences, Vol.3, No.4, 462-469 (2012)

Datnoff L. A. and Rodrigues F. A. (2005).The role of silicon in suppressing rice diseases. APS net Feature Story, 1-28. http://www.apsnet.org/online/feature/silicon/

Denman K. L. , Brasseur G., Chidthaisong A., Ciais P., Cox P. M., Dickinson R. E., Hauglustaine D. C. Heinze C. E. Holland E. D. Jacob D., Lohmann U., Ramachandram S., da Silva Dias P. L.,Wofsy S. C. and Zhang X.(2007).Coupling between changes in the climate system and biogeochemistry. In: Climate change 2007: The physical sciencebasis (Eds.: S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller). Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge, UK/New York: Cambridge University Press. pp. 499-587.

Ding Y., Liu Y. X., Wu W. X., Shi D. Z., and Yang M. (2010). Evaluation of biochar effects on nitrogen retention and leaching in multi–layered soil columns. Water Air Soil Pollu 213:47–55. https://doi:org/ 10.1007/s11270 -010-0366-4

Dobermann A. and Fairhurst T. (2000). Rice: Nutrient Disorders & Nutrient Management. Handbook Series, Potash and Phosphate Institute (PPI), Potash and Phosphate Institute of Canada (PPIC) and International Rice Research Institute, Philippine, p. 191.

Downie A., Crosky A. and Munroe P. (2009). Physical Properties of Biochar. In: Lehmann,J. and Joseph, S., Eds., Biochar for Environmental Management: Science and Technology, Earth scan, London, pp 13-32.

Epstein E. (1994).The anomaly of silicon in plant biology. Proc. Natl. Acad. Sci., 91, 11-17

Fageria, N. K., Carvalho, G. D., Ferreira, E. P. B and Knupp, A. M (2011). Chemistry of lowland rice soils and nutrient availability. Communications in soil Science and Plant Analysis, 49: 1913 – 1933. DOI:10.1080/00103624.2011.591467

FAO (1996). Production year book, Vol. 50. Rome.

FAO 2013. FAOSTAT Database. Rome: Food and Agricultural Organization.

Fearnside, P.M. (2000). Global warming and tropical land-use change: greenhouse gas emissions from biomass burning, decomposition and soils in forest conversion, shifting cultivation and secondary vegetation. Clim. Change 46, 115–158.

FOASTAT (2014). Sugar cane, production quantity (tons) - for all countries. http://www.factfish.com/statistic/sugar%20cane%2C%20production%20quantity. Accessed 20 December 2017.

Food and Agriculture Organization of the United Nations (2018). Rice market monitor, Volume XXI Issue No. 1. Last accessed July 2018.

Gai X., Wang H., Liu J., Zhai L. and Liu S. (2014). Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate. PLOS ONE 9(12): e113888.https://doi:org/10.1371/journal.pone.011388

Ganesan K., Rajagopal K. and Thangavel K. (2007). Evaluation of Bagasse ash a supplementary cementious material. Cement Concrete Composit 29 (6): 515– 524. https://doi:org/10.1016/j.cemconcomp.2007.03.001

Gaskin J W, Speir R A, Harris K, Das K C, Lee R D, Morris L A, Fisher D S. (2010). Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and Yield. Agronomy Journal, 102, 623-633.

Gaskin J. W., Steiner C., Harris K, Das K. C. and Bibens B. (2008). Effect of low-temperature pyrolysis conditions on biochar for agricultural use. Trans. ASABE 51:2061–2069.

Giddel M. R. and Jivan A. P. (2007). Waste to Wealth, Potential of Rice Husk in India a Literature Review. Proc of the Inter Confer on Cleaner Technol and Environ Mgt PEC, Pondicherry, India. 586-590

Glaser B., Lehmann J. and Zech W. (2002). Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal - a review. Bio.Fert.Soils. **35,**219-230.

GRiSP (Global Rice Science Partnership) (2013). Rice Almanac. 4th Edition, International Rice research Institute, Los Banos.

Gunarathne, V., Mayakaduwa S. and Vithanage M. (2017). Biochar's influence as a soil amendment for essential plant nutrient uptake. In: Essential plant nutrient. M. Naeem (eds), Chapter 3 pp. 47 – 67. Springer International publishing. DOI 10.1007/978-3-319-58841-4-_ 3

Güngör K., Jürgensen A. and Karthikeyan K. G. (2007). Determination of phosphorus speciation in dairy manure using XRD and XANES spectroscopy. J Environ Qual 36: 1856-1863.

Guntamukkala and Pusarala (2017). Silicon management in rice. International Journal of chemical studies. 5(6): 1359 – 1361.

Haefele S., Konboon Y., Wongboon W., Amarante S., Maarifat A., Pfeiffer E. and Knoblauch C. (2011). Effects and fate of biochar from rice residues in rice-based systems. Field Crops Res. 121, 430–441.

Hamdan R., El-Rifai H. M., Cheesman A. W., Turner B. L., Reddy K. R., Cooper W. T. (2012). Linking phosphorus sequestration to carbon humification in wetland soils by P-31 and C-13NMR spectroscopy. Environ Sci Technol 46 (9):4775–4782.

