Mountain Journal of Science and Interdisciplinary Research
PRINT ISSN: 2619-7855
ONLINE ISSN: 2651-7744
January-June 2022 • 82 (1) : 74-89

Utilization of Rice Hull Char-Based Compost for Potato (*Solanum tuberosum*) Production

Bennylyn B. Puyongan

Benguet State University - Buguias Campus
Author email address: bennylynp@gmail.com

ARTICLE INFO
Date Received: 05-07-2021
Date Last Revised: 03-04-2022
Date Accepted: 04-07-2022

KEYWORDS
Rice Hull Char-Based Compost (RHCBC)
Potato
Rice hull

Abstract

The study determined the chemical properties of formulated rice hull char-based compost (RHCBC) and its effect on selected physicochemical soil properties, yield, and profitability of RHCBC for organic potato production under La Trinidad conditions. RHCBC consisting of 50% rice hull char, 25% wild sunflower leaves, and 25% chicken manure were formulated and field-tested for potato production at application rates of 0, 5, 10, and 15 tons ha^{-1}. Results revealed that the formulated RHCBC had 6.48 pH, 12.07% organic carbon, 20.76% organic matter, 0.39% total nitrogen, 0.41% total P_2O_5, 0.24% total K_2O, and 1.05% total N-P_2O_5-K_2O. Soil bulk density (Db), soil pH, organic matter (OM), and exchangeable potassium were not significantly affected by RHCBC application. However, the initial Db of 1.12 decreased to 0.91 to 0.97 g cm^{-3}, and the soil pH increased compared with the control. The application of 15 tons ha^{-1} RHCBC had the highest OM relative to the control and higher than the initial OM content of the soil before planting. The exchangeable K of soils applied with different RHCBC rates increased from the initial 170 ppm to 227 ppm to 247 ppm. RHCBC application significantly decreased the available phosphorus (P) content of the soil. High amounts of manganese (42.51 ppm), copper (7.31 ppm), and zinc (4.94 ppm) were obtained from the application of 15 tons ha^{-1} RHCBC. Potato plants applied with 10 tons ha^{-1} RHCBC had the least non-marketable yield, highest marketable yield, most profitable, and significantly the highest return on investment percentage. Subsequent crops may be recommended considering the high amounts of micronutrients in the soil after harvest.

Introduction

Benguet farmers have become dependent on commercial fertilizers making the soil acidic resulting in low soil fertility. Commercial fertilizers can cause soil and water pollution that can affect human health. As cited by Laurean (1987), intensive farming removes most nutrients and plant residues from the soil. To replenish the soil nutrients, farmers usually apply inorganic fertilizers. Excessive application of inorganic fertilizer can result in soil acidity, decreased soil nutrient availability, and to some extent, soil erosion.

The use of organic fertilizers such as biochar, produced from the pyrolysis of rice hulls and some feedstocks available in the area can be a method of safeguarding the soil from destruction and reducing farmers' expenses. Utilizing rice hulls as biochar will lessen agricultural wastes and help mitigate climate change by sequestering carbon in the soil. Sarong and Orge (2015) found that biochar application can enhance the fertility of acidic sandy loam soil. The rice hull biochar holds nutrients in place that are needed for plant growth and development.

Many rice millers consider rice hull, locally known as 'ipa' as one of their primary problems in terms of disposal. In the case of some Nueva Ecija farming areas, rice hull is an expensive commodity in the market and rice milling stations. Records from agriculture research agencies show that at least 3.1 million MT become 'ipa' out of the 14 million MT of palay milled in the country each year (Roque, 2014). Russel (n.d.) mentioned biochar (sometimes called agrichar), short term for Bio-Charcoal referring to a process that takes the carbon captured by living plants and turns the biomass into a solid form of charcoal. Such processes offer one of the most promising carbon capture and sequestration technologies.

Biochar is a carbon-rich product obtained when biomass such as wood, bark, leaves, and animal manures are heated in a closed container with little or no available air. It is fine-grained charcoal high in organic carbon produced through pyrolysis of carbon-based feedstock (biomass) in the absence or low supply of oxygen at temperatures between 350°C and 700°C (Lehmann et al., 2010). The potential impacts of biochar as a soil amendment have been extensively reviewed in the literature by Jeffery et al. (2011). Biochar may alter the physical properties of the soil, including increasing the aeration and water holding capacity of certain soils (Haefele et al., 2011; Jeffery et al., 2011; Verheijen et al., 2009). Moreover, biochar is much more efficient in improving soil quality than any other soil amendment (Lehmann & Joseph, 2009). Previous studies indicate that a bioenergy strategy that includes the use of biochar in soil not only leads to a net sequestration of CO_2 (Woofl et al., 2010) but also may decrease emissions of other more potent greenhouse gases such as N_2O and CH_4 (Spokas et al., 2009).

The study was conducted to utilize rice hull char-based compost for potato (*Solanum tuberosum*) production. It specifically aimed to determine the chemical properties of formulated RHCBC; the effect of RHCBC on selected soil physicochemical properties; the effect of RHCBC on potato yield; and the profitability of RHCBC for potato production.

Methodology

The study was conducted at the Certified Organic Demo Farm of Benguet State University, La Trinidad, Benguet, from September 1, 2018 to March 31, 2019. The organic materials used in the study were rice hull, dry chicken manure, and fresh wild sunflower leaves. Other materials were empty can of lard, cutter, 'bolo', flat galvanized iron sheet, watering can, thermometer, potato tubers var. Granola, identifying tags, measuring devices, farm implements, and recording materials. Laboratory equipment and apparatuses such as triple beam balance, sensitive balance, pH meter, graduated cylinder, core samplers, and soil drying oven were also used in the physicochemical analysis of soil and tuber samples.

Rice hull char-based compost consisting of rice hull char, wild sunflower leaves, and chicken manure were prepared, followed by a field test of the formulated compost for potato production.

Formulation of Rice Hull Char-Based Compost

Rice hulls were collected and air-dried. These were later charred in equipment fabricated from an empty can of lard and a flat galvanized iron sheet. The rice hulls were charred using firewood as fuel and mixed continuously for at least four hours to prevent the rice hull from turning to ashes. Thirty kilograms of rice hull was used per charring equipment resulting in 15kg of rice hull char. The rice char was then left to cool down to mix with other substrates. Meanwhile, the chicken manure was air-dried while fresh disease-free wild sunflower leaves were collected and chopped into a minimum width of one-half inch.

