energies

MDPI

Article

Assessment of Agro-Environmental Impacts for Supplemented Methods to Biochar Manure Pellets during Rice (*Oryza sativa* L.) Cultivation

JoungDu Shin [1,*], SangWon Park [2] and Changyoon Jeong [3]

1 Department of Climate Change and Agro-ecology, National Institute of Agricultural Sciences, WanJu Gun 55365, Korea

2 Chemical Safety Division, National Institute of Agricultural Sciences, WanJu Gun 55365, Korea; swpark@rda.go.kr

3 Red River Research Station Louisiana State University AgCenter, 262 Research Station Driver Bossier City, Louisiana, LA 7112, USA; CJeong@agcenter.lsu.edu

* Correspondence: jdshin1@korea.kr

Received: 19 March 2020; Accepted: 14 April 2020; Published: 21 April 2020

Abstract: The agro-environmental impact of supplemented biochar manure pellet fertilizer (SBMPF) application was evaluated by exploring changes of the chemical properties of paddy water and soil, carbon sequestration, and grain yield during rice cultivation. The treatments consisted of (1) the control (no biochar), (2) pig manure compost pellet (PMCP), (3) biochar manure pellets (BMP) with urea solution heated at 60 °C (BMP-U60), (4) BMP with N, P, and K solutions at room temperature (BMP-NPK), and (5) BMP with urea and K solutions at room temperature (BMP-UK). The NO_3^-–N and PO_4^-–P concentrations in the control and PMCP in the paddy water were relatively higher compared to SBMPF applied plots. For paddy soil, NH_4^+–N concentration in the control was lower compared to the other SBMPFs treatments 41 days after rice transplant. Additionally, it is possible that the SBMPFs could decrease the phosphorus levels in agricultural ecosystems. Also, the highest carbon sequestration was 2.67 tonnes C ha^{-1} in the BMP-UK treatment, while the lowest was 1.14 tonnes C ha^{-1} in the BMP-U60 treatment. The grain yields from the SBMPFs treatments except for the BMP-UK were significantly higher than the control. Overall, it appeared that the supplemented BMP-NPK application was one of the best SBMPFs considered with respect to agro-environmental impacts during rice cultivation.

Keywords: Mitigation of CO_2-equiv.; nutrient release; rice paddy water and soil system; slow-release fertilizer

1. Introduction

Developing methodologies to improve crop productivity and protect soil systems while mitigating environmental pollution is the current direction of research in sustainable agriculture [1–3]. Recently, biomass conversion from agricultural wastes to carbon-rich materials such as biochar has been recognized as a promising option to maintain or increase soil productivity [4], reduce nutrient losses [5], and mitigate greenhouse gas emissions [6] from the agroecosystem. It is estimated that 50 million tonnes of the 80 million tonnes of organic wastes produced in Korea originate from agriculture [7]. Carbon sequestration utilizing recycled organic wastes through biomass conservation technology can greatly mitigate greenhouse gas emissions and the environmental impact of organic waste in Korea. Biochar is made through the pyrolysis under high temperature in oxygen-limited conditions [8]. Converted biochar from agricultural biomass becomes recalcitrant carbonaceous structures. The structures and components of biochars are strongly related to the source of feedstock and the operating conditions that are used in biochar production. Cantrell et al. [9] documented that the biochar made of poultry litter presented a relatively high nutrient content comparable to fertilizer. The reported analytical characterization of biochar is ranges between 5.2–10.3 in pH, 1.1–55.8% in ash content, 23.6–87.5% in carbon content, and 0–642 m^2 g^{-1} in surface area [8,10,11]. Kim et al. [12] reported ranges of 10–69 $cmol_c$ kg^{-1} in the cation exchange capacity (CEC) of biochar. Biochar application can significantly increase plant growth, crop yield, and root biomass by enhancing nutrient use efficiency [13,14]. However, few studies have reported a negative growth response in the early stages of plant growth [15,16]. Thus, research on the incorporation of biochar as a soil amendment in crop fields is still required to improve the production methods and application of biochar in soil. Drift of biochar occurs during field application due to the low density and irregular particle size of biochar. Husk and Major [17] reported that the biochar drift during field application was 25%, while the surface runoff losses due to intense rain events were estimated from 20% to 53% of incorporated biochar [18]. Pelletizing biochar can be a possible solution to minimize losses during field application, and it can also reduce handling and transportation costs [19].

Animal waste composts are recognized as valuable sources of major plant nutrients that reduce the need for synthetic fertilizers [20]. However, environmental problems such as nutrient loss due to surface runoff may arise if excess manure is applied to the agricultural land in sensitive catchment areas. One of the critical issues plaguing animal waste compost application is the lack of an environmentally safe application method to agricultural land in order to mitigate non-point source pollution [21,22]. Most of the nutrients losses from agricultural lands are caused by soil erosion from irrigated agriculture or runoff and leaching after rainfall events [23]. Hence, the top priority was to develop methods that would minimize rapid nutrient loss from animal waste manure application and mitigate nutrient runoff after irrigation or rainfall events. Major pathways of N losses are NH_4^{+-}N and NO_3^-–N leaching, NH_3 volatilization, and runoff losses. New strategies such as biochar-manure pelletizing methods are available to minimize N loss from the application of animal-waste compost. New approaches that would improve the efficiency of compost are significant to agricultural production in Korea, because the amount of animal waste must be disposed in an effective manner with a minimal impact on agricultural eco-systems.

In general, the production of biochar pellets with poultry litter mixed with switch grass (BMP) is relatively simple. Pellet is blended poultry litter with powder of switchgrass, and then BMP is produced with slow pyrolysis [24]. Several scientists reported that the synergistic effects of biochar blended with inorganic fertilizer or biochar mixed with nutrient-rich compost were observed to improve crop yields [25–27]. There is only limited information on the field application of supplemented biochar manure pellets with inorganic fertilizers (SBMPFs). SBMPF provides supplemental nutrients and can also regulate nutrient loss or release rate by functioning as a slow release fertilizer. Slow-release fertilizers gradually discharge nutrients to the soil during the growing season and provide sufficient nutrients to crops while minimizing leaching losses [28], which can increase farmers' profits and minimize environmental impacts [29]. Ultimately, this application ameliorates the loss of income in agro-business and mitigates the potential contamination of agricultural watersheds. SBMPFs thus represent an efficient way to decrease field application costs and biochar loss during soil application [19].

However, only limited information on blended biochar pellets functioning as slow-release fertilizers is available. Kim et al. [30] indicated that the application of a combination of biochar and slow release fertilizers yielded the lowest methane emissions among the treatments due to the inhibition of methanogenic bacteria via increased soil aeration and improved rice yield compared to the control.

Additional benefit for cropland application of biochar is carbon sequestration [31,32]. Biochar has a much longer residency period (up to 1000 years) compared to raw materials because of its recalcitrance to biotic and abiotic degradation [33]. However, biochar is partly degraded and oxidized into CO_2 when incorporated into soils [34] and up to 50% of feedstock carbon may be lost during pyrolysis [31,35]. Therefore, reduction of carbon during biochar production and increasing its stability in the soil would improve its potential for carbon sequestration. In terms of soil carbon sequestration and the mitigation of CO_2-equiv. (carbon dioxide equivalency) emission, biochar incorporated with cow manure compost can sequester 2.3 tonnes C ha^{-1}, and ranges from 7.3 to 8.4 tonnes ha^{-1} for mitigating CO_2-equiv. emission in the cornfield [36]. Shin et al. [37] indicated that the application of biochar pellets blended with organic compost is a promising way to increase carbon sequestration during crop cultivation. For the application of BMP, carbon sequestration and mitigation of CO_2-equiv. emission were 1.65 tonnes ha^{-1} and 6.06 tonnes ha^{-1} greater than those of the control, respectively, during rice cultivation [38]. Soil carbon sequestration from the application of biochar made of wood branch increased from 1.87 to 13.37 tonnes ha^{-1}, while the plots with rice straw application demonstrated decreased soil carbon from 2.56 to 0.92 tonnes ha^{-1} [39].