Han B., Fu L., Zhang D, He X., Chen Q., Peng M. and Zhang J. (2016). Interspecies and intraspecies analysis of trehalose contents and the biosynthesis pathway gene family reveals roles of trehalose in osmotic-stress tolerance in cassava. Int. J. Mol Sci 17:E1077

Haynes R. J., Belyaeva O. N. and Kingston G. (2013).Evaluation of industrial wastes as sources of fertilizer silicon using chemical extractions and plant uptake. J. Plant Nutr. Soil Sci.176, 238–248.

Haysom M. B. C. and Chapman L. S. (1975). Some aspect of calcium silicate trials at Mackay. Proc. QueenslSoc of Sugarcane Technol 42:117-122.

Hongguang C., Davey L. J., Paul H., Mohd S. B. and Cheng L. T. (2017). Influence of biochar produced from different pyrolysis temperature on nutrient retention and leaching, Archives of Agro and Soil Sci.

Hunger S., Sims J. T., Sparks D. L. (2008). Evidence for struvite in poultry litter: Effect of storage and drying. J Environ Qual 37: 1617-1625.

Igwebike-Ossi, C. D. (2017). Elemental Analysis of rice husk using proton-induced X-ray emission (Pixe) spectrometry. International Journal of Applied Chemistry 13(4): 801-811.

Imaizumi K. and Yoshida S. (1958).Edaphological studies on silicon supplying power of paddy field. Bull Natl Inst Agric Sci.; 8: 261–304.

Imolehin, E. D. and Wada A. C. (2000). Meeting the Rice Production and Consumption Demands of Nigeria with Improved Technology. International Rice Commission Newsletter. http://www.fao.org/docrep/x7164t/7164t04.html. Accessed 29/6/2018.

International Rice Research Institute (2013). Rice knowledge bank. Los Bãnos, the Philippines. June 29, 2013. http://www.knowledgebank.irri.org/rkb/rice-milling.html.

Izaurralde, R.C., Rosenberg, N. J. and Lal, R. (2001). Mitigation of climate change by soil carbon sequestration: issues of science, monitoring, and degraded lands. Advances in Agronomy, 70: 1 - 75.

Javed, S. H., Naveed, S. Feroze, N. and Kazmi, M. (2008). Extracting silica from rice husk treated with potassium permanganate. Pak. J. Agri. Sci., 45(4):459 – 462.

Johansen J. M., Jakobsen J. G., Frandsen F. and Glarborg P. (2011). Release of K, Cl, and S during Pyrolysis and Combustion of High-Chlorine Biomass. Energy Fuels 25(11): 4961-4971. https://doi:org/10.1021/ef201098n

Juo A. S. R and Sanchez P.A (1986). Soil nutritional aspects with a view to characterize upland rice environments. In: Progress in upland rice research. Los Banos, Philippines: Intl Rice Res.Inst.85 – 91.

Kajiura M., Wagai R. and Hayashi K. (2015).Optimal thermolysis conditions for soil carbon storage on plant residue burning: modeling the trade-off between thermal decomposition and subsequent biodegradation. J. Environ. Qual.44, 228 –235.

Kammann C. I., Linsel S., Gößling J. W. and Koyro H. W. (2011). Influence of biochar on drought tolerance of Chenopodiumquinoa willd and on soil – plant relations. Plant Soil 345:195–210.https://doi:org/10.1007/s11104-011-0771-5

Karley A. J. and White P. J. (2009). Moving cationic minerals to edible tissues: potassium, magnesium, calcium Current Opinion in Plant Biology, 12, 291-298.

Kasozi, G. N., Zimmerman, A. R., Nkedi-Kizza, P., and Gao, B. (2010). Catechol and humic acid sorption onto a range of laboratory-produced black carbons (biochars) Environ. Sci. Technol. 44(16): 6189-6195

Klotzbucher T., Leuther F., Marxen A., Vetterlein D., Horgan F. G. and Jahn R. (2015). Forms and fluxes of potential plant- available silicon in irrigated lowland rice production (Laguna, the Philippines). Plant Soil.

Knicker H. and Hatcher P. G. (1997). Survival of protein in an organic-rich sediment: Possible protection by encapsulation in organic matter. Naturwissenschaften 84: 213-234.

Knoepp J. D., DeBano L. F. and Neary D. G. (2005). Soil Chemistry, In: Neary, Daniel G.; Ryan, Kevin C.; DeBano, Leonard F., eds. 2005. Wild land fire in ecosystems: effects of fire on soils and water. Gen. Tech. Rep. RMRS-GTR-42- Vol.4. Ogden, UT: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station, pp 53-71.

Korndorfer G. H. and Lepsch (2001).Effect of silicon on plant growth and crop yield. In: Datnoff LE, Snyder GH, Korndorfer GH (eds). Silicon in agriculture. Studies in plant science, 8 Elsevier Amsterdam, pp 133 – 147.

Koutcheiko S., Monreal C. M., Kodama H., McCracken T. and Kotlyar L. (2007). Preparation and characterization of activated carbon derived from the thermo-chemical conversion of chicken manure. BioresourceTechnol98: 2459-2464.

Kudeyarova A. Y. (2007). Application of basic chemical concepts to understanding the formation and transformation mechanisms of humic substances: a revue of publications and own experimental data. Euras Soil Sci40:934–48.