The different organic materials (rice hull char, fresh and disease-free wild sunflower leaves, and dry chicken manure) were prepared based on the formulation of 50% rice hull char + 25% fresh wild sunflower leaves + 25% dry chicken manure. Organic materials mentioned in the formulation were mixed thoroughly and subjected to composting for two months. The mixture was placed and covered with greenhouse plastic. Breathers were installed to provide aeration and heat evacuation. The organic materials were allowed to decompose under greenhouse conditions. After two weeks, the compost materials were mixed again. The organic materials, when fully decomposed, are odorless, black, and soft. Samples were taken for chemical analysis.

Response of Potato to the Different Rates of Rice Hull Char-Based Compost

The formulated RHCBC-50% rice hull char, 25% fresh wild sunflower leaves, and 25% dry chicken manure, was utilized in the field test for potato production.

Land Preparation, Field Lay-out, Planting and Fertilizer Application

An area of 205m² was thoroughly prepared and was divided into 16 plots measuring 2m x 5m, and beds were raised to at least 20cm high. Border plots after every row measuring 0.5m wide were provided. The distance between beds/treatment plots was 50cm, with a canal between beds for easier weeding and hilling up.

The treatments in the field were laid-out following a randomized complete block design with four replications. The application rates of the formulated RHCBC were based on the recommended rate of rice hull char which is 10 tons ha^{-1} (Domingo, 2007). The control was not applied with any RHCBC.

Treatments

T1 - Control (0 tons ha^{-1} RHCBC)
T2 - 5 tons ha^{-1} RHCBC
T3 - 10 tons ha^{-1} RHCBC
T4 - 15 tons ha^{-1} RHCBC

Planting materials used in the study are Granola var. potato tubers with uniform size and weight. Planting was done right after compost incorporation in the soil following the above treatment rates of application. The planting distance was 30cm x 40cm, making 56 hills/plants per plot.

Cultural Management Practices

Hilling up with soil was done one month after planting potato tubers. Weeding was done depending upon the growth and emergence of the weeds. Natural pest and disease management, like manual removal of pests and infected plants, was used to control whatever pests or diseases occurred during the conduct of the study. Such pests and diseases were recorded. The potatoes were harvested 63 days after planting, with issues attributed to the occurrence of late blight in almost 90% of the potato plants. Harvesting was done at random based on the marked subsamples per plot, while transmutation and transcription of data were strictly followed to avoid vague results.

Data Gathered

The data gathered was subjected to statistical analysis using the Statistical Tool for Agricultural Research (STAR) Software program (2014). Analysis of Variance (ANOVA) was used, and a comparison for the mean level of the different treatments was done using Duncan's Multiple Range Test (DMRT).

The data gathered were the chemical properties of the formulated rice hull char-based compost, soil physicochemical properties, potato yield, and return on investment. Initial soil analysis (before land preparation) and final soil analysis (after harvest) were done.

Chemical Properties of the Formulated Rice Hull Char-Based Compost

The formulated rice hull char-based compost samples were brought to the Regional Soils Laboratory of the Department of Agriculture-Regional Field Office, Region 3 (DA-RFO Region 3) for analysis. Analyzed properties were the total nitrogen, total phosphorus, total potassium, organic matter, and organic carbon. The pH of the compost was analyzed at the Department of Soil Science Laboratory, Benguet State University.

Physicochemical Properties of the Soil Before Land Preparation and After Harvesting

Soil samples at a depth of 0-20cm were collected from the area and were analyzed for soil physicochemical properties before land preparation. This analysis served as the initial soil analysis. The analysis was repeated after harvest on every individual treatment and replication. Analyses of soil samples for the bulk density were done at the Department of Soil Science, College of Agriculture, Benguet State University, La Trinidad, Benguet, while the chemical properties were analyzed at the Regional Soils Laboratory, Department of Agriculture-Regional Field Office, Cordillera Administrative Region (DA-RFO CAR), Baguio City. All methods used for the soil chemical analysis were derived from the Bureau of Soil and Water Management (2014). The physicochemical properties of the soil gathered were bulk density, pH, organic matter, available phosphorus, exchangeable potassium, and micronutrients (manganese, copper, and zinc).

Bulk Density of the Soil (g cm^{-3}). The bulk density was taken using the core method. The core sample with soil was oven-dried at 110ºC for 24 hours. It was computed using the formula:

$$Db = \frac{\text{Oven dry weight of the soil (g)}}{\text{Volume of the soil (cm}^3\text{)}}$$

Volume of the soil = volume of core sampler

Volume of core sampler = $(\pi r^2)\, h$

Where: π = 3.1416

r = radius of the core sampler

h = height of the core sampler

Soil pH. The soil pH before land preparation and after harvesting were measured using a pH meter in a 1:1 m/v soil and distilled water solution.

Organic Matter (OM) Soil Content (%). OM was determined using the Walkley Black Method.

Available Phosphorus Content of the Soil (ppm). This parameter was determined using the Olsen method.

Exchangeable Potassium Content of the Soil (ppm). This parameter was determined using the Cold H_2SO_4 method.

Micronutrients (Mn, Cu, and Zn) Content of the Soil (ppm). Micronutrients of the soil such as manganese (Mn), copper (Cu), and zinc (Zn) were determined using the DTPA Extraction-Atomic Absorption Spectroscopy method.

Yield of Potato

Yield parameters gathered were the marketable and non-marketable yields per plot.

Weight of Marketable Tubers per Plot (kg). This parameter was taken by harvesting and weighing the yield of five sample plants with no defects per plot. One plot has an area of 10m² with 56 plants. The weight of marketable tubers per plot was computed as follows:

Weight of marketable tubers per plot (kg) =

$$\frac{\text{Ave. weight of marketable tubers (kg)}}{\text{1 plant}} \times \frac{\text{number of plants}}{\text{plot}}$$

Weight of Non-marketable Tubers per Plot (kg). This parameter was taken by harvesting and weighing the yield of five sample plants with defects per plot. One plot has an area of 10m² with 56 plants. The weight of non-marketable tubers per plot was computed as follows:

Weight of non-marketable tubers per plot (kg) =

$$\frac{\text{Ave. weight of non-marketable tubers (kg)}}{\text{1 plant}} \times \frac{\text{number of plants}}{\text{plot}}$$

Return on Investment (%)

The return on investment was computed using the formula:

$$ROI\ (\%) = \frac{\text{Gross sales - Total Expenses}}{\text{Total Expenses}} \times 100\%$$

Results and Discussion

Chemical Properties of the Formulated Rice Hull Char-Based Compost

Table 1 presents the chemical properties of the formulated rice hull char-based compost. The pH of the compost is considered to be slightly acidic (6.48), which could be attributed to the production of organic acids as supported by the high organic matter content of the compost. The organic carbon of the formulated rice hull char-based compost is high, with a mean value of 12.07%. The presence of large quantities of organic carbon in compost helps improve the physical and chemical properties of the soil. Moreover, the N-P_2O_5-K_2O levels of the compost were considerably low, with mean values of 0.39%, 0.41%, and 0.24%, respectively. The rice char and sunflower leaves, which are plant-based, may justify the low nutrient content of the compost.