The objective of this study was to evaluate the agro-environmental impact of supplemented biochar manure pellet fertilizers (SBMPFs) application on the agro-ecosystems and soil carbon sequestration during the rice growing season. It is hypothesized that the SBMPFs can significantly mitigate non-point pollution sources and increase potential carbon sequestration in agro-ecosystems.

2. Materials and Methods

2.1. Biochar Production

Biochar derived from rice hull was purchased from a local farming cooperative society in Go-chang, JeonBuk, South Korea. The top to bottom pyrolysis method to produce biochar was employed, wherein rice hull is burned from the upper level to bottom, and reduces oxygen flux from the exterior of the pyrolysis system at 29.4 KPa of air suction rate. The maximum temperatures during pyrolysis were from 490 °C at the top and 550 °C at the bottom of the pyrolysis system. The loading volume in each batch was 1.5 m^3 of rice. The biochar was milled with a grinder to pass through a 2-mm sieve before chemical analysis. The same raw materials were used for both the biochar and pig manure compost, and their chemical properties are shown in Table 1 [37,38]. The moisture contents of the biochar and pig manure compost were 5.5% and 27.2%, respectively. The biochar was generally alkaline with a pH of 9.7 and low in total nitrogen (TN), 2.0 g kg^{-1}.

Table 1. Chemical properties of biochar and pig manure compost used [1].

Materials Used	pH	EC (dS m^{-1})	TC (g kg^{-1})	TOC (g kg^{-1})	TIC (g kg^{-1})	TN (g kg^{-1})
Biochar	9.67 ± **0.04** (1:10)	1.4 ± **0.02**	566 ± **5.2**	533 ± **2.4**	33.5 ± **0.8**	2.0 ± **0.01**
Pig manure compost	8.77 ± **0.02** (1:5)	3.4 ± **0.03**	289 ± **11.1**	259 ± **20.7**	30.2 ± **1.6**	29.1 ± **0.3**

[1] EC; Electric conductivity, TC; Total carbon, TOC; Total organic carbon, TIC; Total inorganic carbon, and TN; Total nitrogen. The values were average of triplicates samples with standard deviation.

2.2. Production of Supplemented Biochar Manure Pellet

The processing of SBMPFs is described in Figure 1. Prior to pelleting, biochar was processed in a series of sieves (0.5–5 mm) to ensure even particle distribution. In producing biochar pellets, 40% biochar was mixed with 60% pig manure compost as a binder. The SBMPF was completely mixed by using an agitator while spraying different nutrient solutions in the mixtures, and then feeding it into a commercial pellet mill (7.5 KW, 10HP, KumKang Engineering Pellet Mill Co., Daegu, South Korea). Different biochar pellets (Patent number: 10-1889400) treated with (1) urea solution heated at 60 °C (BMP-U60), (2) N, P, and K nutrient solutions at room temperature (BMP-NPK), (3) urea and K solutions at room temperature (BMP-UK), and (4) pig manure compost only (PMCP) pelletized. The size of BMPFs was approximately Ø 0.51 cm × 0.78 cm. The total carbon, TN (total nitrogen), TP (total phosphorus), and TK (total potassium) contents of BMPF embedded with different treatments are described in Table 2. Their total carbon and nitrogen contents varied from 225 g kg^{-1} to 289 g kg^{-1} and from 29.1 g kg^{-1} to 102.0 g kg^{-1}, respectively. It was observed that the BMP-U60 had the highest nitrogen content of 102.0 g kg^{-1} and BMP-UK had the lowest nitrogen content of 84.0 g kg^{-1}.

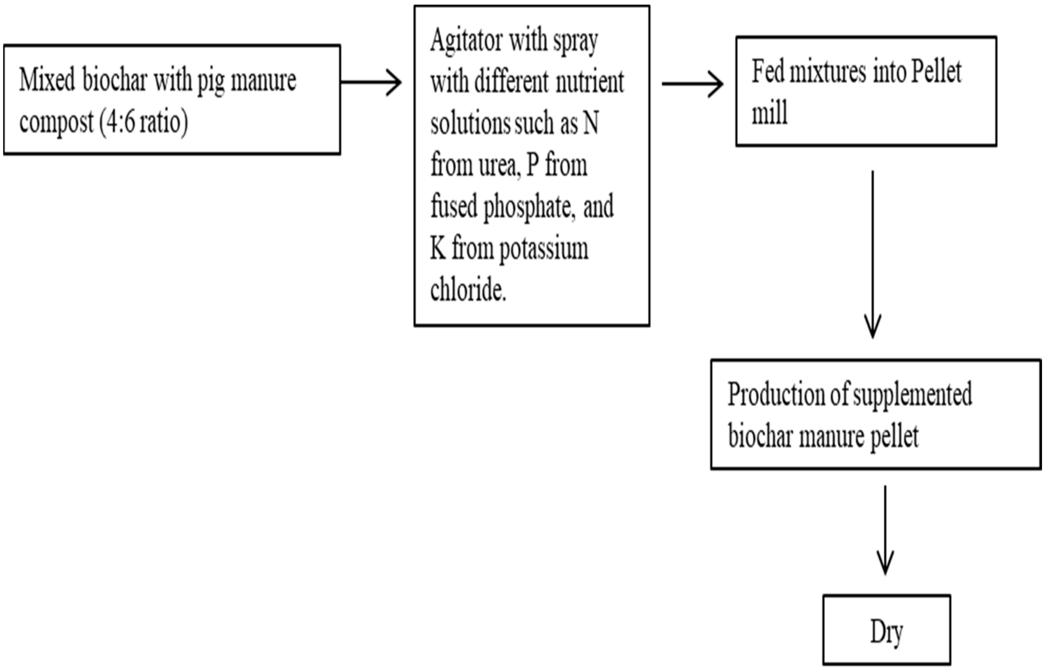

Figure 1. Diagram of processing the supplemented biochar manure pellets with different types of fertilizer.

Table 2. Total carbon, total nitrogen, total phosphorus and total potassium contents of supplemented biochar manure pellet fertilizers [1].

Treatments *	TC (g kg^{-1})	TN (g kg^{-1})	TP(g kg^{-1})	TK(g kg^{-1})
PMCP	289.0 ± 0.3	29.1 ± 0.01	79.4 ± 0.3	20.8 ± 0.2
BMP-U60	226.3 ± 0.2	102.0 ± 0.25	29.5 ± 0.2	11.8 ± 0.3
BMP-NPK	227.8 ± 0.3	75.2 ± 0.03	32.8 ± 0.4	57.2 ± 0.3
BMP-UK	224.7 ± 0.5	84.0 ± 0.05	35.4 ± 0.3	13.5 ± 0.1

[1] TC; Total carbon, TN; Total nitrogen, TP; Total phosphorous, TK; Total potassium; * BMP-U60; BMP blended with urea solution heated at 60 °C, BMP-NPK; BMP blended with N, P and K nutrient solutions at room temperature and BMP-UK, BMP blended with N and P nutrient solutions at room temperature. The values displayed are averages of triplicate samples with standard deviation.

