



# Influence of activated biochar pellet fertilizer application on greenhouse gas emissions and carbon sequestration in rice (*Oryza sativa* L.) production<sup>☆</sup>

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## ABSTRACT

Supplemental activated biochar pellet fertilizers (ABPFs) were evaluated as a method to sequester carbon and reduce greenhouse gas (GHG) emissions, and improve rice production. The evaluated treatments were a control (standard cultivation method, no additives applied), activated rice hull biochar pellets with 40% of N (ARHBP-40%), and activated palm biochar pellets with 40% of N (APBP-40%). The N supplied by the ARHBP-40% and APBP-40% treatments reduced the need for supplemental inorganic nitrogen (N) fertilizer by 60 percent. The ARHBP-40% treatment sequestered as much as 1.23 tonne ha<sup>-1</sup> compared to 0.89 tonne ha<sup>-1</sup> in the control during the rice-growing season. In terms of greenhouse gas (GHG) emissions, CH<sub>4</sub> emissions were not significantly different ( $p > 0.05$ ) between the control and the ARHBP-40%, while the lowest N<sub>2</sub>O emissions (0.002 kg ha<sup>-1</sup>) were observed in the ARHBP-40% during the crop season. Additionally, GHG (CO<sub>2</sub>-equiv.) emissions from the ARHBP-40% application were reduced by 10 kg ha<sup>-1</sup> compared to the control. Plant height in the control was relatively high compared to others, but grain yield was not significantly different among the treatments. The application of the ARHBP-40% can mitigate greenhouse gas emissions and enhance carbon sequestration in crop fields, and ABPFs can increase N use efficiency and contribute to sustainable agriculture.

## 1. Introduction

Greenhouse gas (GHG) emissions from agriculture, forestry, and other land use accounted for 24% of global emissions in 2014 (IPCC, 2014). Specifically, agriculture contributed approximately 12% of total GHG emissions. Of the GHG emissions due to agriculture, approximated 37% can be attributed to soil emission (Paustian et al., 2016; Tubiello et al., 2015). The agricultural contribution to global GHG emissions is expected to increase up to 50% by 2030 (Boko et al., 2007). In particular, the contribution of rice cultivation to GHG emissions has continuously increased, with total GHG emissions from rice paddy increasing at a rate of 26 Tg per decade from 1961 to 2016. Methane (CH<sub>4</sub>) was the primary GHG emitted from rice paddies (FAO, 2016). In early studies on rice paddies, N<sub>2</sub>O emissions were thought to be negligible (Smith et al., 1982). However, current research has shown that N<sub>2</sub>O emissions are a major source of GHG due to increased inorganic N application (Akiyama

et al., 2005). In the previous studies, the mitigation of GHG emissions from agricultural practices was related to control the water regime and the use of organic amendments (Smith et al., 2008; Yan et al., 2005). Feng et al. (2013) reported that the optimized water management strategy could make a significant contribution to the mitigation of CH<sub>4</sub> emission. Frolking et al. (2004) showed the water management significantly influenced to N<sub>2</sub>O emissions. In addition to the conventional strategy, a more integrated strategy is suggested to mitigate GHG emissions effectively.

Biochar is a carbon product obtained when biomass is thermally treated at 300–700 °C under a limited oxygen content (preferably zero). Agricultural biomass, which includes rice husks, manure, wood remains, and crop residues is the most readily available raw material for biochar production. Biochar has attracted attention from agro-environmentalists for its benefits as a soil amendment (Godlewaska et al., 2017) which enhances soil quality (Lehmann and Joseph, 2015), increases crop yield

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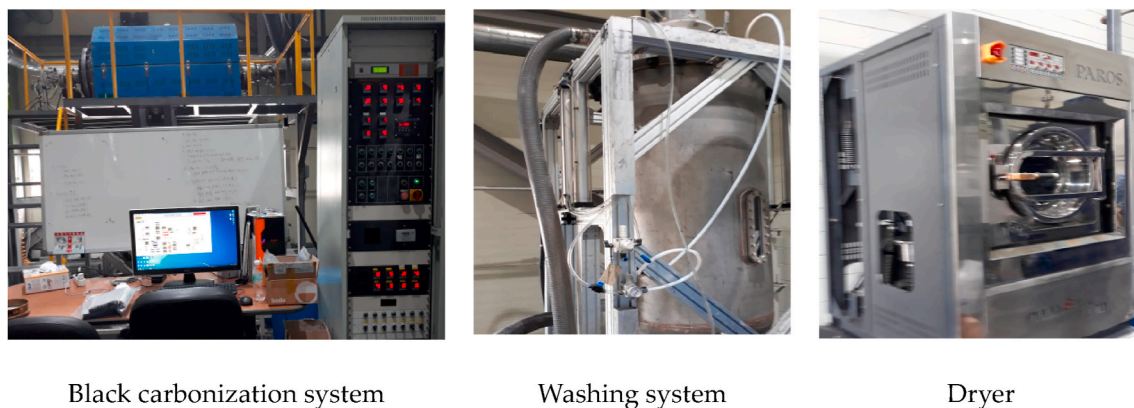


Fig. 1. Automatic pyrolysis system to enhancing the porosity of biochar.