Labiano and Gayonan (2019) found that pure rice hull biochar has a much higher pH value of 7.16 compared to the present study. According to Singh et al. (2010), the pH and electrical conductivity of the biochar depend on the content and composition of the mineral fraction or ash fraction, which in turn depends on the type of feedstock and process conditions under which the biochar is produced. The nutrient contents of biochars are also largely influenced by the type of feedstocks and pyrolysis conditions (Singh et al., 2010); whereas the availability of nutrients in biochars is related to the type of bonds associated with the element involved (DeLuca et al., 2009; & Yao et al., 2012). Furthermore, the total N-P_2O_5-K_2O of the rice hull char-based compost is lower than the 5% required for a material to be considered organic (Bureau of Agriculture and Fisheries Standards [BFAR], 2016).

Table 1

Chemical Properties of the Formulated Rice Hull Char-based Compost

Parameters	Chemical Contents
pH	6.48
Organic carbon (%)	12.07
Organic matter (%)	20.76
Total N (%)	0.39
Total P, P_2O_5(%)	0.41
Total K, K_2O (%)	0.24
Total N – P_2O_5 – K_2O (%)	1.05

Physicochemical Properties of the Soil

Bulk Density of the Soil

Soil bulk density (Db) was not significantly affected by the RHCBC application rates (Table 2). However, it was observed that the initial Db decreased from 1.12 to a range of 0.91 to 0.97g cm^{-3} whether with or without rice hull char-based compost. The decrease in soil Db could be attributed to the properties of biochar, which is porous and has a large specific surface area, and the presence of micropores. Biochar enhances granulation and aggregation of the compacted soil, specifically that the soil was left fallow for almost three years and had been managed as a pasture area for horses. In addition, soil Db values (0.91-0.97g cm^{-3}) of soil amended with RHCBC fall under the ideal Db for silt to clay soil which is <1.10-1.4g cm^{-3}. The general texture of the soil used in the study is silty clay loam to clay loam. Low soil Db reduces root impedance and increases soil aeration and drainage, and in the end, enhances nutrient/water uptake by the plant.

Moreover, the lowest soil Db was noted from

Table 2

Soil Db as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	Bulk Density (g cm^{-3})
Control (0 tons RHCBC ha^{-1})	0.95 ^{a}
5 tons RHCBC ha^{-1}	0.96 ^{a}
10 tons RHCBC ha^{-1}	0.91 ^{a}
15 tons RHCBC ha^{-1}	0.97 ^{a}
Initial	1.12
CV (%)	4.86

Note: Means with the same letters are not significantly different at the 5% level by DMRT

soil treated with 10 tons ha-1 rice hull char-based compost. Such finding corroborates Herath et al. (2013) that biochar amendment at 10 tons ha^{-1} significantly reduced soil Db in an Alfisol poor in organic carbon but not in an Andosol high in organic carbon. In addition, Canqui (2017) stated that biochar application reduced Db by 3 to 31% in 19 out of 22 soils. Further, Aslam et al. (2014) reported that biochar application at 1-2% (w/w) decreases the soil bulk density and increases soil porosity and infiltration rate by increasing the total soil porosity.

Soil pH

The different rates of RHCBC did not significantly affect the soil pH compared with the control (Table 3). The initial pH decreased with or without RHCBC application. Such a decrease could be associated with the release of organic acids from root exudates. Relative to the control, all soils treated with compost, regardless of rates of compost, had increased in soil pH by 3.40%. The highest percent increase (3.90%) of pH from the control was from the application of 10 tons ha^{-1} rice hull char-based compost, and the lowest increase over the control was from the application of 5 tons ha^{-1} compost (2.72%).

Prasetyo and Suriadikarta (2006) and Yusran (2008), as cited by Ifansyah (2013), stated that the main constraints in the development of ultisols are low pH, high P fixation, high content of Al, Fe, and Mn, and low cation exchange capacity. Brady and Weil (2008) also mentioned that soil pH of 6.05 to 6.12 from those applied with RHCBC is considered slightly acidic soil. Moreover, Hillel (2008) emphasized that soil acidification solubilizes and leaches out some nutrients and increases the concentration of potentially toxic metal ions such as Mn, Cu, Zn, Al, Cr, and Ni. Further, Gapew (2013) stated that poultry litter char-based organic fertilizer applied at 10 tons ha^{-1} had the highest value attributed to the high pH of the formulated compost.

Organic Matter Content of the Soil

Table 4 presents the soil OM content as affected by the RHCBC application rates. The result indicates that the OM content of the soil was not affected by the application of the different RHCBC rates. However, the application of 15 tons ha^{-1} has the highest OM relative to the control and is higher than the initial OM content of the soil. This result signifies that the soil OM content can be further retained even after harvest if the rate of compost applied is 15 tons ha^{-1} or more. A lower than 15 tons ha^{-1} compost rate will yield to OM depletion after harvest.

Moreover, treatment mean values of OM in the plots applied with compost decreased by 8.14% over the control plots. Organic matter content of the soil applied with 5 tons ha-$^{-1}$ had the highest percent decrease (15.20%). Conversely, the OM content of char-amended soil with 10 tons ha^{-1} had the least decrease (0.16%) over the control plots. This result implies that the potato crop utilized the high amounts of organic

Table 3

Soil pH as Affected by Application Rates of Rice Hull Char-based Compost

Treatment	pH
Control (0 tons RHCBC ha^{-1})	5.89[a]
5 tons RHCBC ha^{-1}	6.05[a]
10 tons RHCBC ha^{-1}	6.12[a]
15 tons RHCBC ha^{-1}	6.10[a]
Initial	6.21
CV (%)	2.76

Note: Means with the same letters are not significantly different at the 5% level by DMRT

Table 4

OM Content of the Soil as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	OM(%)
Control (0 tons RHCBC ha^{-1})	3.42[a]
5 tons RHCBC ha^{-1}	2.90[a]
10 tons RHCBC ha^{-1}	2.86[a]
15 tons RHCBC ha^{-1}	3.11[a]
Initial	2.95
CV (%)	14.55

Note: Means with the same letters are not significantly different at the 5% level by DMRT

C and OM present in the compost for its growth and development. Furthermore, OM values (2.86%-3.42%) after harvest with or without compost are moderately low according to the interpretation of results issued by the Regional Soils Laboratory, DA-RFO CAR.