2.3. Field Experiment

The experimental field was cultivated with rice monoculture, and it has clay loamy soil. It is located at 35°49.510′ N of latitude and 127°2.536′ E of longitude in the National Institute of Agricultural Sciences (NIA), Rural Development Administration (RDA), Jeonju, Republic of Korea. The precipitation amount and average temperature were 718 mm and 22.3 °C during the rice cultivation season, respectively. Additionally, the solar radiation quantity and duration of sunshine are measured at 2753.2 MJ and 949.9 h during the cultivation period, respectively. The rice variety used in this experiment was Shindongjin, with a planting distance of 30 × 60 cm. The experimental design was a block design with five treatments consisting of (1) the control, (2) PMCP, (3) BMP-U60, (4) BMP-NPK, and (5) BMP-UK with three replications and 16 m^2 of the plot size. The amount of fertilizer and manure compost applied in the control and PMCP treatment were 90-45-57 kg ha^{-1} (N-P-K) and 2600 kg ha^{-1}, respectively, which was based on National Institute of Agricultural Sciences (NIA) recommended rates for rice cultivation [40]. The SBMPFs were incorporated into the soil based on 90 N kg ha^{-1} for whole basal application at 5 days prior to rice transplanting. Water logging time was 6 days prior to rice transplanting. The date of rice transplant was May 23, and drainage times were 14 days, 35 days, and 93 days after transplanting with one-week drainage. Rice was harvested 154 days after transplanting period. To evaluate the agricultural impact of different SBMPFs, major plant nutrients were analyzed from the surface water and soil in the paddy during rice cultivation. For rice growth responses, the plant height and number of tillers were measured about 100 days after rice transplanting, while the grain yield and dry weight of rice straw were weighed after harvest. For the effect of SBMPF applications in the paddy, the physicochemical properties of the soil used are presented in Table 3.

Table 3. Soil physicochemical properties of experimental field [1].

Soil Type	pH	EC ($dS\ m^{-1}$)	NH_4^+–N ($mg\ kg^{-1}$)	NO_3–N ($mg\ kg^{-1}$)	P_2O_5 ($mg\ kg^{-1}$)	K_2O ($mg\ kg^{-1}$)	TC ($g\ kg^{-1}$)	TOC ($g\ kg^{-1}$)
Clay Loam	7.0 ± 0.4	0.6 ± 0.03	10.6 ± 0.1	ND	97.8 ± 0.6	26.1 ± 0.1	20.7 ± 0.3	16.6 ± 0.2

[1] EC; electric conductivity, TC; Total carbon, TOC; Total organic carbon and ND; Non detected with 1 mg kg^{-1} of detection limit. The values displayed are averages of triplicate samples with standard deviation.

2.4. Chemical Analysis of Paddy Soil and Water

After rice transplantation in the paddy, surface soil and water samples were collected every 20 days. The collected water samples were filtered through Whatman 2. The surface water was analyzed for NH_4^+–N, NO_3^-–N, K^+, and SiO_2 content using a UV spectrophotometer (C-Mac, Dae-Jeon, Korea) throughout the cropping season. The wet soil samples were extracted by using a 2M KCl solution (1:5, soil: extractant ratio). Those samples were analyzed directly for NH_4^+–N and NO_3^-–N by using the Bran-Lubbe Segmented Flow Auto Analyzer (Seal Analytical Ltd., Wisconsin, USA), and then the NH_4^{+}—N and NO_3—N concentrations were calculated by compensation for moisture contents of wet soil. The extractant using the Mehlich III method [41] from dried soil samples that passed through 2 mm sieves were stored in a refrigerator at 4 °C until PO_4^-, K^+ and SiO_2 were analyzed using a UV spectrophotometer (C-Mac, Dae-Jeon, Korea). Total carbon (TC) in soils was analyzed with total organic carbon (TOC) analyzer (Elementa vario TOC cube, Hanau, Germany). The combustion temperature was 950 °C and tungsten trioxide (WO_3) was used as the catalyst. With 350mg of soil samples, total nitrogen (TN) contents were determined by dry combustion with 250mg of L-Glutamic acid, standard compound, by using vario Max CN (Elementar, Hanau, Germany).

2.5. Data Processing and Carbon Balance Calculations

The soil carbon sequestration via BMPFs application was calculated from the difference of the residual amount of soil carbon between the control and different treatments after rice harvest by using the following equation [38]:

$$SS_{TC} = \left\{ \sum_{i=0}^{n} T_{TC}\ (Li - Ii) - NT_{TC}\ (Li - Ii) \right\} \times SW \tag{1}$$

where SS_{TC} (kg ha^{-1}) is the potential sequestration amount of soil carbon, T (kg ha^{-1}) is the treatment of SBMPFs, NT (kg ha^{-1}) is the control, $_{TC}$ is total carbon content (g kg^{-1}), i is the sampling date, Li and Ii are carbon contents of the last and initial samplings which analyzed the soil carbon content (g kg^{-1}), and SW is the soil weight (bulk density, 1.3; 10cm of plowing soil depth, kg ha^{-1}).

The mitigation of CO_2 emission for SBMPFs application was also estimated using equation [38]:

$$CO_2 = SS_{TC} \times CF_{SC} \tag{2}$$

where SS_{TC} is the amount of soil carbon sequestration (tonnes ha^{-1}) and CF_{SC} is the conversion factor of CO_2 emission from soil carbon (1 kg C = 3.664 kg CO_2-equiv.).

Profit analysis for the mitigation of CO_2 emission was also calculated by using the equation [38]:

$$P = AM \times MP \tag{3}$$

where P is the profit of carbon dioxide trading (\$ ha^{-1}), AM is the amount of mitigation of CO_2 emission (tonnes ha^{-1}), and MP is the market prices of CO_2 offsets (\$ per tonnes CO_2). Also, the trading prices of CO_2 offsets in the European Climate Exchange (ECX) varied between \$4.1 and \$7.9 per tonnes CO_2 in 2016 [42] while the Korean Climate Exchange (KCX) ranged from \$7.9 to \$19.3 per 1 Korean Allowance Unit (KAU) [43].

2.6. Statistical Analysis

Statistical analysis was conducted using SAS version 9.2 Software (SAS, Inc., Cary, NC, USA), with an ANOVA with Duncan multiple range tests for the comparison of treatments with carbon contents at 1st day of rice transplanting and day after harvesting, carbon sequestration, and growth components during rice cultivation. Standard deviation was used for comparisons of paddy water and soil chemical properties.

3. Results and Discussions

3.1. Effects of Essential Nutrients in the Paddy Water and Soil

3.1.1. Paddy Water Quality

The NH_4^+–N and NO_3^-–N concentrations in the surface paddy water are presented in Figure 2. At the first day of rice transplanting, the NH_4^+–N concentration of surface paddy water in the MBP-NPK was significantly higher than the other treatments, but its control showed nearly the same values than the other treatments. However, the NO_3^-–N concentrations in the control and PMCP were only significantly higher than those in the SBMPF treatments. It was observed that NH_4^+–N concentrations in the treatments were higher on the first day of rice transplants, but similar to the rest of the days. The loss of nitrogen under the application of SBMPF was almost complete within 21 days after rice transplantation. This might be due to the adsorption of NH_4^+–N by the applied biochar in the soil. Regardless of the treatments at 112 days of rice transplanting, the NO_3^-–N concentrations were higher compared with other sampling days (93 days) due to the start of drainage of the surface water in the rice paddy. The study showed that the application of SBMPs can be a solution to mitigate the loss of nitrogen and phosphorus [44].

The PO_4^-–P, K^+, and SiO_2 concentrations in the surface paddy water under application of BMPFs are described in Figure 3. The measured PO_4^-–P concentration in the control and PMCP treatment was 2.8–5.3 times higher than the value in BMP-U60, BMP-UK, and BMP-NPK, respectively, until 21 days after rice transplantation. The PO_4^-–P concentrations were not significantly different ($p > 0.05$) from 41 days to 93 days after rice transplanting among the treatments. The greatest differences in K+ concentrations can be seen at 41 days after transplant. The higher values in the control and PMCP were 28.5 mg L^{-1}, and the lowest in the BMP-U60 was 9.6 mg L^{-1}, but not significantly different ($p > 0.05$) with that of BMP-UK.