(Jeffery et al., 2011), mitigates nitrous oxide emission (Woolf et al., 2010), and increases the carbon sequestration capacity (Lehmann and Joseph, 2015; Shin et al., 2019). Specifically, rice husk biochar has a potential value as a soil amendment because of its high phosphorus, silicon, and potassium contents (Lehmann et al., 2009). However, biochar may cause dust issues during its application on fields; approximately 25% of biochar can be lost during application (Kammann et al., 2015). Pelletized biochar has been suggested as a method to ameliorate this problem (Reza et al., 2012). In particular, pelletized biochar combined with pig manure compost and fertilizer has been reported as a slow-release fertilizer to improve the functionality (Shin et al., 2019). A slow-release fertilizer gradually discharges nutrients to soils during the crop season, minimizing nutrient loss through runoff water and leachate (Fernandez-Escobar et al., 2004). Biochar-pellets blended with pig manure compost and fertilizer (BCP) show higher  $\text{NH}_4^+$  use efficiency compared to a traditional inorganic fertilizer (Shin et al., 2019). Nutrient use efficiency is essential for improving crop yields, reducing non-point source pollution, and achieving sustainable agriculture (Jiang et al., 2019).

Biochar from crop residues can increase soil carbon, while enhancing the rate of soil carbon mineralization via accommodating microorganisms (Majumder et al., 2019). Consequently, transforming crop residues or feedstock to biochar can be a promising avenue to sequester soil carbon. With respect to soil organic carbon changes, raising soil capability to sequester carbon in crop fields can be an important part of a strategy of mitigating the impacts of climate change (Pekkan et al., 2021). Increasing carbon sequestration in crop fields is a promising approach to mitigate GHG emissions, with several researchers having conducted studies on the application of biochar to enhance carbon sequestration in agricultural fields (Majumder et al., 2019; Kan et al., 2020; Yang et al., 2020). Shin et al. (2019) reported that the amount of sequestered carbon and profit could reach  $1.65 \text{ tonne ha}^{-1}$  and  $\$145.59 \text{ ha}^{-1}$  (KAU, Korean Allowance Unit), respectively, compared to the control for rice cultivation under the application of the BCP.

Several studies on the fertilizer application with biochar were conducted to improve the nutrient use efficiency and mitigate GHG emissions (Chen et al., 2018; Yang et al., 2020). A few studies reported that the application of biochar with inorganic fertilizers functioned as a slow-release fertilizer, and the combined application showed an improved nutrients-use efficiency, mitigated methane gas emission, and increased rice yield (Kim et al., 2017; Chen et al., 2018; Yang et al., 2016). The amendment of wheat straw-biochar decreased  $\text{CH}_4$  and  $\text{N}_2\text{O}$  emissions by 11.2–17.5% and 19.5–26.3%, respectively (Wu et al., 2019a, 2019b). Zhang et al. (2012) also observed that biochar application in rice paddies resulted in a significant decrease of overall global warming potential (GWP) from 18.7% to 7.1%, and greenhouse gas intensity (GHGI) from 34.8% to 12.4%. Wu et al. (2019a, 2019b) reported biochar application in soil increased the adsorption capacity of

$\text{NH}_4^+$  and  $\text{N}_2\text{O}$  from the field experiment. Biochar application in the wheat field showed a significant impact on mitigating  $\text{CH}_4$  and  $\text{N}_2\text{O}$  gas emissions and increasing crop production (Wang et al., 2012).

Another branch of active research is the modification of biochar surface to increase the absorption/adsorption of chemicals including nitrogen. Kim et al. (2020a, 2020b) reported that activated rice hull biochar showed increased surface area and enhanced  $\text{NH}_4^+$  adsorption capacity due to its improved adsorption capacity after physiochemically treatment with KOH at high temperatures. Although several studies have reported that biochar has the potential to be used as a slow-release fertilizer (Zhang et al., 2012; Shin et al., 2019; Yang et al., 2020), pelletized biochar increases the efficiency of its functionality as a slow-release fertilizer. The newly developed ABPFs can be improved the adsorption capacity of  $\text{NH}_4^+$  due to its increased surface area compare to the conventional biochar and its pellets. The cost of producing activated biochar can be a critical factor in making biochar technologies of a valuable avenue to reduce non-point source pollution and mitigate GHG emissions. Currently, most biochar studies focused on the value-added or modified biochar properties to improve the absorption capacity (Yao et al., 2013; Rajapaksha et al., 2016; Yang et al., 2016; Shin et al., 2018). Several studies have been conducted to reduce landfill leachate using biomass-based activated carbon (Mahdavi et al., 2018; Deng et al., 2018). Additionally, activated biochar was successfully applied to eliminate organic micro-pollutants from wastewater (Hagemann et al., 2020). Compared to conventional coal-based activated carbon, activated biochar releases significantly lower amounts of GHG emissions during the production process (Hagemann et al., 2020). The environmental benefits of using activated biochar fertilizers have also been evaluated (González-Cencerrado et al., 2020). The activated carbon materials using renewable feedstock such as low-cost agricultural by-products can be an alternative high potential strategy to mitigate GHG emissions and reduce environmental pollutants in soil and water system (Li et al., 2015; Tran et al., 2017). However, few studies have been conducted on the ABPFs to improve soil and water conservation and agro-ecosystems, especially in terms of carbon sequestration and GHG emissions in agricultural practices.