Patricio (2018) reported that 88-110 tons ha^{-1} cacao pods biochar is needed to increase the OM content of the soil. In addition, Brady (1985), as cited by Laurean (1987), claimed that the inherent capacity of soils to produce good crops is closely related to their OM and N contents. Hence, preservation and proper management of OM should always be considered in soil fertility. Further, Persaud et al. (2018) claimed that application of rice husk biochar increased OM, soil pH WHC, exchangeable cations, N, P, cation exchange capacity but decreased bulk density and Fe concentration.

Available Phosphorus Content of the Soil

The available phosphorus (P) content of the soil was significantly decreased by the rates of rice hull char-based compost (Table 5). Available P in soils applied with 5 tons ha^{-1} rice hull char-based compost differed significantly from available P contents of plots applied with 10 and 15 tons ha^{-1}, but it did not differ significantly from the available P from the control plots. It was observed that as the RHCBC rate increases, the amount of P retained in the soil after harvest tends to decrease significantly. Five tons per hectare of compost application for potato production was the optimum substitution to maintain a relatively higher P in the soil after cropping.

In addition, an increase in soil pH decreases the adsorption of P by Fe/Al oxides. Phosphorus availability in most soils is at a maximum near pH 6.5. The retention results mainly from the eaction with Fe/Al oxides and precipitations of $AlPO_4$ and $FePO_4$ at low pH values. As pH increases, the activity of Fe and Al decreases, which results in lower P adsorption/precipitation and higher P concentration in solution. Notably, Fe/Al oxides have the capacity to adsorb large amounts of P in the soil solution resulting in P fixation and hence unavailable for plant uptake. Phosphorus fixation is further enhanced by rice hull char's large specific surface area. However, the formulated RHCBC has 25% chicken manure, which could have also been one of the sources of very high P (33.67-73.16 ppm) of plots

Table 5

Available Phosphorus Content of the Soil as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	P (ppm)
Control (0 tons RHCBC ha^{-1})	77.75 ^{a}
5 tons RHCBC ha^{-1}	73.16 ^{a}
10 tons RHCBC ha^{-1}	54.15 ^{b}
15 tons RHCBC ha^{-1}	33.67 ^{c}
Initial	40.01
CV (%)	15.93

Note: Means with the same letters are not significantly different at the 5% level by DMRT

applied with compost, based on the Regional Soil Laboratory, DA-RFO CAR. Available *P* values greater than 20ppm are considered very high based on analysis using the Olsen method.

The factors that greatly affect the retention of available P in the soil are soil minerals and pH (Havlin et al., 1999). Effective utilization of P is attained by phosphatic fertilizers when combined with animal manures. Animal manures increase the availability of P for plant utilization through granulation, a property that tends to retard closer contact of the element with the soil (Brady, 1985). Further, Liu et al. (2017) found out that rice hull biochar had a positive effect on phosphate solubilizing bacteria and contributed to increasing P availability.

Exchangeable Potassium Content of the Soil

The exchangeable potassium (K) content of the soil was not significantly affected by the RHCBC application rates (Table 6). However, it was observed that the exchangeable K increased from the initial mean value of 170ppm to those applied with rice hull char-based compost, which ranges from 227ppm to 247ppm, with the highest of 247ppm from the 10 tons ha^{-1}. This data corroborates with the soil Db, marketable yield, and ROI, wherein 10 tons ha^{-1} improved the soil Db and gave the highest marketable yield and the highest ROI.

For the descriptive word of the values of exchangeable P from plots applied with compost (227.50-247.00ppm), it is high since it is greater

Table 6

Exchangeable Potassium Content of the Soil as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	K (ppm)
Control (0 tons RHCBC ha^{-1})	255.00^{a}
5 tons RHCBC ha^{-1}	227.50^{a}
10 tons RHCBC ha^{-1}	247.50^{a}
15 tons RHCBC ha^{-1}	240.00^{a}
Initial	170.00
CV (%)	22.12

Note: Means with the same letters are not significantly different at the 5% level by DMRT

than 75ppm as indicated in the interpretation of the laboratory analysis results. Further, the percent decreases in the exchangeable K from soils treated with compost at 5, 10, and 15 tons ha^{-1} rates were 10.78%, 2.94%, and 5.88%, respectively, over the exchangeable K from untreated plots. Such decreases in exchangeable K in the soil treated with compost over the control could be due to the uptake of potatoes. Potatoes are known to be luxury consumers of K, especially during the bulking stage of the crop.

Sopher and Baird (1978), as cited by Laurean (1987), reported that most crops remove K from the soil more than any other plant nutrient elements, except N. Under conditions of heavy N fertilization and removal of the forage, K removal may exceed N removal. Moreover, the exchangeable K and Db of the biochar-amended soil were significantly improved (Nitura & Perlas, 2018).

Manganese Content of the Soil

Highly significant differences were observed in the manganese (Mn) content of the soil after harvest as affected by the RHCBC application rates. The Mn content of the soil applied with 15 tons ha^{-1} was higher than the other treatments (Table 7). However, Mn contents obtained from soils applied with 10 tons ha^{-1}, 5 tons ha^{-1}, and the unfertilized (control) are not significantly different. Such a result has the same trend with the copper and zinc content of the soil as subsequently presented. Moreover, soil Mn availability was highly affected by soil pH and OM.

Table 7

Manganese Content of the Soil as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	Mn (ppm)
Control (0 tons RHCBC ha^{-1})	21.65^{b}
5 tons RHCBC ha^{-1}	19.59^{b}
10 tons RHCBC ha^{-1}	24.39^{b}
15 tons RHCBC ha^{-1}	42.51^{a}
Initial	42.86
CV (%)	21.55

Note: Means with the same letters are not significantly different at the 5% level by DMRT

Like other micronutrient cations, Mn availability is enhanced in acidic soils and precipitates as MnO_2 when pH increases. Reactions with OM can also influence the availability of Mn. Further, the absorption potential of biochar brought by the large specific surface area also contributes to the increased Mn availability in the soil after harvest.