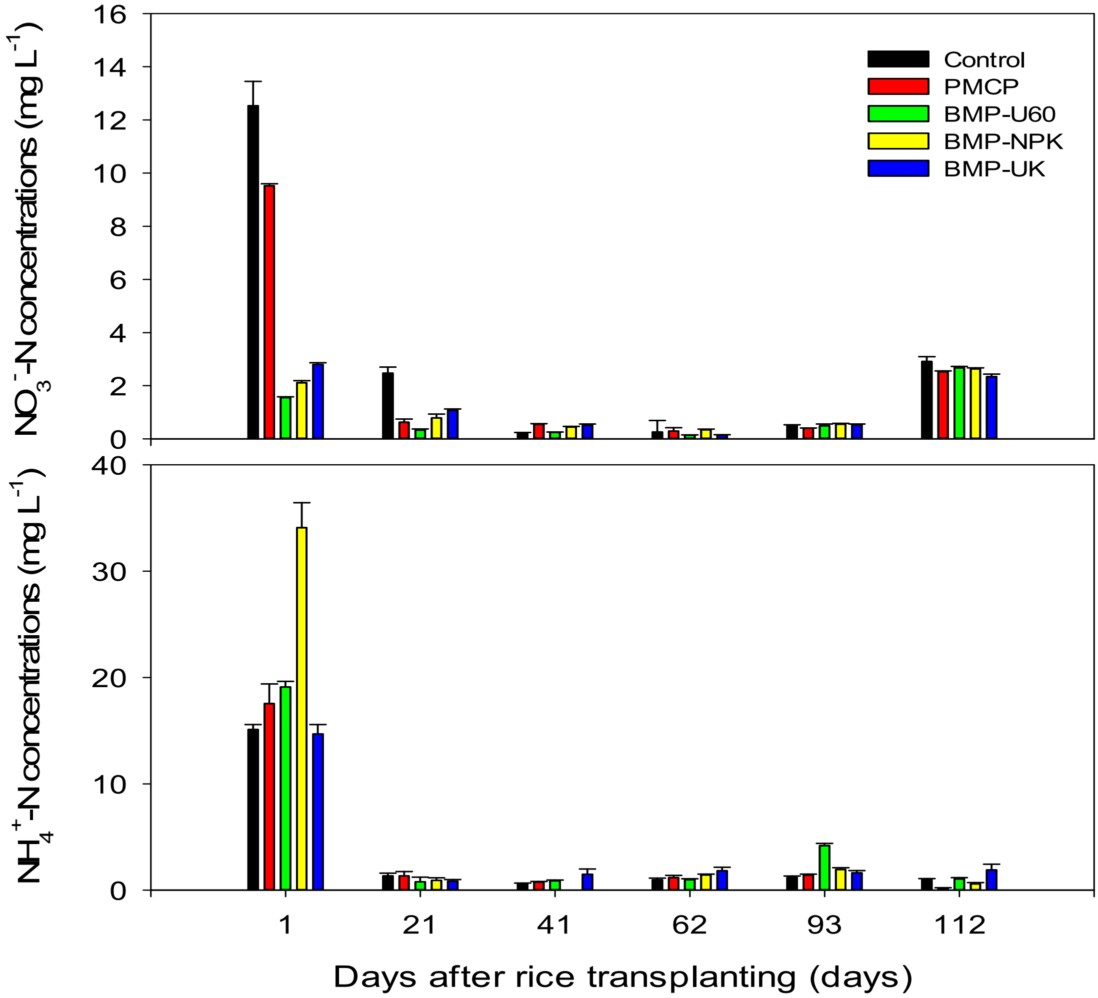

Figure 2. Effects of different treatments on NH_4^+–N and NO_3^-–N contents in rice surface paddy water during rice cultivation. The values displayed are averages of triplicate samples with standard deviation.

Silicon (Si) in soil exists in an unavailable form, but the Si in crop residues is a useful structure (H_4SiO_4) compared with Si fertilizer for crop uptake [45]. This recycled Si is leached into soil after the decomposition of crop residues. It is observed that SiO_2 concentration ranged from 10 mg L^{-1} to 35 mg L^{-1} during the cultivation period, and the highest SiO_2 concentration was 34.4 mg L^{-1} in the BMP-UK at after 41 and 112 days of rice transplanting. However, SiO_2 concentrations in the paddy water under the application of SBMPFs were higher than those of the control and PMCP at 112 days after transplant. The most commonly used silicon fertilizer is wollastonite for soil application because of its high solubility for plant uptake (2.3–3.6%) [46]. Recently, much attention has been paid to biochar as an alternative soil ameliorant because it could slowly release 43 mg kg^{-1} for the available plant uptake of silica [47]. The 1% KOH solution treated biochar application to soil significantly increased available form of silicon in the plant [48]. In this study, the SiO_2 concentration was significantly increased at the harvesting time under the application of SBMPFs. Thus, the incorporation of SBMPFs had the potential ability to recycle silica. Overall, the PO_4—P, K^+, and SiO_2 concentrations were significantly higher than the other sampling days (93 days) due to the start of drainage of the surface water in the paddy field.