Kumar S., Sangwan P., Dhankhar R.Mor V. and Bidra S. (2013). Utilization of Rice Husk and Their Ash: A Review in Res J Chem Env Sci, 1 (5): 126-129.

Lehmann J, Gaunt J, and Rondon M. (2006). Biochar sequestrationin terrestrial ecosystems: a review. Mitig Adapt Strategy Global Change. 11: 403–27.

Lehmann J., Kern D. C., German L. A., McCann J., Martins G. C. and Moreira A.(2003).Soil Fertility and Production Potential. In: J. Lehmann, D.C. Kern, B. Glaser and W.I. Woods (eds.), Amazonian Dark Earths: Origin, Properties, Management. Dordrecht, Kluwer Academic Publishers. pp. 105-124

Lehmann J., Rillig M. C., Thies J., Masiello C. A., Hockaday,W. C. and Crowley D. (2011). Biochar effects on soil biota – A review. Soil Bio and Biochem 43:1812–1836.

Lehmann, J., and Joseph, S. (2009). Biochar for environmental management: An introduction. pp. 1–12. In J. Lehmann and S. Joseph (eds.), Biochar for Environmental Management: Science and Technology. Earthscan Publ., London.

Lei O. and Zhang R. (2013). Effects of biochars derived from different feedstocks and pyrolysis temperatures on soil physical and hydraulic properties. J Soil Sediment 13: 1561– 1572. https://doi:org/10.1007/s11368-013-0738-7.

Li H., Ye X., Geng Z., Zhou H., Guo X., Zhang Y., Zhao H. and Wang G.(2016). The influence of biochar type on long-term stabilization for Cd and Cu in contaminated paddy soils, J. of Hazardous Materials. 304: 40–48.

Liang Y. C., Ma T. S., Li F. J. and Feng Y. J.(1994).Silicon availability and response of rice and wheat to silicon in calcareous soils. Communications in Soil Sci. and Plant Analysis.25: 2285 – 2297.

Liang Y., Sun W. and Zhu Y. (2007).Mechanisms of silicon-mediated alleviation of abiotic stresses in higher plants: a review, Environ Poll; 147: 422 – 428. Linkages, Opportunities, and Constraints. IFPRI, New York, USA.

Liu, E., Changrong, Y., Xurong, M., Wenqing, H., So, H.B., Linping, D., Qin, L., Shuang, L. and Tinglu, F. (2010). Long term effect of chemical fertilizer, straw, and manure on soil chemical and biological properties in north-west China. Geoderma 150, 173–180.

Lutgens, Frederick K and Tarbuck Edward J. (2000). Essentials of Geology, 7th Ed., Prentice Hall.

Ma J. F. (2004). Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses. Soil Science and Plant Nutrition.50: 11 -18.

Ma J. F. and Takahashi E. (2002). Soil, fertilizer and plant silicon research in Japan. Elsevier, Amsterdam .

Ma J.F. (2004).Role of silicon in enhancing the resistance of plants to biotic and abiotic stresses. Soil Science and Plant Nutrition 50: 11 -18.

Ma, J.F. and Yamaji, N. (2006).Silicon uptake and accumulation in higher plants. Trends in Plant Science, 11:392–397.

Marxen A., Klotzbücher T., Jahn R., Kaiser K., Nguyen V. S., Schmidt A., Schädler M. and Vetterlein D.(2016).Interaction between silicon cycling and straw decomposition in a silicon deficient rice production system. Plant Soil. 398: 153-163.

Meng, J.J., Liu, J.Y., Huang, S.P. (2010). Study on biochar under the low-carbon economy. Proceedings of Academic Conference on Low-carbon in Shanxi Province, China 88–92.

Mihara C., Xhui C., Yuki S., Syuhei M. and Akira W. (2017). Relationship between plant-available silicon and reducible iron in irrigated paddy soils, Soil Sci. and Plant Nutr. 63(1), 67-74.

Mukome F. N. D, Zhang X., Silva L. C. R., Six J. and Parikh S. J. (2013). Use of chemical and physical characteristics to investigate trends in biochar feedstocks. J of Agri and Food Chem. https://doi.org/10.1021/jf3049142.

Muthadhi A., Anitha R. and Kothandaraman S. (2007). Rice husk ash properties and its uses: a review. J of the Inst of Eng 88(5): 50-56.

Muthayya, S., Hall, J. Bagriansky, J. Sugimoto, J. Gundry, D., Matthias, D., Prigge, S., Hindle, P., Fanner, M. and Maberly, G. (2012). Rice Fortification—an emerging opportunity to contribute to the elimination of vitamin and mineral deficiency worldwide. Food Nutr. Bull. 33: 296–307

Muthayya, S., Sugimoto, J. D., Montgomery, S. and Maberly, G. F. (2014). An overview of global rice production, supply, trade, and consumption. Annals of the New York Academy of Sciences, 1324(1), 7-14

National Agricultural Extension and Research Liaison Services and Projects Coordinating Units (2004). Field situation study. NAERLS/PCU. October 13, 2003 – January 9, 2004.

National Institute of Agro-Environmental Sciences (NIAES) (1987). Official Methods of Analysis of Fertilizers, 124: 36-48. Foundation Nohrin Kohsaikai, Tsukuba.