Havlin et al. (1999) reported that the low availability of Mn in high-OM soils is attributed to the formation of unavailable chelated Mn^{2+} compounds. It may also be held unavailable organic complexes in peat or muck soils. The addition of natural organic materials such as peat moss, compost, and wheat clover straw had increased the solution of exchangeable Mn. In addition, Al-wabel et al. (2014) reported that biochar could be effectively used as a soil amendment for heavy metal immobilization and for reducing phytotoxicity.

Copper Content of the Soil

Copper (Cu) content of the soil after harvest was significantly increased by the application of the highest rate (15 tons ha^{-1}) of rice hull char-based compost (Table 8). The Cu contents of plots treated with 5 and 10 tons ha^{-1} were not significantly different from the Cu content of the control plots. However, the Cu content of soil applied with 15 tons ha^{-1} was significantly different from the Cu content of 5, 10 tons ha^{-1}, and the control. The highest Cu of 7.31ppm was from the application of 15 tons ha^{-1}, which was the same as the initial Cu content of the soil.

Table 8

Copper Content of the Soil as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	Cu (ppm)
Control (0 tons RHCBC ha^{-1})	6.62^{b}
5 tons RHCBC ha^{-1}	6.16^{b}
10 tons RHCBC ha^{-1}	6.54^{b}
15 tons RHCBC ha^{-1}	7.31^{a}
Initial	7.31
CV (%)	6.39

Note: Means with the same letters are not significantly different at the 5% level by DMRT

This result could be attributed to the competition of Cu with other micronutrients such as Fe, Mn, and Zn for plant uptake; hence Cu was not highly absorbed by the potato plants. Moreover, the concentration of Cu in the soil olution decreases with increasing pH. Its supply to plants is reduced because of the decreased solubility and increased adsorption, especially with RHCBC, wherein biochar has a large specific surface area for adsorption of positively charged elements. Furthermore, the high amounts of Fe in the soil solution also depress Cu absorption by plant roots and may intensify Cu deficiency.

Enhanced Cu retention by biochar amendment resulted in the following mechanisms: electrostatic interactions between Cu and negatively charged soil and biochar surfaces, absorption of minerals (ash) components, complexation of Cu by surface functional groups, and precipitation (Uchimiya et al., 2011). The Cu removal in the soil is a strongly pH-dependent process associated with variability of chemical Cu forms and various reactivities of organic molecules. The Cu adsorption amount was higher on silty Haplic Luvisol than on sandy Haplic Podzol mainly due to higher content of organic carbons, functional groups, clay and silt fractions, and larger surface area. Moreover, the biochar addition increased the soil surface charge linearly and contributed to higher Cu adsorption in the whole range of investigated ion concentrations (Tomczyk & Sokolowska, 2019).

Zinc Content of the Soil

The zinc (Zn) content of the soil was significantly increased by applying the highest RHCBC rates (Table 9). The highest significant Zn of 4.94ppm was obtained from soils applied with 15 tons ha^{-1}, but it is comparable with 4.25ppm Zn from 10 tons ha^{-1} char-amended soil. Further, Zn content from 10 tons ha^{-1} application of RHCBC is comparable with the Zn contents from soils applied with 5 tons ha^{-1} RHCBC and the unfertilized soil. It could also be noted that a slight increase from the initial Zn was noted from 15 tons ha^{-1} char-amended soils. Zn availability in the soil could be affected by the pH, OM, and interaction with other nutrients.

Havlin et al. (1999) stated that the availability of Zn^{2+} decreases with increased pH; chelation of Zn^{2+} brought about by the OM; some antagonistic effect with Cu^{2+}, Fe^{2+}, and Mn^{2+} which inhibits Zn^{2+} uptake due to competition for the same carrier site. Moreover, Puga et al. (2015) reported that biochar application reduced the uptake of Cd, Pb, and Zn by plants with the jack bean translocating high proportions of metals to shoots. Biochar application during mine soil remediation reduces plant concentrations of potentially toxic metals.

Table 10 presents the standard concentrations of micronutrients in the Philippine soils based on BSWM (2014). Very high Fe concentrations of soil amended with RHCBC were noted, ranging from 148.77ppm to 195.30ppm. For the Mn content of the soil amended with compost, it registered as low, ranging from 19.59ppm to 42.51ppm. Moreover, the Cu content of the soils applied

Table 9

Zinc Content of the Soil as Affected by the Application Rates of Rice Hull Char-based Compost

Treatment	Zn (ppm)
Control (0 tons RHCBC ha^{-1})	4.01^{b}
5 tons RHCBC ha^{-1}	3.55^{b}
10 tons RHCBC ha^{-1}	4.25^{ab}
15 tons RHCBC ha^{-1}	4.94^{a}
Initial	4.67
CV (%)	12.00

Note: Means with the same letters are not significantly different at the 5% level by DMRT

Table 10

Standard Concentration Ranges of Micronutrients in the Philippines Soils

Micronutrient	VL	L	M	H	VH
Mn (ppm)	1.00 – 4.90	5.00 – 55.00	55.10 – 170.00	170.10 – 300.00	>300.00
Cu (ppm)	<1.00	1.00 – 5.90	6.00 – 13.90	14.00 – 30.90	>31.00
Zn (ppm)	<0.50	0.50 – 1.15	1.16 – 4.80	4.81 – 20	>20.00

Legend: VL – very low; L – low; M – medium; H – high; and VH – very high
Source: BSWM (2014)

with RHCBC after harvest registered as medium ranging from 6.16ppm to 7.31ppm. Further, Zn contents were medium to high in the soils amended with compost after harvest, ranging from 3.55ppm to 4.94ppm. These results imply that high amounts of micronutrients were retained in the soil after harvest, especially the Fe. Planting subsequent crops requiring high micronutrients can be recommended to utilize these nutrients further. However, if the next choice of crop is sensitive to high amounts of micronutrients, remediating the soil can be done to minimize the contents of such cations in the soil but with another application of higher rates of compost.