Therefore, the objective of this study was to investigate the impact of the ABPFs application on rice cultivation, specifically by exploring the changes in nitrogen use efficiency, amount of sequestered carbon, greenhouse gas emissions, and plant growth characteristics. It is hypothesized that the use of activated biochar can enhance  $\text{NH}_4^+$  adsorption capacity, control nutrient release, and mitigate GHG emissions.

## 2. Materials and methods

### 2.1. Processing activated biochar production

Rice hull biochar was purchased from U-Gi industry Co. (Gochang,

**Table 1**

Chemical properties of the activated rice hull biochar, the activated palm biochar, and the pig manure compost used.

Materials used	pH (1:10)	EC (dS m <sup>-1</sup> )	TC	TOC	TIC	TN
			g kg <sup>-1</sup>			
Activated rice hull biochar	8.79 ± 0.06	7.25 ± 1.63	327.1 ± 2.39	294.7 ± 0.45	33.0 ± 0.21	2.0 ± 0.04
Activated palm biochar	9.06 ± 0.72	5.98 ± 1.79	329.6 ± 9.23	310.2 ± 13.81	19.4 ± 0.32	0.6 ± 0.01
Pig manure compost	8.77 (1:5 ratio)	3.4 ± 0.05	289.0 ± 0.42	259 ± 0.31	30.2 ± 0.12	29.1 ± 0.31

Legend: EC: electric conductivity; TC: total carbon; TOC: total organic carbon; TIC: total inorganic carbon, and TN: total nitrogen. The values were average of triplicate samples with standard deviation ( $p < 0.05$ ).

**Table 2**

Major nutrient contents of the ABPFs.

Input materials*	TC	TN	TP	TK
	g kg <sup>-1</sup>			
ARHBP	325.0 ± 0.23	89.21 ± 0.13	10.8 ± 0.02	293.6 ± 0.51
APBP	376.0 ± 0.14	87.15 ± 0.42	11.6 ± 0.04	270.4 ± 0.32

Legend: ARHBP: activated rice hull biochar pellets; APBP: activated palm biochar pellets; TC: total carbon; TN: total nitrogen; TP: total phosphorous; TK: total potassium. The values were average of triplicate samples with standard deviation ( $p < 0.05$ ).

Jeonbuk, Republic of Korea), and activated palm biochar was bought from Green biochar Co. (Hwasung, Gyeonggi, Republic of Korea). Following previous NH<sub>4</sub>-N adsorption experimental results (Kim et al., 2020a, 2020b), a 6M KOH solution (1: 2 ratios, 6M KOH: biochar) was sprayed into rice hull biochar and left overnight to complete sorption. Then, 30 kg treated rice hull biochars with 6M KOH were then placed in a reactor heated from room temperature to 850 °C at a rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> flow at a flow rate of 5 ml min<sup>-1</sup>. After pyrolysis, the activated rice hull biochar was removed from the reactor after cooling and then transferred to the washing system. Residual KOH was removed from the activated rice hull biochar with 3 washes of deionized water. Finally, the activated rice hull biochar was placed in the dryer to evaporate any remaining moisture. These processes were conducted via an automatic pyrolysis system (Fig. 1).

The chemical properties of the activated rice hull biochar, the activated palm biochar, and the pig manure compost used are shown in Table 1. The activated rice hull biochar was generally alkaline with a pH 8.8 and low total nitrogen (TN) at 2.0 g kg<sup>-1</sup>, while the pH and TN in the activated palm biochar were 9.1 and 0.6 g kg<sup>-1</sup>, respectively. Furthermore, the TN content of the pig manure compost was 14.6 times higher than that of the activated rice hull biochar.

## 2.2. Supplemental activated biochar pellet fertilizers

Before pelletizing, the activated rice hull and palm biochars (4:6, activated biochar: pig manure compost) were separately mixed with pig manure compost using an agitator, while spraying nutrient solutions into the mixture. The mixtures are fed into a commercial pellet mill (7.5 KW, 10HP, KumKang Engineering Pellet Mill Co., Daegu, South Korea) for producing the ABPFs. The primary nutrient contents of the ABPFs are described in Table 2. The total nitrogen contents were 89.2 g kg<sup>-1</sup> and 87.2 g kg<sup>-1</sup> in the activated rice hull biochar pellet (ARHBP) and the activated palm biochar pellet (APBP), respectively. These nitrogen contents were 1.2–1.4% higher than the N contents from the value-added biochar pellet (BMP-NPK) (Shin et al., 2020) because the ABPFs were treated with 6M KOH during the process. It was shown that the

**Table 3**

Physicochemical properties of paddy soil before used\*.