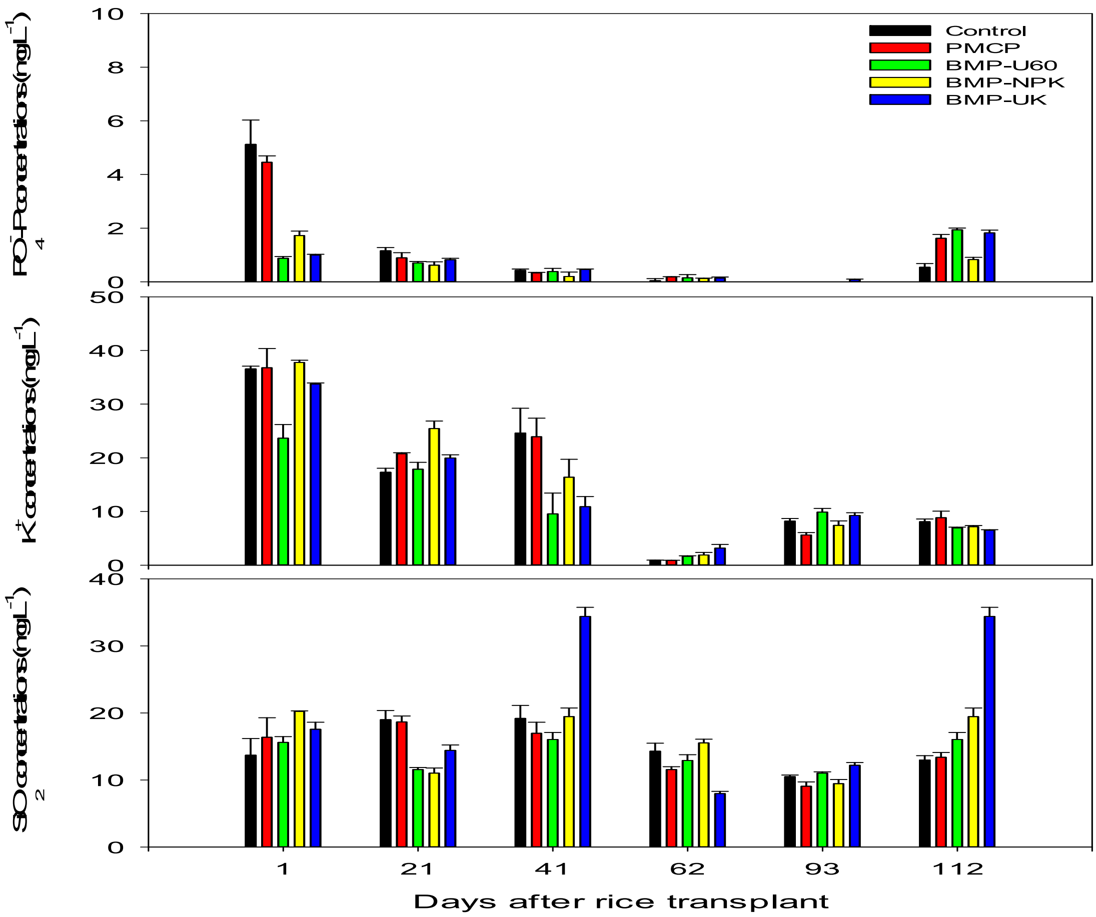

Figure 3. Effects of different treatments on PO_4^-–P, K^+ and SiO_2 concentrations in surface paddy water during rice cultivation. The values displayed are averages of triplicate samples with standard deviation.

3.1.2. Nutrients in Paddy Soil

Urea application is usually the main source of ammonium ions because urea can be hydrolyzed into NH_4^+ and OH^- by the ammonification reaction within short periods after application in the paddy soil. The major nutrient concentrations in the soil are described in Figure 4. NH_4^+–N concentration in the BMP-NPK was highest among the treatments at 41 days after rice transplanting. Total nitrogen losses were reduced with the incorporation of rice straw in the rice paddy soil due to increasing immobilization [49] and denitrification [50]. P_2O_5 concentrations except the PMCP were not significantly different during 21 days after rice transplanting among treatments. The K_2O concentrations in the soil treated with BMPFs continuously decreased during rice cultivation due to the K^+ solubility, except for the BMP-U60 treatment. Biochar application increased the availability of K^+ and P because it was a net source of cations due to increased soil capacity to hold exchangeable cations [51,52]. The application of biochar produced from rice straw increased the available P and K^+ by 15.3% and 28.6% in the soil, respectively. However, biochar application did not significantly increase total nitrogen compared with the control in the rice paddy [53]. Overall, the release of major nutrients to soil under the application of SBMPFs was significantly lower compared with those from the control and PMCP.

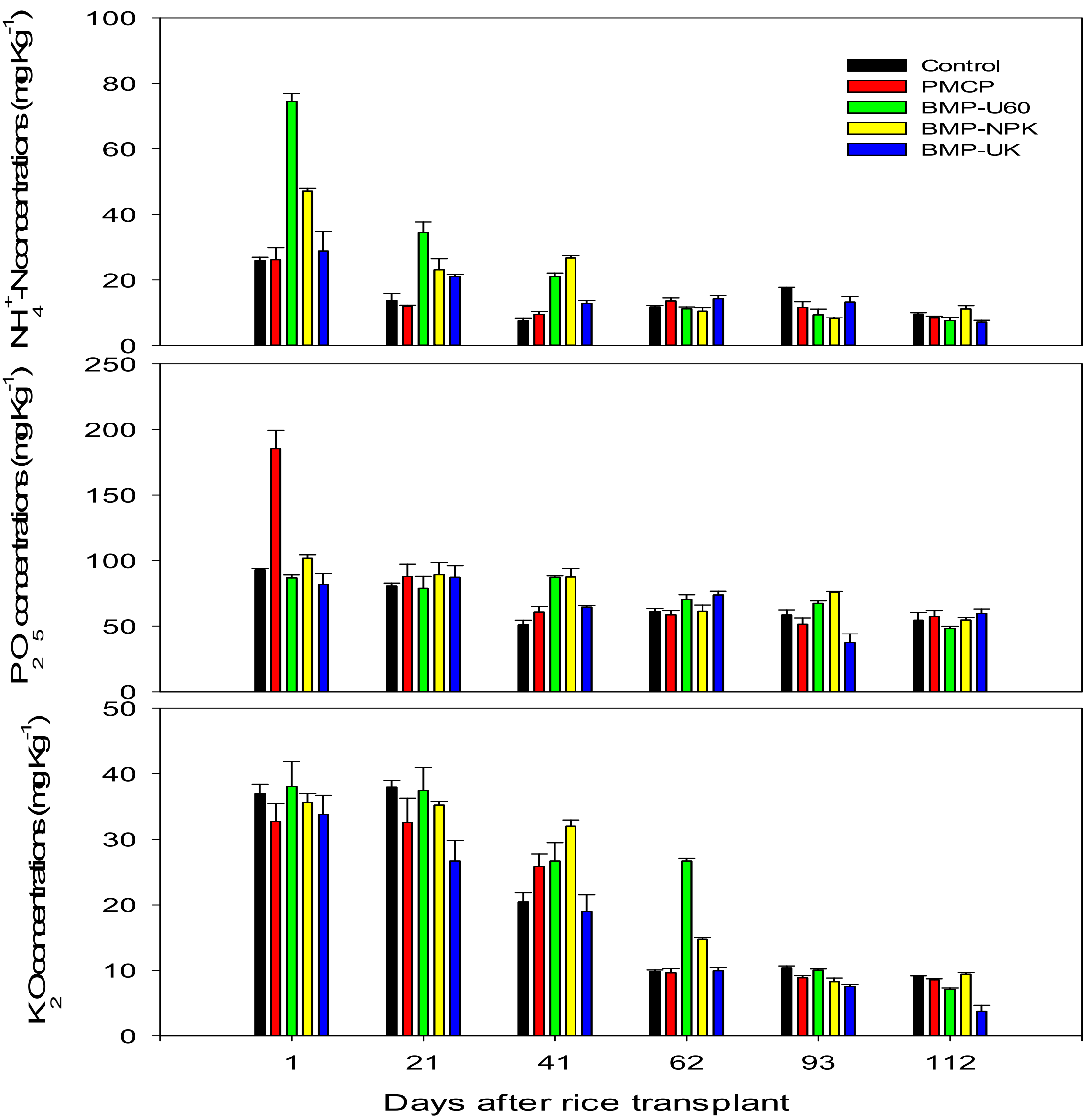

Figure 4. $NH_4{}^+$–N, P_2O_5 and K_2O concentrations under different treatments in the paddy soil during rice cultivation. The values displayed are averages of triplicate samples with the standard deviation.

3.2. Carbon Sequestration and Profit Analysis

Soil carbon sequestration was only considered after soil analysis from rice paddy incorporated SBMPFs at day 1 of rice transplanting and the day after harvesting. Changes of total carbon contents in paddy soil under different treatments at the initial stage and after harvesting are described in Table 4. The carbon contents on first day of rice transplanting and the day after harvesting were significantly ($p < 0.001$) different in the treatments. There was minimal difference in total carbon content in the control between the first day of rice transplanting and after harvesting.

The application of biochar incorporated to the soil has been suggested as a promising method for carbon sequestration as well as another method for mitigating greenhouse gas, increasing crop yields and enhancing the sorption of pollutants [49,54]. Regarding carbon sequestration, it might be distinguished that short term released CO_2 refers to the retention time of sequestrated carbon in soil from organic matter decomposition, while long term, it is stored as biochar from thermal conversion materials [38].

Table 4. Carbon contents in the soils treated with different supplemented biochar manure pellet fertilizers on first day of rice transplant and day after harvest *.