Ning D. F., Song A., Fan F. L., Li Z. J. and Liang Y. C.(2014).Effects of slag-based silicon fertilizer on rice growth and brown-spot resistance. PLos One,9 (7). 102681.

Nwajiaku, I.M, Sato, K., Tokunari, T., Kitano, S. and Masunaga, T. (2018). Improvement of Rice Husk Residue Silicon Availability for Replenishing Available Silicon in Paddy Soil. International journal of plant and soil Science 24(2): 1-11

O'Donoghue E. and Hansen J. (2017). *USDA Agricultural Projections to 2026 by* USDA Agricultural Projections No. (OCE-2017-1) 106 pp

Ogawa, M. and Okimori Y. (2010). Pioneering works in biochar research in Japan. Australian Journal of Soil Research, 48: 489-500

Ohno, T., and Grunes, D.L. (1985). Potassium-magnesium interactions affecting nutrient uptake by wheat forage. Soil Sci. Soc. Am. J. 49:685-690

Okigbo, B.N. (1982). In the developmental effectiveness of food in Africa, p. 11-67. New York, Agricultural Development Council.

Okuno T., Sonoyama N., Hayashi J. I., Li C. Z., Sathe C. and Chiba T. (2005). Primary release of alkali and alkaline earth metallic species during the pyrolysis of pulverized biomass. Energ Fuel 19: 2164-2171. https://doi:10.1007/s001140050384

Olarieta, J.R.; Padro, R.; Masip, G.; Rodriguez-Ochoa, R. and Tello E. (2010). 'Formiguers', a historical system of soil fertilization (and biochar production) Agriculture, Ecosystems and Environment 140:27-33.

Olsen S. R. and Sommers L. E. (1982). Determination of available phosphorus.In "Method of Soil Analysis", Vol. 2, Ed. A. L. Page, R. H. Miller, and D. R. Keeney, Madison,WI: American Society of Agronomy, pp 403.

Palm C. A., Gachengo C. N., Delve R. J., Cadisch G. and Giller K. E. (2001). Organic inputs for soil fertility management in tropical agroecosystems: application of an organic resource database. Agriculture, Ecosystems and Environment 83, 27–42.

Parry D.W. and Smithson F. (1964). Types of opaline silica deposition in the leaves of British grasses. Ann Bot London, 28:169-185.

Patcharin W., Wisaroot P. and Akhapon M. (2009). Characterization for post treatment effect of bagasse ash for silica extraction. World Acad Sci, Eng Technol 3: 339-349.

Patrick Jr., W. H. and Mikkelsen, D. S. (1971). Plant nutrient behavior in flooded soil. In Fertilizer technology and use, 2nd ed., ed. R. A. Olson, 187–215. Madison, Wisc.: Soil Science Society of America.

Pender, J. (2009). The World Food Crisis, Land Degradation, and Sustainable Land Management: Linkages, opportunities and constraints. IFPRI, New York, USA.

Peng, F., He, P., Luo, Y., Lu, X., Liang, Y. and Fu, J. (2012). Adsorption of phosphate by biomass char deriving from fast pyrolysis of biomass waste. Clean – Soil Air Water 40, 493–498.

Ponamperuma F. N. (1982). Some aspect of physical chemistry of paddy soils. In proceedings of symposium on paddy soils. Science Press, Beijing. pp 59 – 94.

Ponnamperuma F. N. (1965). Dynamic aspects of flooded soils and the nutrition of the rice plant. In Proceedings of the Symposium Mineral Nutrition of the Rice Plant (1964) John Hopkins Press, Baltimore.pp. 295-328.

Rodrigues F. A. and Datnof L. E. (2015). Silicon and Plant Diseases. Berlin: Springer.

Sahebi M., Hanafi M. M., Akmar A. S. N., Rafii M. Y., Azizi P., Tengoua F. F., Azwa J. N. M. and Shabanimofrad M. (2015). Importance of silicon and mechanisms of biosilica formation in plants. Biomed. Res. Intl.; 1-16.

Saito K., Yamamoto A., Sa T. and Saigusa M.(2005). Rapid, Micro-methods to estimate plant silicon content by dilute hydrofluoric acid extraction and spectrometer molybdenum method. Soil Sci Plant Nutr. 51(1), 29 – 36.

Sakamoto, K. (1958). Studies on the relation between the silica content in the rice plant and the insect pests. Part 6.Jpn J Appl Entomol Z 2:88-92

Savant A. S., Snyder G. H. and Datnoff L. E. (1997). Silicon management and sustainable rice production. Adv, Agron. 58: 151 – 199.

Savant N. K., Korndorfer G. H., Datnoff L. E. and Snyder G. H. (1999).Silicon nutrition and sugarcane production: A Review. J. Plant Nutr. 22 (12):1853-1903.

Sharma D, Jamra G, Singh UM, Sood S, Kumar A, (2017). Calcium Biofortification: Three Pronged Molecular Approaches for Dissecting Complex Trait of Calcium Nutrition in Finger Millet (Eleusine coracana) for Devising Strategies of Enrichment of Food Crops Frontiers in Plant Science, 7, 2028.

Singh B., Singh B. P. and Cowie A. L. (2010). Characterization and evaluation of biochars for their applications a soil amendment. Aust J Soil Res 48: 516–525.