Soil type	pH (1: 5)	EC (dS m <sup>-1</sup> )	TN (g kg <sup>-1</sup> )	P <sub>2</sub> O <sub>5</sub> (mg kg <sup>-1</sup> )	K <sub>2</sub> O (g kg <sup>-1</sup> )
clay loam	5.1 ± 0.05	58.0 ± 0.40	7.6 ± 0.02	58.8 ± 0.12	10.6 ± 0.04

Legend: TC: total carbon; TN: total nitrogen. The values were average of triplicate samples with standard deviation ( $p < 0.05$ ).

total potassium contents in the ABPFs were 4.7–5.1 times higher than that of the BMP-NPK.

## 2.3. Field experiment

The experimental cultivation field has clay loam soil and is located at 35° 49.515'N of latitude and 127° 2.532'E of longitude in the National Institute of Agricultural Sciences (NAS), Rural Development Administration (RDA), Jeonju, Republic of Korea. The average precipitation and temperature were 4.3 mm and 22.2 °C, respectively, during the crop growing season. Additionally, the average solar radiation quantity and duration of sunshine are measured at 16.6 MJ and 6.6 h during the cultivation period, respectively. The rice variety used in this experiment was 'Shindongjin', and the planting distance was 30 cm × 60 cm, and one or two rice plants were planted at each point in the paddy field. The experimental design was a randomized block design with three replications. The treatments consisted of, 1) control (90-45-57 kg ha<sup>-1</sup> of N-P-K and 2500 kg ha<sup>-1</sup> of pig manure compost application), 2) activated rice hull biochar pellet (ARHBP-40%, 36 kg ha<sup>-1</sup> based on TN requirement), and 3) activated palm biochar pellet (APBP-40%, 36 kg ha<sup>-1</sup> based on TN requirement). The choice to use a 40% application rate of ABPFs is based on 30–35% of nitrogen (urea) use efficiency for rice (Qin et al., 2001) as a slow-release fertilizer. The application amount of pig manure compost in the control was 2600 kg ha<sup>-1</sup> based on NAS recommended application rates for rice cultivation (NAS, 2010). The water was irrigated by pumping from groundwater well in the paddy fields during the rice cultivation periods. The physicochemical properties of the soil before the experiment are presented in Table 3.

## 2.4. Chemical analysis of surface paddy soil

Surface soil samples were collected every 20 days after transplant in the paddy throughout the cropping season. The wet soil samples were extracted using a 2M KCl solution (1:5, soil: extractant ratio). The extracted solutions from soil samples were analyzed by the Bran-Lubbe Segmented Auto Analyzer (Seal Analytical Ltd., Wisconsin, USA) to detect NH<sub>4</sub>-N and NO<sub>3</sub>-N concentrations. The concentrations of NH<sub>4</sub>-N and NO<sub>3</sub>-N from wet soil extractions are compensated with soil moisture contents. The dried ABPFs samples were milled with a grinder to pass through a 2 mm sieve before chemical analysis. The milled samples were extracted using the Mehlich III method (Mehlich, 1984), and the extracted solutions were stored in a refrigerator at 4 °C until analyzing P and K<sup>+</sup> by the UV spectrophotometer (C-Mac, Dae-Jeon, Republic of Korea). Total nitrogen (TN) and total carbon (TC) in biochar and soil were analyzed with total organic carbon (TOC) analyzer (Elementa Vario TOC cube, Hanau, Germany). The combustion temperature was 950 °C with a tungsten trioxide (WO<sub>3</sub>) catalyst. Total nitrogen (TN) contents of biochar and soils were determined by the dry combustion method using the Vario Max CN analyzer (Elementar, Hanau, Germany). Total P and K contents in ABPFs were analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, IntegraXL, GBC Ltd., Braeside, Australia) after digesting the samples with nitric and hydrochloric acids.