Treatments Control	First Day of Rice Transplant (g kg^{-1})	Day After Harvest (g kg^{-1})
	10.30 ± 0.02 a	10.38 ± 0.02 c
PMCP	9.45 ± 0.07 d	10.49 ± 0.07 c
BMP-U60	9.87 ± 0.13 b	10.83 ± 0.13 b
BMP-NPK	9.90 ± 0.06 b	11.80 ± 0.09 a
BMP-UK	9.66 ± 0.05 c	11.83 ± 0.03 a
F-value	55.33	235.30
Pr > F	<0.001	<0.001

* Mean values followed by different letters, which indicate significant differences ($p < 0.05$) among treatments with One way ANOVA by the mean comparison for all pairs using Tukey-Kramer HSD analysis for total carbon contents on first day of rice transplant and the day after harvest.

For the application of different types of SBMPFs, carbon sequestration, mitigation of CO_2, and profit analysis were calculated by using Equations (1)–(3), respectively (Table 5). The analysis of carbon sequestration showed 2.67 tonnes C ha^{-1} in the BMP-UK as the best treatment for carbon sequestration, and 1.14 tonnes C ha^{-1} in the BMP-U60 as the worst. It appeared that their recovery rates varied from 25.4% to 48.5% of SBMPFs applied to the rice paddy. It was observed that the mitigation of CO_2 increased with the application of BMPFs, and the highest was 5.09 tonnes C ha^{-1} in the BMP-UK. The profit under SBMPFs application was estimated to range from $6.56 ha^{-1} to $68.80 ha^{-1} during rice cultivation for KAU. The target of the Korean government is to reduce greenhouse gas emissions by 1.48 million tonnes CO_2-equiv. (5.2%) of the 28.49 million tonnes CO_2-equiv. total greenhouse emissions in the agricultural sector by 2020 [55]. Therefore, it is estimated that the 482,085 ha^{-1} (29.3%) of 1,644,000 ha^{-1} total area of rice cultivation with the BMP-NPK application in Korea [56] is required to accomplish this goal.

In order to establish carbon trading in the agriculture sector, policymakers should prepare a draft policy specifically for mitigating greenhouse gas emissions by providing support to farmers of about $58 per hectare of cultivated rice paddy through the application of BMP-NPK. The application of BMPFs did not only increase carbon storage, but also enhanced rice yield and soil fertility [38].

Table 5. Evaluation of carbon sequestration and its profit analysis for application of supplemented biochar manure pellet fertilizers during rice cultivation.

Treatments	Carbon Sequestration (Tonnes ha^{-1})	Mitigation of CO_2 (Tonnes ha^{-1})	Profit ($ ha^{-1})	Additional Profit for SBMPF Application ($ ha^{-1})
Control	1.28 ± 0.11 b	4.70 ± 0.12 b	63.59 ± 2.50 b	-
PMCP	1.24 ± 0.08 b	4.54 ± 0.29 b	61.47 ± 3.96 b	-
BMP-U60	1.41 ± 0.12 b	5.18 ± 0.44 b	70.06 ± 5.98 b	6.56
BMP-NPK	2.45 ± 0.18 a	8.98 ± 0.66 a	121.46 ± 8.92 a	57.87
BMP-UK	2.67 ± 0.12 a	9.78 ± 0.44 a	132.36 ± 5.95 a	68.77
F-value	55.06	55.06	55.06	-
Pr > F	<0.001	<0.001	<0.001	-

kg C = 3.664 kg CO_2-eqiv., 1 tonnes CO_2 = KAU = 23,000 (8.12) = $13.53.

3.3. Rice Growth Responses to Supplemented Biochar Manure Pellet

Growth responses to the application of SBMPFs are shown in Table 6. The plant height in BMP-U60 was 15.2% higher than the control, and rice yield in the BMP-U60 was increased by 15.7% compared with the control, even when the application amount of pig manure compost applied was reduced to about 1000 kg ha^{-1}. This result might be due to the enhanced nutrient use efficiency under application of BMPFs functioning as a slow release fertilizer. Min et al. [4] reported that supplemented BMPFs application enhanced rice yield. Shin et al. [38] also reported similar results in their study. With the whole basal application of SBMPFs in the rice field prior to rice transplanting, it could prevent additional fertilizer application. Puga et al. [57] conducted similar research to evaluate the effects of biochar-based N fertilizers on nitrogen use efficiency (NUE) and maize yield. Their results showed that an average maize yield was increased 26% in the application of biochar-based N fertilizers (51% biochar with 10% N) compared with urea only treatment, and the NUE was 12% improved. Pokharel and Chang [58] also reported that manure pellet with wood chip biochar significantly increased plant grain yield by 36.3 and 16.1%, compared to the control, while woodchip with biochar applications significantly decreased plant grain yield.

Table 6. Characteristics of rice growth to supplemented biochar manure pellet fertilizer application.

Treatments	Plant Height (cm)	Number of Tillers	Dry Weight of Rice Straw (Tonnes ha^{-1})	Grain Yield (Tonnes ha^{-1})
Control	92.33 ± 0.58 b	11.67 ± 1.53 b	9.73 ± 0.51 a	6.63 ± 0.14 b
PMCP	100.00 ± 2.00 ab	12.33 ± 2.52 ab	9.55 ± 0.11 a	6.68 ± 0.49 ab
BMP-U60	106.33 ± 8.15 a	16.00 ± 2.65 ab	6.85 ± 0.43 b	7.67 ± 0.36 a
BMP-NPK	103.67 ± 5.51 ab	13.00 ± 3.46 ab	5.96 ± 0.51 c	7.13 ± 0.33 a
BMP-UK	104.67 ± 5.03 ab	17.67 ± 3.51 a	5.32 ± 0.53 c	6.52 ± 0.65 b
F-value	3.69	2.49	63.02	3.69
Pr > F	0.043	0.110	<0.001	0.043

4. Conclusions

Different supplemented biochar manure pellet fertilizers were tested to assess their agro-environmental impacts on paddy water and soil systems during rice cultivation. With regard to the water quality of paddy, the NO_3^-–N and PO_4^-–P in control and PMCP were relatively higher than those of the SBMPFs applied plots. Non-point pollutants in runoff water to small stream near the rice cultivation area were reduced with application of SBMPFs. Considering the soil chemical properties, NH_4^+–N concentration in control was lower compared with the SBMPFs treatment at 41 days after rice transplant. However, the available P_2O_5 concentrations were almost stage-state among all the treatments from 21 days after rice plant until the harvest period, except for the first day of rice transplant in the PMCP. It is possible that the SBMPFs can be applied with whole basal application without additional application of chemical fertilizers. Also, the highest carbon sequestration was 2.67 tonnes C ha^{-1} in BMP-UK treatment, and the lowest was 1.14 tonnes C ha^{-1} in the BMP-U60 treatment. The grain yields from the SBMPF applied plots, except for BMP-UK, were significantly higher than the yield from the control even though amounts of pig manure compost applied were decreased from 1881.8 kg ha^{-1} to 2070.8 kg. Therefore, the application of SBMPFs can contribute to reducing the agro-environmental impacts of runoff as well as enhance carbon sequestration and rice yield in agro-ecosystems.

Author Contributions: Project leader and original draft writing, J.S.; Statistics and visualization, S.P.; review and editing, C.J. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded beyond Research Program of Agricultural Science & Technology Development (Project No. PJ013814012020) in Korea.

Acknowledgments: We are thankful to the National Institute of Agricultural Sciences, Rural Development Administration in Korea.