Singh, B. N., Fagde, S, Ukwungwu, M. N., William C., Jagtap, S. S., Oladimeji, O., Effisue, A. and Okhidievbie, O (1997). Rice growing environments and biophysical constraints in different agroecological zones of Nigeria. Met. J., 2(1): 35-44.

Sohl M. (2005). Rice is life in 2004 and beyond. Int. Rice commission Newsletter. 54: 1-10.

Somado, E. A., R.G. Guei and S.O. Keya (eds.) (2008). NERICA: the New Rice for Africa – a Compendium, 2008 edition, Africa Rice Center (WARDA).

Sombroek, W. G. (1966). Amazonian soils. Centre for agricultural publication and documentation. Wageningen: Wageningen University.

Somebroek W (1993). Amounts, dynamics and sequestering of carbon in tropical and subtropical soils. Ambio 22:417–426

Spokas, K.A., W.C. Koskinen, J.M. Baker, and D.C. Reicosky. (2009). Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. Chemosphere 77:574–581.

Takahashi E. (1987). Silica accumulator. In Siliciphilous plant and Calciphilous plant. Noubunkyo, Tokyo, pp. 54 – 103.

Takahashi E. and Okuda A. (1966).The role of silicon. Symposium on the mineral nutrition of rice plant. (International Rice research Institute). Johns Hopkins Press pp. 123 – 146.

Takahashi E., Ma J. F. and Miyake Y. (1990).The possibility of silicon as an essential element for higher plants. Comments on Agric. and food chem. 2: 99 – 122.

Takahashi J. (1961). Physiological disease of rice in Taiwan. Soils Fert. Taiwan. 10 – 14.

Tavakoli E., Lyons G., English P. and Guppy C. N. (2011). Silicon nutrition of rice is affected by soil pH, weathering and silicon fertilisation. J. Plant Nutr. Soil Sci. 174, 437–446.

Tejirian, A., and Xu, F. (2010). Inhibition of cellulase-catalyzed lignocellulosic hydrolysis by iron and oxidative metal ions and complexes. Appl. Environ. Microbiol.76 (23), 7673- 7682.

Thangalazhy-Gopakumar S., Adhikari S., Ravindran H., Gupta R. B., Fasina O., Tu M. and Fernando S. D. (2010). Physiochemical properties of bio-oil produced at various temperatures from pinewood using an auger reactor. Bioresour Technol 101 (21): 8389– 8395. https://doi.org/10.1016/j.biortech.2010.05.040

Tiessen, H., Cuevas, E. and Chacon, P. (1994). The role of soil organic matter in sustaining soil fertility. Nature 371, 783–785.

Todkar B.S., Deshmukh S. M. and Deorukhka O.A. (2016). Extraction of silica from rice husk. Int J Eng Res Dev 12:69–74

Tsai W. T., Liu S. C., Chen H. R., Chang Y. M. and Tsai Y. L. (2012). Textural and chemical properties of swine-manure derived biochar pertinent to its potential use as a soil amendment. Chemosphere 89(2): 198 – 203.

Tsujimoto Y., Muranaka S., Saito K. and Asia H. (2014).Limited Si-nutrient status of rice plants in relation to plant-available Si of soils, nitrogen fertilizer application, and rice-growing environments across Sub-Saharan Africa. Field Crops Research Vol. 155:1 – 9.

Tuck, C. O., Perez E., Horvath, I. T., Sheldon, R. A. and Poliakoff, M. (2012). Valorization of biomass: deriving more value from waste. Science 337:695–699.

UNEP (2009). Converting Waste Agricultural Biomass into Resource: Compendium of Technologies. United Nations Environmental Programme 2009, Division of Technology, Industry and Economics International Environmental Technology Centre Osaka/Shiga, Japan, pp 441.

Van Lith S. C., Jensen P.A., Frandsen F. and Glarborg P. (2008). Release to the Gas Phase of Inorganic Elements during Wood Combustion Part 2: Influence of Fuel Composition. Energ Fuel 22 (3):1598–1609.https://doi:org/10.1021/ef060613i

Van Zwieten L., Singh B., Joseph S., Kimber S., Cowie A. and Chan K. Y. (2009). Biochar and emissions of non-CO_2 greenhouse gases from soil. In: Lehmann J, Joseph S (eds) Biochar for environmental management-science and technology. Earthscan, London, pp 227 –249.

Vigil M. F. and Kissel D. E. (1991). Equations for the amount of nitrogen mineralized from cropresidues. Soil Sci. Soc. Am. J. 55, 757 – 761.

Walsh M. E., Perlack R. L., Turhollow A., de la Torre Ugarte D., Becker D. A., Graham R. L., SlinskyS. E. and Ray D. E. (2000). Biomass feedstock availability in the United States: 1990 State level analysis. Oak Ridge National Laboratory, Oak Ridge. Available via bioenergy.ornl.gov

Wang Y., Xiao X. and Chen B. (2018). Biochar impacts on soil silicon dissolution kinetics and their interaction mechanism. Science Report 1. 1 – 11.

Weaver R. M., Syers J. K. and Jackson M. (1968). Determination of silica in citrate-bicarbonate- dithionite extracts of soils. Soil Sci. Soc. Am. Proc. 32,497-501.

Wickramasinghe D. B. and Rowell D. L. (2006).The release of silicon from amorphous silica and rice straw in Sri Lankan soils, Biol. Fertil. Soils. 42, 231-240.