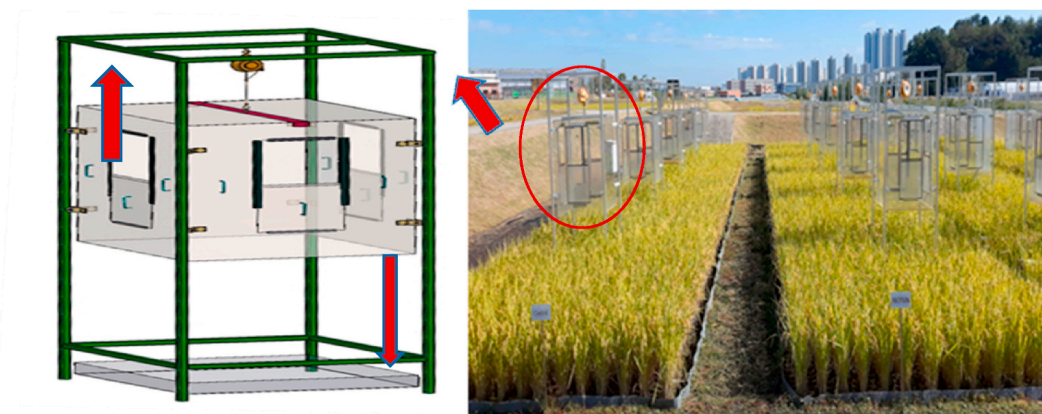


Fig. 2. Diagram of the up-down type of greenhouse gas collection chamber in the cropland (Pattern number: 20-2019-0002155).

## 2.5. Calculation of carbon balance

The potential soil carbon sequestration among the treatments was calculated with the difference of the residual amount of soil carbon for each treatment between the initial sample after transplant and the last sample after rice harvest using the following equation (Shin et al., 2019):

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

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

The efficiency of soil carbon sequestration amount via the ABPFs was calculated by the difference between the treatment and control using the following equation:

$$ESCS = TSS_{TC} - NTSS_{TC} \quad (2)$$

where,  $ESCS$  ( $\text{kg ha}^{-1}$ ) is the efficiency of soil carbon sequestration under the ABPFs application,  $SS_{TC}$  ( $\text{kg ha}^{-1}$ ) is the sequestered soil carbon amount in soil,  $T$  is the treatments, and  $NT$  is the control.

The mitigated amount of  $\text{CO}_2$  emission was also estimated using the equation (Shin et al., 2017):

$$\text{CO}_2 = SS_{TC} \times CF_{SC} \quad (3)$$

where,  $SS_{TC}$  is the amount of soil carbon sequestration ( $\text{tonne ha}^{-1}$ ), and  $CF_{SC}$  is the conversion factor of  $\text{CO}_2$  emission from soil carbon ( $1 \text{ kg C} = 3.664 \text{ kg CO}_2\text{-equiv}$ ).

Profit estimation for mitigated  $\text{CO}_2\text{-equiv}$  emission was also calculated using the equation (Shin et al., 2017):

$$P = AM \times MP \quad (4)$$

where,  $P$  is the potential revenue from  $\text{CO}_2$  reduction and trading ( $\text{\$ ha}^{-1}$ ) through the soil carbon sequestration,  $AM$  is the amount of mitigated  $\text{CO}_2$  equiv. emission ( $\text{tonne ha}^{-1}$ ), and  $MP$  is the market price of  $\text{CO}_2$  trading ( $\text{\$ per tonne CO}_2$ ).

## 2.6. Analysis of greenhouse gas emissions in the rice paddy

For greenhouse gas emissions, gases were collected every week from the up-down type of greenhouse gas chamber facilitated in the rice paddy. The up-down type of greenhouse gas collection chamber was designed to eliminate the temperature differences between the interior and exterior of the chamber during rice cultivation periods (Fig. 2).

The chamber consists of a polyvinyl chloride base square ( $100 \text{ cm} \times 100 \text{ cm} \times 120 \text{ cm}$  of high), enclosing a volume of  $1,200\text{L}$ . Each side of the chambers was fitted with two rubber stopper ports: one for the thermometer and another for the gas sampling using a syringe. Gas samplings were accomplished between 9:00 and 11:00 in the morning, which are representative of average daily emissions (Yagi and Minami, 1990). Gas samples and temperatures were collected and recorded before and after placement of the chamber, transported to the laboratory, and analyzed  $\text{CH}_4$  and  $\text{N}_2\text{O}$  concentrations within 24 h using gas chromatography (Agilent 7890B, Santa Clara, CA, USA) equipped with a flame ionization detector (FID) for  $\text{CH}_4$  and electron capture detector (ECD) for  $\text{N}_2\text{O}$ . Before analyzing gases, the standard curves were prepared using the certified standards of known concentrations to calibrate gas chromatography (Daedeok Gas Co., Daejeon, Korea). Greenhouse gas emissions per hour in rice paddy were calculated using the following equation:

$$F = \rho \times \frac{273}{(273 + \text{initial temperature} + \text{late temperature})/2} \times \frac{V}{A} \times \frac{\Delta C}{h} \quad (5)$$

where,  $F$  is greenhouse gas emissions per hour ( $\text{mg m}^{-2} \text{ hr}^{-1}$ ),  $\rho$  is the density of gases at 273K, which is 0.714 for  $\text{CH}_4$ , 1.96 for  $\text{N}_2\text{O}$ ,  $V$  is the volume of greenhouse gas collection box ( $\text{m}^{-3}$ ),  $A$  is the surface area of greenhouse gas collection box ( $\text{m}^{-2}$ ),  $\Delta C$  is difference concentrations after and before analyzing the greenhouse gases (ppm), and  $h$  is sampling period (hour).