Yield of Potato

Marketable Yield, Non-Marketable Yield, and Total Yield per Plot of Potatoes

Table 11 presents the tuber yield (marketable, non-marketable, and total yield) per plot as affected by the different RHCBC application rates (Table 11) (Figure 1-4). Significant difference effects of the RHCBC rates were only noted on the non-marketable yield per plot. The application of 5 tons ha^{-1} and 15 tons ha^{-1} of compost on plants are comparable with the control plot, while plants applied with 10 tons ha^{-1} compost yielded the least non-marketable weight of tubers. The plants applied with 10 tons ha^{-1} produced the heaviest weight of tubers, which could be attributed to the improved soil physicochemical properties after the RHCBC application, specifically on soil Db, pH, available K, and high amounts of Mn, Cu, and Zn. These properties affect plant height and vigor, which result in tall and vigorous plants and eventually higher yield. Marketable yield directly affected the return on investment, with 10 tons ha^{-1} application having the highest ROI. Further, the noted decrease in the marketable yield in the plants applied with 15 tons ha^{-1} could be attributed to micronutrient toxicities, the volatile properties of biochar, the slightly acidic RHCBC, and waterlogging history of the site. High inherent micronutrient contents (especially Mn) of the soil could have limited the further increase in yield.

Barker and Pilbeam (2007) mentioned that potato is one indicator plant for Mn toxicity. Waterlogging leads to Fe accumulation due to compaction, lowering root growth and eventually inhibiting iron uptake. In addition, Ding et al. (2016) cited that the decrease in crop yield might be attributed to the high volatile matter an toxic and harmful substances in biochar, which can reduce nutrient uptake and inhibit plant growth. Moreover, Rondon et al. (2007) also cited that instances of decreasing yield due to a high biochar application rate were reported when the equivalent of 165 tons ha^{-1} biochar were added to poor soil. At this high application rate, yields decreased to the level of the unamended control. The application of 165 tons ha^{-1} biochar is a very large amount, which is unlikely to be practically feasible in the field for at least a one-time amendment. Further, Asai et al. (2009) reported greater upland rice yields with 4 tons ha^{-1} biochar, but when 8 or 16 tons ha^{-1} were applied, yields were not different from the unamended control in Laos. Gaskin et al. (2010), in their study on poor and acidic soil in the USA, showed that peanut hull and pine chip biochar applied at 11 and 22 tons ha^{-1} could reduce corn yields below those obtained in the control plots under standard fertilizer management. Biederman and Harpole (2012) cited that alkaline biochars are more effective at increasing biomass than acidic biochars.

Table 11

Marketable, Non-marketable, and Total Yield of Potatoes as Affected by the Different Application Rates of Rice Hull Char-based Compost

Treatment	Marketable Yield (kg/plot)	Non-Marketable Yield (kg/plot)	Total Yield (kg/plot)
Control (0 tons RHCBC ha^{-1})	7.21^{a}	2.10^{ab}	9.31^{a}
5 tons RHCBC ha^{-1}	9.46^{a}	2.73^{a}	12.19^{a}
10 tons RHCBC ha^{-1}	10.28^{a}	0.53^{b}	10.81^{a}
15 tons RHCBC ha^{-1}	8.09^{a}	2.77^{a}	10.86^{a}
CV (%)	21.46	50.11	15.63

Note: Means with the same letters are not significantly different at the 5% level by DMRT

Figure 1

Samples of Potato Tubers (Marketable and Non-marketable) from the Control Plots

Figure 2

Samples of Potato Tubers (Marketable and Non-marketable) from Plots Applied with 5 tons ha^{-1} RHCB Compost

Figure 3

Samples of Potato Tubers (Marketable and Non-marketable) from Plots Applied with 10 tons ha⁻¹ RHCB Compost

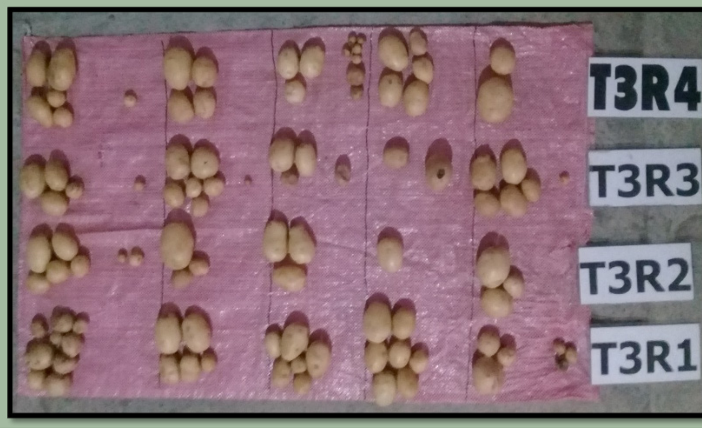
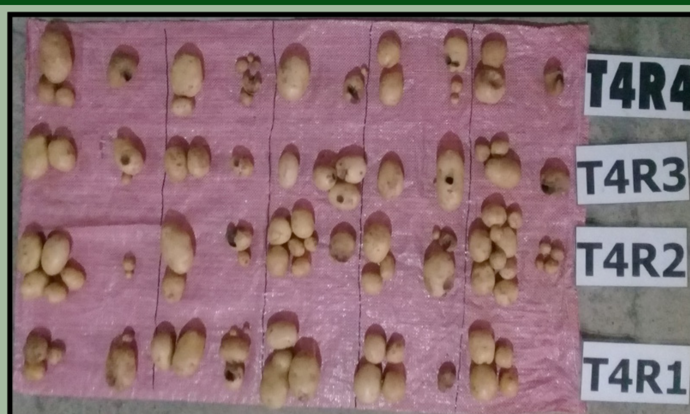


Figure 4

Samples of Potato Tubers (Marketable and Non-marketable) from Plots Applied with 15 tons ha⁻¹ RHCB Compost



Other Observations

During the conduct of the study, some other observations were noted. One of the observations noted was the occurrence of late blight, which started the 2nd week after planting and affected all plants on the 4th week after planting. One liter of oriental herbal nutrient (OHN) was sprayed once after the onset of blight, but it was not enough to control the disease. Based on the actual observation in the field, during the 2nd week and 4th week after planting potato tuber, the occurrence of heavy fog was observed, which could have triggered the spread of late blight in all plants. According to some organic potato farmers nearby, they have also encountered late blight on their farms.

Generally, potato plants growing under short days are more susceptible to blight than those growing under long days (Singh et al., 2010). The study was conducted during the short days, January to March. The onset of blight started from robustly growing plants before it spread to all blocks. Phytopthora infestans, the causal organism of blight, could have been one factor in decreasing marketable tubers and increasing non-marketable tubers.

Table 12 presents the agrometeorological data obtained from Benguet State University-PAG-ASA Agromet station. Rainfall only occurred right after planting during the onslaught of typhoon Usman (last week of December 2018) in the locality. Relative humidity (RH) ranged from 75.71% to 89.79%, which could have been one factor in the occurrence of late blight. Accordingly, high relative humidity favors the growth of spores, and at low RH, the growth of the spores of the pathogen will hasten faster, which causes blight. The temperature ranged from 16.38ºC in the 5th week after planting to 18.96ºC on the planting days.