Wu W., Yang M., Feng Q., McGrouther K., Wang H., Lu H. and Chen Y.(2012).Chemical characterization of rice straw-derived biochar for soil amendment, Biomass Bioenerg. 47,268–276.

Xiao X., Chen B. and Zhu L. (2014).Transformation, Morphology and Dissolution of silicon and carbon in rice straw-derived biochars under different pyrolytic temperatures. Environ. Sci. Technol. 48, 3411-3419.

Xiao, R.; Bai, J.H.; Wang, Q.G.; Gao, H.F.; Huang, L.B., and Liu, X.H., (2011). Assessment ofheavy metal contamination of wetland soils from a typical aquatic-terrestrial Ecotone in Haihe River basin, North China. CLEAN—Soil, Air, and Water, 39(7), 612–618.

Yan L., Yan B. Y., Peng Y. L., Ji Z. J., Zeng Y. X., Wu H. L. and Yang C. D. (2017). Molecular screening of blast resistance genes in rice germplasms resistant to Magnaporthe oryzae. Rice Sci, 24(1):41–47.

Yao X., Xu K. and Liang Y. (2016). Comparing the therm-physical properties of rice husk and rice straw as feedstock for thermochemical conversion and characterization of waste ashes from combustion. Bio. Resource 11(4): 10549 – 10564.

Yao, Y.; Gao, B.; Chen, J.; Zhang, M.; Inyang, M.; Li, Y.; Alva, A. and Yang, L. (2013). Engineered carbon (biochar) prepared by direct pyrolysis of Mg-accumulated tomato tissues: Characterization and phosphate removal potential. Bioresour. Technol., 138, 8−13.

Yoshida S. (1965). Chemical aspects of the role of silicon in physiology of rice plant. Bull. Natl. Inst. Agric. Sci. Series B.; 15: 1 – 58 (J. E).

Yuan J., Xu R. and Zhang H (2011). The forms of alkalis in the biochar produced from crop residues at different temperatures. BioresourceTechnol 102:3488-3497.

Summary in English

Rice is an increasing important crop in many countries in Sub-Saharan Africa (SSA) including Nigeria. This is because of all the staple crops; rice has risen to a position of preeminence due to change in consumer's preference. However, domestic production has never been able to meet the demand, leading to considerable imports. Silicon (Si) has been proven by many researchers to be a beneficial element for rice but local farmers in SSA are not concern on the use of Si fertilizer despite the Si risk deficiency in the area. This may be attributed to the unawareness of farmers on the high demand of Si by rice plant. Aside from Si deficiency risk, soil degradation is also a major challenge facing local rice farmers in SSA. SSA soils are generally low in soil nutrient due to high organic matter mineralization. Application of fertilizers is recommended to tackle the challenges facing low rice production in SSA but the high cost of the fertilizers makes its application difficult for local farmers. To sustain rice production in SSA, there is need to research on alternative local source which are locally available and affordable. The conversion of wastes generated from agricultural produce into biochar and returning it to fields is a practical solution. This is a potentially valuable agricultural practice that can positively affect both the physical and chemical properties of the soil as well as enhance carbon sequestration into the soil. This waste conversion approach will benefit not only the agricultural sector but also play a very important role in handling environmental issues like waste management.

This study examined change in the elemental composition of rice husk biochar (RHB) and sugarcane bagasse biochar (SBB) at varying pyrolysis temperature, with emphasis on evaluating the potentials of these biochars to improve the nutrient status of the soil as well as its uptake by rice plant. In this study, the rice husk and sugarcane bagasse, used were pyrolyzed at 300 – 700°C and 350 – 700°C for RHB and SBB using an experimental electric furnace, respectively.

In an exploratory study, the effect of pyrolysis temperature on two agricultural wastes was assessed. This was done to ascertain possible change in the elemental composition of the produced biochar that can improve rice plant growth and yield. The result reveals that pyrolysis temperature changes induce change in the elemental composition of the used agricultural waste biomass (rice husk (RH) and sugarcane bagasse (SB)). From the result, it was found that biochar yield and total nitrogen decreased significantly ($p < 0.05$) with increasing pyrolysis temperature. The biochar yield ranged from 55% at 300°C to 35% at 700°C and from 27% at 350°C to 22% at 700°C with total nitrogen ranging from 4.9 g kg^{-1} to 3.6 g kg^{-1} and from 6.0 g kg^{-1} to 3.8 g kg^{-1} as well in RHB and SBB, respectively. The ash content, pH, EC, total carbon, 1M ammonium acetate extractable (hereafter, extractable) Ca, Mg, Na, available phosphorus and Si were significantly ($p < 0.05$) increased with increasing pyrolysis temperature in both biochars (RHB and SBB). The maximum ash content (35.6%), pH (10.7), EC (0.40dS m^{-1}), extractable Mg (29 mg kg^{-1}), extractable Na (38 mg kg^{-1}) and available phosphorus (1842 mg kg^{-1}) were from RHB at 700°C while maximum extractable Ca (180 mg kg^{-1}) was from SBB at 700°C. In RHB, extractable K increased significantly ($p < 0.05$) with increasing pyrolysis temperature, while in SBB it decreased. In RHB, the increased in extractable K ranged from 165 to 684 mg kg^{-1} while the SBB extractable K decreased significantly from 396 to 251 mg kg^{-1}. Among the three extractants (0.01M $CaCl_2$, 0.5M HCl and 0.1M citric acid) used for available Si, its maximum in 0.01M $CaCl_2$ was observed in RHB at 700°C (3124 mg kg^{-1}) while 0.5M HCl and 0.1M citric acid were from SBB (7262 mg kg^{-1} and 9313 mg kg^{-1}) respectively at 700°C. In summary, an increase in pyrolysis temperature leads to the generation of biochar with high nutrient content. In all, RHB at high pyrolysis temperature may produce nutrient-rich biochar, with high pH, EC, ash content, extractable base cations, available Si and phosphorus. It could be an option to increase Si availability through acid pre-treatment as the amount of Si extracted from biochar was higher in acid extraction.