The cumulative greenhouse gas emissions in rice paddy were calculated using the following equation:

$$CGE = \sum_{i=1}^n \{(F \times 24)(1 + NSP)\} \quad (6)$$

where,  $CGE$  is cumulative greenhouse gas emissions ( $\text{g m}^{-2}$  for  $\text{CH}_4$  or  $\text{mg m}^{-2}$  for  $\text{N}_2\text{O}$ ),  $F$  is greenhouse gas emissions per hour ( $\text{mg m}^{-2} \text{ hr}^{-1}$ ),  $i$  is the sampling date, and  $NSP$  is the next sampling periods (days).

## 2.7. Statistical analysis

Statistical analysis was conducted using SAS version 9.2 Software (SAS, Inc., Cary, NC, USA) with a one-way ANOVA test for comparison among treatments with carbon sequestration and responses of growth characteristics during rice cultivation. Duncan multiple range tests were used to compare the carbon sequestration and rice yield components under the influence of different treatments. The standard deviation was used for comparing between chemical properties of soil and greenhouse gas emissions at each sampling date among the treatments.

**Table 4**

The application amounts of major nutrient components such as N, P, K, and pig manure compost in the rice paddy.

Treatments	Application amount of ABPFs	N	P	K	Pig manure compost
		kg ha <sup>-1</sup>			
Control	–	90.0	45.0	57.0	2600.0
ARHBP-40%	403.6	36.0	4.4	118.5	242.2
APBP-40%	412.8	36.0	4.8	111.6	247.7

Legend: N: nitrogen; P: phosphorus; K: potash. ARHBP-40%: activated rice hull biochar pellet with 40% of N; APBP-40%: activated palm biochar pellet with 40% of N.

### 3. Results and discussions

#### 3.1. Application effect of ABPFs in the paddy soil

The major nutrient components in the ABPFs and control treatment are summarized in Table 4. The nitrogen contents in the ABPFs treatments were 40% of N levels in the control treatment. Applied amounts of phosphorous in the control were much higher at 9.4 and 10.2 times than those of the ARHBP-40% and APBP-40%, respectively. Pig manure compost was only applied 242.2 and 247.7 kg ha<sup>-1</sup> in the ARHBP-40% and APBP-40%, respectively. However, the applied amount of potash in the ARHBP-40% and APBP-40% was twice the level of the control. There was the remaining KOH in the final product of the activated biochar even if the activated biochar was washed with deionized water three times to remove residual KOH.

The effects of the ARHBP-40% and APBP-40% application on the NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N concentrations in paddy soil during rice cultivation are described in Fig. 3. The NH<sub>4</sub><sup>+</sup>-N concentration in the control was abruptly decreased from 177.7 mg kg<sup>-1</sup> to 49.4 mg kg<sup>-1</sup>, while NO<sub>3</sub><sup>-</sup>-N concentration was highest, 13.2 mg kg<sup>-1</sup> in 14 days after transplant. Almost 72% of NH<sub>4</sub><sup>+</sup>-N was lost within 14 in the control field treated with inorganic fertilizer and manure. However, NH<sub>4</sub><sup>+</sup>-N in soil was retained 64% higher in the ARHBP-40% and 72% higher in the APBP-40% treatments compared to the control. It seems that the activated biochar pellet retains more NH<sub>4</sub><sup>+</sup>-N in soils by preventing volatilization. Ammonia (NH<sub>3</sub>) emission is the largest component of N loss from fertilized crop fields. An extensive study has been conducted on ammonia (NH<sub>3</sub>) emissions after the application of manures (Misselbrook

et al., 2005; Pedersen et al., 2020). Applied nitrogen in the soil can be generally converted into NH<sub>4</sub><sup>+</sup>-N via the mineralization process, which is subsequently nitrified to NO<sub>3</sub><sup>-</sup>-N. Once urea is applied in paddy soil, it is hydrolyzed to NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> via the mineralization reaction within 20 days after application in paddy soil (Shin et al., 2019).