Return on Investment

Table 13 presents the return on investment ROI) obtained from applying different RHCBC rates. Plots applied with 10 tons ha^{-1} exhibited the highest ROI (58.09%), while those applied with 15 tons ha^{-1} had the lowest ROI (24.35%). The high ROI could be ascribed to the high marketable yield of plants applied with 10 tons ha^{-1} and the stable market price of organically produced potato, unlike the commercially produced potato with an unstable price.

There was a notable increase in the net income and ROI from applying 10 tons ha^{-1}, but a drastic decrease was observed in the 15 tons ha^{-1}. Such a decrease could be attributed to the decrease in the marketable yield related to the late blight infection and some negative effects of elements and volatile substances in the biochar.

Table 12

Meteorological Observations of Benguet State University-PAG-ASA Agromet Station

	Week After Planting								
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th
Tº (ºC)	18.96	17.95	18.07	17.35	16.38	17.02	17.46	16.93	17.35
RH (%)	86.00	75.71	84.14	89.43	88.14	81.86	76.50	86.50	89.79
Rainfall	0.71	0	0	0	0	0	0	0	0

Table 13

Return on Investment as Affected by Rice Hull Char-based Compost Application Rates in Potato

Treatment	Yield (kg/plot)	Total Expense (PhP)	Gross Income (PhP)	Net Income (PhP)	ROI (%)
Control (0 tons RHCBC ha^{-1})	7.21	478.75	721	242.25	50.60
5 tons RHCBC ha^{-1}	9.46	649.93	946	296.07	45.55
10 tons RHCBC ha^{-1}	10.28	650.28	1028	377.72	58.09
15 tons RHCBC ha^{-1}	8.09	650.58	809	158.42	24.35

Note: The market price used for organic potato was from BIGS market, which is Php. 100.00 per kg.

Conclusions

Based on the findings of the study, formulated rice hull char-based compost (RHCBC) is slightly acidic and has high amounts of organic carbon and organic matter but low total N-P_2O_5-K_2O levels. Soil bulk density (Db), soil pH, organic matter (OM), and exchangeable potassium were not significantly affected by the RHCBC application. The application rate of 15 tons ha^{-1} of formulated RHCBC significantly improved the soil's Mn, Cu, and Zn after harvest. Potato plants applied with formulated RHCBC at 10 tons ha^{-1} resulted in the highest nitrogen uptake of tuber, produced the highest marketable yield, and exhibited the highest ROI percentage.

Recommendations

Application of 10 tons ha^{-1} rice hull char-based compost is recommended for potato production under La Trinidad, Benguet conditions. Applying more than 10 tons ha^{-1} compost will further decrease the yield. The amounts of organic materials from animal manures should be increased to improve the nutrient contents of the charred compost and yield higher amounts of N-P_2O_5-K_2O.

Acknowledgment

The author thanks Mrs. Magdalena D. Pandosen, Prof. Alexander W. Fagyan, Dr. Belinda A. Tad-awan and Dr. Bernard S. Tad-awan for their comments on the research and the earlier version of this manuscript; and the BSU-Department of Soil Science; and the Department of Agriculture-Regional Field Office, Cordillera Administrative Region chemists Ms. Maribel P. Mananguit and Ms. Jennika Lou D. Javier for their technical assistance.

References

Al-Wabel, M., Usman, A., El-Naggar, A., Aly, A., Ibrahim, H., Elmaghraby, S., & Al-Omran, A. (2014). Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. *Saudi Journal of Biological Sciences, 22*(4), 503-511. https://doiorg/10.1016/j.sjbs.2014.12.003

Asai, H., Samson, B., Stephan, H., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y., Shiraiwa, T., & Horie, T. (2009). Biochar amendment techniques for upland rice production in Northern Laos, 1. Soil physical properties, leaf SPAD and grain yield. *Field Crop Research, 111* (1-2), 81-84. https://doi.org/10.1016/jfcr2008.10.008

Aslam, Z., Khalid, M., & Aon, M. (2014). Impact of biochar on soil physical properties. *Scholarly Journal of Agricultural Science, 4*(5), 280-284.

Barker, A., & Pilbeam, D. (2007). *Handbook of plant nutrition*. CRC Press.

Biederman, L. & Harpole, W. (2012). Biochar and its effect on plant productivity and nutrient cycling: A meta-analysis. *Global Change Biology Bioenergy, 5*(2), 202-214. https://doiorg/10.1111/gcbb.12037

Brady, N.C. (1985). T*he nature and properties of soils* (9th ed.). Macmillan Publishing Co.

Brady, N. & Weil, R. (2008). *The nature and properties of soils* (14th ed.). Pearson Education, Inc.

Bureau of Agriculture And Fisheries Standards. (2016). *Philippine National Standards*. PNS BAFS 40:2016. http://organic.da.gov.phimages/downloadables/PNS/PNS-Organic-SoilAmendments-PNS-BAFS-40-2016.pdf

Bureau of Soil and Water Management. (2014). *Updated manual on soil, water, fertilizer and plant tissue analysis*.

Canqui, H. B. (2017). Biochar and soil physical properties. *Soil Science Society of America Journal, 81*(4), 687-711. https://doiorg/10.2136/sssaj2017.01.0017

DeLuca, T., Mackenzie, M., & Gundale, M. (2009). *Biochar effects on soil nutrient transformations.* In J. Lehmann & S. Joseph (Eds.), *Biochar for environmental management science and technology*. (pp 251 – 265). Earthscan. http://www.css.cornell.edu/faculty/lehmann/publ/First%20proof%2013-01-09.pdf

Ding, Y., Liu, Y., Liu, S., Li, Z., Tan, X., Huang, X., Zeng, G., Zhou, L., & Zheng, B. (2016). Biochar to improve soil fertility. *A review. Agronomy for Sustainable Development, 36*(36). https:/doi.org/10.1007/s13593-016-0372-z

Domingo, O. (2007). *Carbonized Rice Hull: from Waste to Soil Conditioner*. http://i-makeadifferenceblogspot.com/2008/07/carbonizedrice-hull-from-waste-to-soil.html

Gapew, H.C. (2013). *Formulation and effect of poultry litter char-based organic fertilizers for organic production of Cabbage (Brassica oleracea L.)*. Unpublished Master' Thesis. Benguet State University - La Trinidad.