Subsequently in this study, a pot experiment was conducted in an experimental glasshouse. The pot experiment aimed at investigating how pyrolysis could enhance the Si availability in rice husk for the improvement of soil available Si. RHB pyrolyzed at varying temperature (300°C – 700°C) was used for this experiment. The experiment units in the pot experiment were replicated into three and arranged in a complete randomized design. The result revealed that RHB could serve as a Si source as its effect on maintaining soil available Si remained after harvest. RHB at 400°C significantly ($p < 0.05$) increased the soil available Si by 61% compared to the original content (93.8 mg SiO_2 pot^{-1}) of the used soil. Also the application of RHB not only improve soil available Si but also improve Si uptake by rice plant. The cumulative amount of Si (soil available Si and the uptake by plant) ranged from 1971.7 of the control to 2478.8 mg SiO_2 pot^{-1} in RHB treatment. The increment in RHB treatments against the control ranged from 30.6 to 455.9 mg SiO_2 pot^{-1}. This increment is because of the cumulative Si release by the biochar throughout the cropping season and also enhancement of available Si release from the soil through the effect of RHB on soil physicochemical properties. In summary, the percentage Si release from treatments was much higher in RHB than RH treatments during the cropping season. Hence, the application of RHB as Si releasing agent to increase soil available Si will improve rice plant growth. The role RHB and SBB played in improving the soil fertility was also investigated in a pot experiment. The result revealed that even though RHB and SBB can be used as amendment; its efficacy could not be generalized. This is because the physical and chemical characteristics of biochar vary widely in the soil and their interaction with soils on improving crop and soil productivity need to be uniquely evaluated.

Finally, based on the results obtained from this study, pyrolysis of agricultural waste biomass is one of the strategies of locally source alternative to silicate fertilizer as well as soil amendment. The present studies confirmed that increasing pyrolysis temperature changes the elemental composition of the agricultural waste biomass. It also affirms that the application of its products (biochar) can improve soil available Si and Si uptake in rice. Therefore, developing an innovative process, which can control the best pyrolysis temperature, would be a key factor for the local communities for optimum utilization of the produced biochar.

Summary in Japanese

米は、ナイジェリアを含むサハラ以南のアフリカの多くの国で重要な作物となってきている。これは消費者の嗜好の変化により、すべての穀物のなかでの米の立場が優先的になってきたためである。しかし、国内生産は決して需要を満たすことができず、かなりの量の輸入につながっている。ケイ素(Si)は、多くの研究者によって稲にとって有用元素であることが証明されているが、サハラ以南のアフリカ地域の農家は、Si不足のリスクにもかかわらずケイ酸肥料の使用に関心を払ってきていない。これは、稲が高いSiの要求度を知らない事が原因である。Si欠乏のリスクとは別に、土壌の劣化もナイジェリアの米農家が直面する大きな課題である。ナイジェリアの土壌は、有機物の分解が速いため一般的に土壌肥沃度が低い。ナイジェリアの低い米生産の課題に取り組むためには、施肥が推奨される。しかし、肥料コストが高いため、地元の農家には容易ではない。ナイジェリアで持続的に米を生産するためには、現地で入手可能で手頃な価格の代替ローカルソースを調査する必要がある。農産物から発生する廃棄物をバイオ炭に転換し農地に還元する事は現実的な解決作である。これは土壌の物理化学性の両方に良い影響を与えると共に土壌への炭素貯留を強化する価値のある農法となり得る。また、この廃棄物を転換するアプローチは農業セクターに利益をもたらすだけでなく廃棄物管理のような環境問題対応にも重要な役割を果たしうる。

本研究では、炭化温度を変化させた籾殻バイオ炭（RHB）およびサトウキビバガスバイオ炭（SBB）の元素組成の変化を調査し、これらのバイオ炭による土壌の養分状態と稲の養分吸収の改善の可能性を評価した。本研究では、籾殻およびサトウキビバガスを電気炉を用いてそれぞれ300-700℃、350-700℃で炭化させた。

まず、ナイジェリアで一般的に生産される 2 つの農業廃棄物を対象に、稲の生育と収量を改善する要因となるバイオ炭の養分組成の変化に対する炭化温度の影響を評価した。その結果、炭化温度の変化は農業廃棄物バイオマス（籾殻（RH）およびサトウキビバガス（SB））の元素組成を変化させる事が明らかとなった。炭化物の収率と全窒素は炭化温度の上昇と共に有意($p< 0.05$）に減少した。炭化物の収率はRHB と SBB でそれぞれ、300℃の 55% から 700℃の 350℃35% と 350℃の 27% から 700℃の 22%、同様に全窒素含量は 300℃の 4.9 g kg^{-1} から 700℃の 3.6 g kg^{-1} と 300℃の 6.0 g kg^{-1} から 700℃の 3.8 g kg^{-1} の範囲で変化した。灰分、pH、EC、全炭