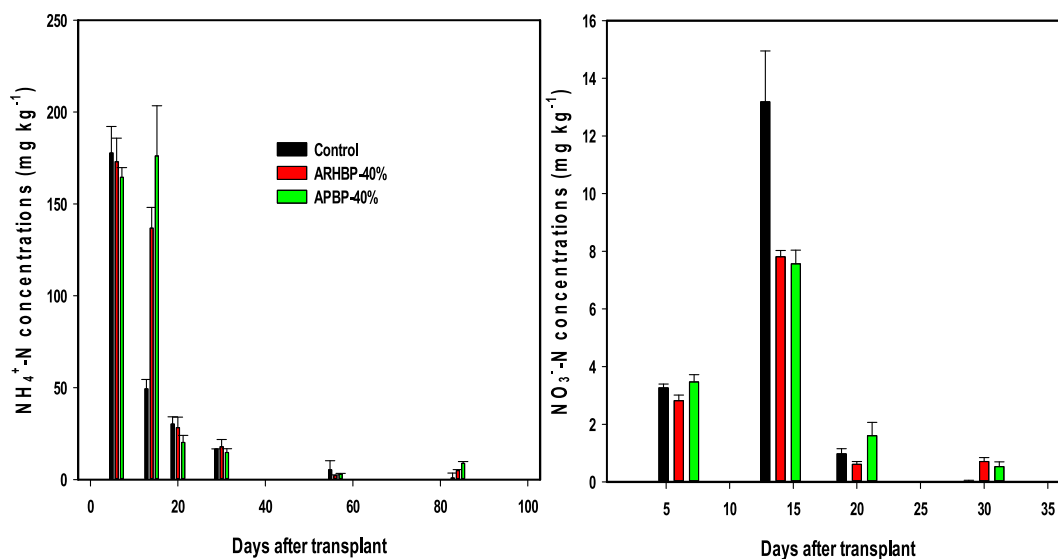
However, the evolution of NO<sub>3</sub><sup>-</sup>-N concentration in the soil was significantly different compared to the changes in NH<sub>4</sub><sup>+</sup>-N concentration in the soil due to the different chemical processes involved. The retained NO<sub>3</sub><sup>-</sup>-N concentration in soil was 39.4% more in the ARHBP-40% and 40.9% more in the APBP-40%, respectively, 14 days after transplant compared to the control. It appeared that the retention of NO<sub>3</sub><sup>-</sup>-N in soil was higher in the APBP-40% treatment at 20 days after transplant compared to the retention in the ARHBP-40%. In fact, NO<sub>3</sub><sup>-</sup>-N in soil was still available in the ARHBP-40% and APBP-40% treated soils, while the available NO<sub>3</sub><sup>-</sup>-N was relatively lower in the control treatment (Fig. 3). This implies that the ARHBP-40% and APBP-40% can be possibly adapted as a slow-release fertilizer to improve nitrogen use efficiency for rice cultivation. An assessment of the environmental benefit with a developing new fertilizer revealed that the reduction of nitrogen losses achieved was 63% in the application of the ABPFs. The improved nutrient use efficiency may be due to the NH<sub>4</sub><sup>+</sup>-N adsorption capacity of applied biochar (Shin et al., 2018).

**Table 5**

Carbon contents in the soils treated with the ABPFs on the first day of rice transplants and the day after harvest during rice cultivation.

Treatments*	First day of rice transplant	133 days after transplant
	g kg <sup>-1</sup>	
Control	10.05 ± 0.30 a	10.74 ± 0.17 a
ARHBP-40%	9.61 ± 0.35 a	10.56 ± 0.35 a
APBP-40%	8.54 ± 0.15 b	9.29 ± 0.19 b
F-value	30.17***	28.86***
Pr > F	<0.0007	<0.0008

Legend: Note \*  $p < 0.05$ , \*\*  $p < 0.01$ , \*\*\*  $p < 0.001$ . 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 Duncan's multiple range test for total carbon contents on the first day of transplant and the day after harvest.



**Fig. 3.** Effects of the ABPFs application on NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N concentrations in paddy soil during rice cultivation. The values were average of three replications, and error bars display standard deviation ( $p < 0.05$ ).

**Table 6**

Estimation of carbon sequestration and its profit analysis for application of the ABPFs during rice cultivation.

Treatments <sup>a</sup>	Carbon sequestration tonne ha <sup>-1</sup>	Mitigation of CO <sub>2</sub> -equiv.	Profit (\$ ha <sup>-1</sup> )
Control	0.89 ± 0.19 b	3.27 ± 0.68 b	92.36 ± 19.33 b
ARHBP-40%	1.23 ± 0.14 a	4.49 ± 0.53 a	126.57 ± 14.89 a
APBP-40%	0.98 ± 0.06 ab	3.58 ± 0.23 ab	101.00 ± 6.37 ab
F-values	4.44	4.48	4.48
Pr > F	0.0656	0.0645	0.0646

Legend: kg C = 3.664 kg CO<sub>2</sub>-equiv., 1 tonnes CO<sub>2</sub> = KAU=33,000 (1.6, 2020) = \$28.21. Note <sup>a</sup>p < 0.05, <sup>\*\*</sup>p < 0.01, <sup>\*\*\*</sup>p < 0.001.

<sup>a</sup> Mean values followed by different letters, which indicate significant differences (p < 0.05) among treatments with a one-way ANOVA by the mean comparison for all pairs using Duncan's multiple range test for carbon sequestration and mitigation of CO<sub>2</sub>-equiv.

### 3.2. Carbon sequestration and profit analysis

Changes of the carbon contents in the soils treated with the ABPFs on the first day of transplant and the day after harvest during rice cultivation are described in Table 5. The carbon contents on both the first day of transplant and the day after harvest were significantly different (p < 0.001) among the treatments. The highest carbon content was 10.1 g kg<sup>-1</sup> in the control, while the lowest content was 8.5 g kg<sup>-1</sup> in the APBP-40% on the first day of the transplant. The increased carbon contents under the different treatments were 0.95% in the ARHBP-40%, 0.75% in ARBP-40%, and 0.69% in the control.