Gaskin, J., Speir, R., Harris, K., Das, C., Lee, R., Morish, L., & Fisher, D. (2010). Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. *Agronomy Journal, 102*(2), 623-633. https://doiorg/10.2134/agronj2009.0083

Haefele, S., Konboon, Y., Wongboon, W., Amarante, S., Maarifat, A., Pfeiffer, E., & Knoblauch, C. (2011). Effects and fate of biochar from rice residues in rice-based systems. *Field Crops Research, 121*(3), 430-440. https://doiorg/10.1016/j.fcr.2011.01.014

Havlin, J., Beaton, J., Tisdale, S., & Nelson, W. 1999). *Soil fertility and fertilizers: An introduction to nutrient management* (6th ed.). Prentice Hall, Inc.

Herath, H., Arbestain, M., & Hedley, M. (2013). Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol. *Geoderma, 209-210*, 188-197. https://doiorg/10.1016/j.geoderma.2013.06.016

Hillel, D. (2008). *Soil in the environment: crucible of terrestrial life*. Elsevier. Inc.

Ifansyah, H. (2013). Soil pH and Solubility of Aluminum, Iron, and Phosphorus in Ultisols: the Roles of Humic Acid. *Journal of Tropical Soils, 18*(3), 203-208. https://media.neliticom/media/publications/134295-EN-soil-phand-solubility-of-aluminum-iron.pdf

Jeffery, S., Verheijen, F., Van Der Velde, M., & Bastos, A. (2011). A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystem & Environment, 144*(1), 175-187. https://doiorg/10.1016/j.agee.2011.08.015

Labiano, A., & Gayonan, C. (2019). *Nitrogen mineralization in paddy soil as affected by the application of agricultural waste-derived biochar*. 22nd Philippine Society of Soil Science and Technology, Inc. (PSSST) Annual Meeting and Scientific Conference. Paper presentation. Junior Category.

Laurean, C.P. (1987). *Formulation and utilization of organic fertilizers*. Unpublished Master's Thesis. Benguet State University, La Trinidad, Benguet.

Lehmann, J., & Joseph, S. (2009). *Biochar from environment management: an introduction in biochar for environment management: Science and Technology*. Earthscan Publishers Ltd.

Lehmann, J., Major, J., Rondon, M., Molina, D., & Riha, S. (2010). Maize yield and nutrition during 4 years after biochar application to a Colombian Savannah Oxisol. *Plant and Soil, 333*, 117-128. https://doi.org/10.1007/s11104-0100327-0

Liu, S., Meng, J., Jiang, J., Yang, X., Lan, Y., Cheng, X., & Chen, W. (2017). Rice husk biochar impacts soil phosphorus availability, phosphatase activities and bacterial community characteristics in three different soil types. *Applied Soil Ecology, 116*, 12-22. https://doi.org/10.1016/japsoil.2017.03.020

Nitura, D., & Perlas, F. (2018). *Chicken feather biochar: percentage recovery, characteristics and effect on soil properties and growth and yield of upland rice*. 21st Philippine Society of Soil Science and Technology, Inc. (PSSST) Annual Meeting and Scientific Conference. pp. 24 – 25.

Patricio, A.C. (2018). *Nutrient analysis of acidic* *soil amended with varying rates of two biochar sources*. 21st Philippine Society of Soil Science and Technology, Inc. (PSSST) Annual Meeting and Scientific Conference. pp. 21 – 23.

Persaud, T., Homenauth, O., Fredericks, D., & Hamer, S. (2018). Effect of rice husk biochar as an amendment on a marginal soil in Guyana. *World Environment,* 8(1), 20-25. http://articlesapub.org/10.5923.j.env.20180801.03.html#Ref

Puga, A., Melo, L., De Abreu, C., & Beesley, L. (2015). Biochar application to a contaminated soil reduces the availability and plant uptake of zinc, lead and cadmium. *Journal of Environmental Management, 159*, 86-93. https://doi.org/10.1016/j.jenvman.2015.05.036

Rondon, M., Lehmann, J., Ramirez, J., & Hurtado, M. (2007). Biological nitrogen fixation by common beans (Phaseolus vulgaris L.) increases with bio-char additions. *Biology and Fertility of Soils, 43*, 699-708. https://doiorg/10.1007/s00374-006-0152-z

Roque, A. (2014). Even prices of rice hull increasing. *Philippine Daily Inquirer*.

Russel, P. (n.d.). *BioChar*. https://www.peterrussell.com/Earth/BioChar.php

Sarong, M., & Orge, R. (2015). Effect of rice hull biochar on the fertility and nutrient holding capacity of sandy soils. OIDA International *Journal of Sustainable Development, 8*(12), 33-44. https://ssrn.com/abstract=2730687

Singh, B., Hatton, B., Balwant, S., Cowie, A., & Kathuria, A. (2010). Influence of biochars on nitrous oxide emission and nitrogen leaching from two contrasting soils. *Journal of Environmental Quality, 39*(4), 1224-1235. https://doi.org/10.2134/jeq2009.0138

Spokas, K., Koskinen, W., Baker, J., & Reicosky, D. (2009). Impacts of woodchip biochar additions on greenhouse gas production and sorption degradation of two herbicides in a Minnesota soil. *Chemosphere, 77*(4), 574-581. https:/doi.org/10.1016/j.chemosphere.2009.06.053

Tomczyk, A., & Solowska, P. (2019). Biochar efficiency in copper removal from Haplic soils. *International Journal of Environmental Science and Technology, 16*, 4899-4912. https:/doi.org/10.1007/s13762-019-02227-4

Uchimiya, M., Wartelle, L., Klasson, K., & Lima, I. (2011). Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. *Chemosphere, 82*(10), 1431-1437. https://doi.org/10.1016/j.chemosphere.2010.11.050

Verheijen, F., Jeffery, S., Bastos, A., Van Der Velde, M., & Diafas, I. (2009). *Biochar application to soils-a critical scientific review of effects on soil properties, processes and functions.* European Commision Publication Office.

Woofl, D., Amonette, J., Sreet-Perrott, F., Lehmann, J., & Joseph, S. (2010). Sustainable biochar to mitigate global climate change. *Nature Communication, 1*, 56. https://doi.org/10.1038/ncomms1053

Yao, Y., Gao, B., Zhang, M., Inyang, M., & Zimmerman, A. (2012). Effect of biochar amendment on sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere, 89*(11), 1467-1471. https://doi.org/10.1016/j. chemosphere.2012.06.002