素、1M 酢酸アンモニウム抽出（以下 extr.）Ca、Mg、Na、可給性リンおよび可給性 Si が炭化温度の上昇と共に有意（$p< 0.05$）に増加。灰分(35.6%)、 pH（10.7）、EC（0.40dS m-1）、extr. Mg（29 mg kg^{-1})extr.Na（38 mg kg^{-1}）と phosphorus（1842 mg kg^{-1}）の最大値は 700℃ の RHB であり、extr. Ca（180 mg kg^{-1}）の最大値は 700℃ の SBB であった。RHB では、extr.K は炭化温度の上昇と共に 165 から 684 mg kg^{-1} に有意（$p< 0.05$）に増加したが、SBB では 396 から 251 mg kg^{-1} に減少した。可給性 Si 測定に用いた 3 種類の抽出方法(0.01M $CaCl_2$、0.5M HCl、 0.1M クエン酸)のそれぞれの最高値は 0.01M $CaCl_2$ では 700℃ の RHB で 3124 mg kg^{-1}、0.5M HCl と 0.1M クエン酸では 700℃ の SBB でそれぞれ 7262 mg kg^{-1} と 9313 mg kg^{-1} であった。要約すると、炭化温度の上昇は養分含有量の高いバイオ炭を生成した。高い炭化温度での RHB は、高 pH、EC、灰分、extr.塩基類、および可給性 Si,P 含有量が高い養分豊富なバイオ炭を生成できる。酸での抽出による Si の抽出量が大きかったので、酸の前処理は有効性 Si を増加させる選択肢になり得ると考えられた。

次に、実験用ガラス室でのポット試験により炭化がどのようにして土壌中可給性 Si の改善に資するもみ殻中の可給性 Si 含量を増強するかを評価した。300℃ - 700℃ で炭化されたも RHB 試験に供試した。試験は 3 連で乱塊法により実施された。結果、RHB は収穫後の土壌中可給性 Si 維持に効果的な Si 供給源として役立つことが明らかになった。RHB at 400℃ で炭化した RHB は土壌中の有効性 Si を元の土壌中の含有量(93.8 mg SiO_2 pot^{-1}）から有意($p < 0.05$)に 61%増加させた。また、RHB の施用は、土壌中可給性 Si を改善するだけでなく、稲の Si 取り込みを改善した。土壌中可給性 Si と植物による Si 吸収量は RHB を施用していない対象区の 1971.7 から RHB 処理区の 2478.8 mg SiO_2 pot^{-1} であり、RHB 処理による増加分は、対象区に対して 30.6 から 455.9 mg SiO_2 pot^{-1} の範囲であった。この増加は、RHB からの収穫期を通じての累積 Si 放出と、RHB が土壌の物理化学的性質に及ぼす効果による土壌からの可給性 Si 放出の増大のためである。要約すると、作期中の Si 放出率は、RH より RHB 処理ではるかに高かった。したがって、RHB の施用は Si 放出剤として土壌中可給性 Si を増加させ稲の生育を改善する。

ポット試験で RHB と SBB の土壌肥沃度改善効果について調べた結果、RHB と SBB は改良資材として使用できるものの、その有効性を一般化することはできなかった。これは、biochar の物理化学的特性が土壌で広く変化するためであり、作物および

土壌生産性の改善に対するバイオ炭と土壌との相互作用は今回の試験とは分けて評価される必要がある。

　最後に、この研究から得られた結果に基づいて、農業廃棄物バイオマスの炭化は、Si 肥料や土壌改良材の地元の資材を用いる代替戦略の一つとなりえることが示された。本研究において、炭化温度の上昇が農業廃棄物バイオマスの元素組成を変化させることを確認した。また、バイオ炭の施用は、土壌中可給性 Si および稲の Si 吸収を改善できることを確認できた。したがって、最適な炭化温度を制御できる革新的なプロセスを開発することは、生産されたバイオ炭の最適な利用のために、地域社会にとって鍵となります。

List of publications

Ifeoma Monica Nwajiaku, John Seye Olanrewaju, Kuniaki Sato, Takeo Tokunari, Shigeru Kitano and Tsugiyuki Masunaga. 2018. Change in nutrient composition of biochar from rice husk and sugarcane bagasse at varying pyrolytic temperatures. International Journal of Recycling of Organic Waste in Agriculture, Vol 7(4). pp 269 - 276. DOI:10.1007/s40093-018-0213-y (This article covers Chapter 2)

Ifeoma Monica Nwajiaku, Kuniaki Sato, TakeoTokunari, Shigeru Kitano and Tsugiyuki Masunaga. 2018. Improvement of rice husk residue silicon availability for replenishing available silicon in paddy soil. International Journal of Plant & Soil Science, Vol. 24(2): 1-11. DOI:10.9734/IJPSS/2018/43220 (This article covers Chapter 3)