Conflicts of Interest: The author certifies that there are no affiliation with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

References

1. Edgerton, M.D. Increasing crop productivity to meet global needs for feed, food, and fuel. *Plant Physiol.* **2009**, *149*, 7–13. [CrossRef] [PubMed]
2. O'Connor, D.; Peng, T.; Zhang, J.; Tsang, D.C.W.; Alessi, D.S.; Shen, Z.; Bolan, N.S.; Hou, D. Biochar application for the remediation of heavy metal polluted land: A review of in situ field trials. *Sci. Total Environ.* **2018**, *619*, 815–826. [CrossRef] [PubMed]
3. Zhao, B.; O'Connor, D.; Zhang, J.; Peng, T.; Shen, Z.; Tsang, D.C.W.; Hou, D. Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar. *J. Clean. Prod.* **2018**, *174*, 977–987. [CrossRef]
4. Min, H.; Liu, Y.; Qin, H.; Jiang, L.; Zou, Y. Quantifying the effect of biochar amendment on soil quality and crop productivity in Chinese rice paddies. *Field Crops Res.* **2013**, *154*, 172–177.
5. Li, Z.; Gu, C.; Zhang, R.; Ibrahim, M.; Zhang, G.; Wang, L.; Zhang, R.; Chen, F.; Liu, Y. The benefic effect induced by biochar on soil erosion and nutrient loss of slopping land under natural rainfall conditions in central China. *Agric. Water Manag.* **2017**, *185*, 145–150. [CrossRef]
6. Liu, X.; Zhou, J.; Chi, Z.; Zheng, J.; Li, L.; Zhang, X.; Zheng, J.; Cheng, K.; Bian, R.; Pan, G. Biochar provided limited benefits for rice yield and greenhouse gas mitigation six year following an amendment in a rice paddy. *Catena* **2019**, *179*, 20–28. [CrossRef]
7. MIFAFF. Annual statistics in food, agriculture, fisheries and forestry in 2009. Korean Ministry for Food, Agriculture, Fisheries and Forestry. *Environ. Sci. Pollut. Res.* **2010**, *16*, 1–9.
8. Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota—A review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836. [CrossRef]
9. Cantrell, K.B.; Hunt, P.G.; Uchimiya, M.; Novak, J.M.; Ro, K.S. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour. Technol.* **2012**, *107*, 419–428. [CrossRef] [PubMed]
10. Brewer, C.; Unger, R.; Schmidt-Rohr, K.; Brown, R. Criteria to select biochars for field studies based on biochar chemical properties. *Bioenergy Res.* **2011**, *4*, 312–323. [CrossRef]
11. Xie, T.; Reddy, K.R.; Wang, C.; Yargicoglu, E.; Spokas, K. Characteristics and applications of biochar for environmental remediation: A review. *Crit. Rev. Env. Sci. Tech* **2015**, *45*, 939–969. [CrossRef]
12. Kim, P.; Johnson, A.M.; Essington, M.E.; Radosevich, M.; Kwon, W.T.; Lee, S.H.; Rials, T.G.; Labbe, N. Effect of pH on surface characteristics of switchgrass-derived biochars produced by fast pyrolysis. *Chemosphere* **2013**, *90*, 2623–2630. [CrossRef] [PubMed]
13. Blackwell, P.; Joseph, S.; Munroe, P.; Anawar, H.M.; Storer, P.; Gilkes, R.J.; Solaiman, Z.M. Influences of biochar and biochar-mineral complex on mycorrhizal colonization and nutrition of wheat and sorghum. *Pedosphere* **2015**, *25*, 686–695. [CrossRef]
14. Chan, K.; van Zwieten, L.; Meszaros, I.; Downie, A.; Joseph, S. Agronomic values of green waste biochar as a soil amendment. *Aust. J. Soil Res.* **2007**, *45*, 629–634. [CrossRef]
15. Deenik, J.L.; McClellan, T.; Uehara, G.; Antal, M.J.; Campbell, S. Charcoal volatile matter content influences plant growth and soil nitrogen transformations. *Soil Sci. Soc. Am. J.* **2010**, *74*, 1259–1270. [CrossRef]
16. Solaiman, Z.M.; Murphy, D.V.; Abbott, L.K. Biochars influence seed germination and early growth of seedlings. *Plant Soil* **2012**, *353*, 273–287. [CrossRef]
17. Husk, B.; Major, J. *Commercial Scale Agricultural Biochar Field Trial in Quebec, Canada, over Two Years: Effects of Biochar on Soil Fertility, Biology, Crop Productivity and Quality*; Blue Leaf: Quebec, QC, Canada, 2008.
18. Major, J.; Lehmann, J.; Rondon, M.; Goodale, C. Fate of soil-applied black carbon: Downward migration, leaching and soil respiration. *Glob. Chang. Biol.* **2010**, *16*, 1366–1379. [CrossRef]
19. Reza, M.T.; Lynam, L.G.; Vasquez, V.R.; Coronella, C.J. Pelletization of biochar from hydrothermally carbonized wood. *Environ. Prog. Sustain. Energy* **2012**, *31*, 225–234. [CrossRef]
20. Khalil, M.; Gutser, R.; Schmidhalter, U. Effects of urease and nitrification inhibitors added to urea on nitrous oxide emissions from a loess soil. *J. Plant Nutr. Soil Sci.* **2009**, *172*, 651–660. [CrossRef]
21. Harmel, R.D.; Torbert, H.A.; Haggard, B.E.; Haney, R.; Dozier, M. Water quality impacts of converting to a poultry litter fertilization strategy. *J. Environ. Qual.* **2004**, *33*, 2229–2242. [CrossRef]
22. Wang, Y.; Lin, Y.; Chiu, P.C.; Imhoff, P.T.; Guo, M. Phosphorus release behaviors of poultry litter biochar as a soil amendment. *Sci. Total Environ.* **2015**, *512*, 454–463. [CrossRef] [PubMed]

23. EPA. A Long-Term Vision for Assessment, Restoration, and Protection under the Clean Water Act Section 2013, 303(d) Program. Available online: https://19january2017snapshot.epa.gov/new-version-cwa-303d-program-updated-framework-implementing-cwa-303d-program-responsibilities_html (accessed on 14 April 2020).
24. Cantrell, K.B.; Martin, J.H., II. Poultry litter and switchgrass blending and pelleting characteristics for biochar production. In Proceedings of the ASABE Annual International Meeting, Dallas, TX, USA, 29 July –1 August 2012.
25. Hua, L.; Wu, W.X.; Liu, Y.X.; McBride, M.; Chen, Y.X. Reduction of nitrogen loss and Cu and Zn mobility during sludge composting with bamboo charcoal amendment. *Environ. Sci. Pollut. Res.* **2009**, *16*, 1–9. [CrossRef] [PubMed]
26. Ro, K.S.; Cantrell, K.B.; Hunt, P.G. High-temperature pyrolysis of blended animal manures for producing renewable energy and value-added biochar. *Ind. Eng. Chem. Res.* **2010**, *49*, 10125–10131. [CrossRef]
27. Faloye, O.T.; Alatise, M.O.; Ajayi, A.E.; Ewulo, B.S. Synergistic effects of biochar and inorganic fertilizer on maize (zea mays) yield in an alfisol under drip irrigation. *Soil Tillage Res.* **2017**, *174*, 214–220. [CrossRef]
28. Fernandez-Escobar, R.; Benlloch, M.; Herrera, E.; Garcia-Novelo, J.M. Effect of traditional and slow-release N fertilizers on growth of olive nursery plants and N losses by leaching. *Sci. Hortic.* **2004**, *101*, 39–49. [CrossRef]
29. Mortain, L.; Dez, I.; Madec, P.J. Development of new composites materials, carriers of active agents from biodegradable polymers and wood. *Comptes Rendus Chim.* **2004**, *7*, 635–640. [CrossRef]
30. Kim, J.; Yoo, G.; Kim, D.; Ding, W.; Kang, H. Combined application of biochar and slow-release fertilizer reduces methane emission but enhances rice yield by different mechanisms. *Appl. Soil Ecol.* **2017**, *117*, 57–62. [CrossRef]
31. Zhao, L.; Cao, X.; Zheng, W.; Kan, Y. Phosphorus-assisted biomass thermal conversion: Reducing carbon loss and improving biochar stability. *PLoS ONE* **2014**, *9*, e115373. [CrossRef]
32. Brassard, P.; Godbout, S.; Raghavan, V. Soil biochar amendment as a climate change mitigation tool: Key parameters and mechanisms involved. *J. Environ. Manage.* **2016**, *181*, 484–497. [CrossRef]
33. Harvey, O.R.; Kuo, L.J.; Zimmerman, A.R.; Louchouarn, P.; Amonette, J.E.; Herbert, B.E. An index-based approach to assessing recalcitrance and soil carbon sequestration potential of engineered black carbons (biochars). *Environ. Sci. Technol.* **2012**, *46*, 1415–1421. [CrossRef]
34. Cross, A.; Sohi, S.P. A method for screening the relative long term stability of biochar. *Gcb Bioenergy* **2013**, *5*, 215–220. [CrossRef]
35. Lehmann, J.; Joseph, S. *Biochar for Environmental Management: Science, Technology and Implementation*; Routledge: New York, NY, USA, 2015.
36. Shin, J.; Hong, S.; Lee, S.; Hong, S.; Lee, J. Estimation of soil carbon sequestration and profit analysis on mitigation of CO_2-eq. emission in cropland incorporated with compost and biochar. *Appl. Biol. Chem.* **2017**, *60*, 467–472. [CrossRef]
37. Shin, J.; Choi, E.; Jang, E.S.; Hong, S.G.; Lee, S.; Ravindran, B. Adsorption characteristics of ammonium nitrogen and plant responses to biochar pellet. *Sustainability* **2018**, *10*, 1331. [CrossRef]
38. Shin, J.; Jang, E.; Park, S.; Ravindran, B.; Chang, S. Agro-environmental impacts, carbon sequestration and profit analysis of blended biochar pellet application in the paddy soil-water system. *J. Environ. Manag.* **2019**, *244*, 92–98. [CrossRef] [PubMed]
39. Thammasom, N.; Vityakon, P.; Lawongsa, P.; Saenjan, P. Biochar and rice straw have different effects on soil productivity, greenhouse gas emission and carbon sequestration in Northeast Thailand paddy soil. *Agric. Nat. Resour.* **2016**, *50*, 192–198. [CrossRef]
40. NAAS. *Recommended Application Amounts of Fertilizers for Crop Cultivation (eds)*; National Academy of Agricultural Sciences, Rural Development Administration: New Delhi, India, 2010; p. 16.
41. Mehlich, A. Mehlich III soil test extractant: A modification of Mehlich II extractant. *Commun. Soil Sci. Plant Anal.* **1984**, *15*, 1409–1416. [CrossRef]
42. EEX. EU Emission Allowances—Primary Market Auction. European Energy Exchange. 2017. Available online: https://www.eex.com/en/marketdata/environmental-markets/auction-market/ (accessed on 7 March 2017).
43. KRX. Korea Allowance Unit. Korean Exchange. Available online: http://marketdata.krx.co.kr/mback; http://open.krx.co.kr/contents/OPN/01/01050401/OPN01050401.jsp#document=070301 (accessed on 7 March 2017).
44. Kaneki, R.; Iwama, K.; Minagawa, A.; Sudo, M.; Odani, H.; Kobayashi, A.; Tanaka, A.; Ikeda, K.; Muranaga, M. Effect of mass balance in paddy fields and rice plant yields by reduced fertilizer use and non-puddling cultivation. *J. Jpn. Soc. Hydrol. Water Resour.* **2013**, *26*, 201–211. [CrossRef]

45. Epstein, F. Silicon: Its manifold roles in plants. *Ann. Appl. Biol.* **2009**, *155*, 155–160. [CrossRef]
46. Wang, J.; Wang, D.; Zhang, G.; Wang, Y.; Wang, C.; Teng, Y.; Christie, P. Nitrogen and phosphorous leaching losses from intensively managed paddy fields with straw retention. *Agri. Water Manag.* **2014**, *141*, 66–73. [CrossRef]
47. Hasegawa, K.; Kobayashi, M.; Nakada, H. Influence of applying organic matter in a paddy field on the water quality (2). Influence of applying rice-straw on the leaching of nitrate nitrogen from draining soil and on the denitrification of nitrate nitrogen in flooded soil. *Bull. Shiga. Agric. Exp. Stn.* **1981**, *23*, 30–37.
48. Xu, G.; Wei, L.L.; Sun, J.N.; Shao, H.B.; Chang, S.X. What is more important for enhancing nutrient bioability with biochar application into a sandy soil: Direct or indirect mechanism? *Ecol. Eng.* **2013**, *52*, 119–124. [CrossRef]
49. Major, J.; Steiner, C.; Downie, A.; Lehmann, J. Biochar effects on nutrient leaching. In *Biochar for Environmental Management: Science and Technology*; Lehmann, J., Joseph, S., Eds.; Earchscan Publ.: London, UK, 2009; pp. 271–287.
50. Liu, Y.; Lu, H.; Yang, S.; Wang, Y. Impacts of biochar addition on rice yield and soil properties in a cold waterlogged paddy for two crop seasons. *Field Crops Res.* **2016**, *191*, 161–167. [CrossRef]
51. Sebastian, D.; Rodrigues, H.; Kinsey, C.; KorndÖrfer, G.; Pereira, H.; Buck, G.; Datnoff, L.; Miranda, S.; Provance-Bowely, M. A 5-day method for determination of soluble silicon concentrations in non-liquid fertilizer materials using a sodium carbonate-ammonium nitrate extractant followed by visible spectroscopy with heteropoly blue analysis; single-laboratory validation. *J. AOAC Int.* **2013**, *96*, 251–259. [CrossRef] [PubMed]
52. Xiao, X.; Chen, B.; Zhu, L. Transformation, morphology, and dissolution of silicon and carbon in rice straw-derived biochars under different pyroltytic temperatures. *Environ. Sci. Technol.* **2014**, *28*, 3411–3419. [CrossRef] [PubMed]
53. Wang, M.; Wang, J.; Wang, X. Effect of KOH-enhanced biochar on increasing soil plant-available silicon. *Geoderma* **2018**, *321*, 22–31. [CrossRef]
54. Kan, T.; Strezov, V.; Evans, T.J. Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. *Renew. Sustain. Energy Rev.* **2016**, *57*, 1126–1140. [CrossRef]
55. MAFFa. *Report of Road Map to Accomplish the Reduction Goal of Greenhouse Gas Emissions in Korea*; Korean Ministry for Food, Agriculture, Fisheries and Forestry: Gwacheon, Korea, 2014; pp. 57–60.
56. MAFFb. *Annual Statistics in Food, Agriculture, Fisheries and Forestry in 2015*; Korean Ministry for Food, Agriculture, Fisheries and Forestry: Sejong, Korea, 2015.
57. Puga, A.P.; Grutzmacher, P.; Cerri CE, P.; Ribeirinho, V.S.; de Andrade, C.A. Biochar-based nitrogen fertilizers: Greenhouse gas emissions, use efficiency, and maize yield in tropical soils. *Sci. Total Environ.* **2020**, *704*, 135375. [CrossRef]
58. Pokharel, P.; Chang, S.X. Manure pellet, woodchip and their biochars differently affect wheat yield and carbon dioxide emission from bulk and rhizosphere soils. *Sci. Total Environ.* **2019**, *659*, 463–472. [CrossRef]