For the application of the ABPFs in the rice paddy, carbon sequestration, mitigation of CO<sub>2</sub>, and profit-analysis are calculated by equations (1), (3) and (4), respectively (Table 6). The effect of biochar on soil carbon sequestration in cropland was established internationally by the Intergovernmental Panel on Climate Change in 2019 (IPCC, 2019). Results showed that the highest carbon sequestration was 1.23 tonne ha<sup>-1</sup> in the ARHBP-40%, while the lowest was 0.89 tonne ha<sup>-1</sup> in the control during rice cultivation. The efficiency of the ABPFs application was calculated by equations (2) and (3), and the values of carbon sequestration and mitigation of CO<sub>2</sub>-equiv. emission were 0.34 and 1.22 tonnes ha<sup>-1</sup> in the ARHBP-40%, respectively, during rice cultivation. Compared to previous

data, the current results showed 40% lower in CO<sub>2</sub>-equiv. emission because the application of inorganic N amount of the ABPFs was 60% less compared with the amount in the control. Profit-analysis performed using the market price of CO<sub>2</sub> (KRXETS, 2020) revealed that profits for CO<sub>2</sub> trading in the ABPFs treatments were higher in the range of 1.09–1.37 times than that of the control.

### 3.3. Effects of greenhouse gas emissions

For the estimation in the reduction of greenhouse gas emissions on the application of the ABPFs in the rice paddy, the cumulative CH<sub>4</sub> and N<sub>2</sub>O emissions in a rice paddy during rice cultivation are described in Fig. 4. The CH<sub>4</sub> and N<sub>2</sub>O emissions in paddy treated with the ABPFs during rice cultivation are calculated by Eqs. (4) and (5). The highest cumulative CH<sub>4</sub> emission was 16.64 g m<sup>-2</sup> in the APBP-40%, while there was not a significantly (p > 0.05) difference between the control and ARHBP-40% during rice cultivation. However, the lowest cumulative N<sub>2</sub>O emission was 78.96 mg m<sup>-2</sup> in the ARBPH-40% for rice cultivation periods. It was observed that the order of N<sub>2</sub>O emissions was Control > APBP-40% > ARHBP-40% during rice cultivation in the paddy. N<sub>2</sub>O emissions in the ARHBP-40% was 27% lower than that of the control. This reduction may be due to the ability of activated rice hull biochar to adsorb NH<sub>4</sub>-N (Kim et al., 2020a,b), but activated palm biochar can only adsorb PO<sub>4</sub>-P in aqueous solutions (Kim et al., 2020a,b).

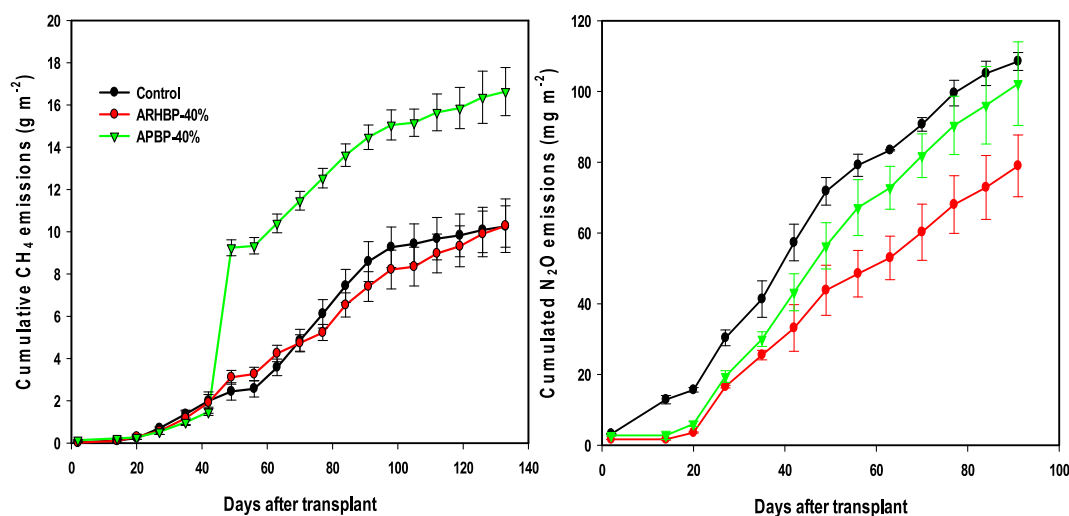
Estimation of total greenhouse gas emissions on the application of the ABPFs during rice cultivation is presented in Table 7. For comparison among the treatments, it was observed that the lowest N<sub>2</sub>O emission was

**Table 7**

Estimation of greenhouse gas emissions on the application of the ABPFs during rice cultivation.

Treatments	CH <sub>4</sub> emission (tonne ha <sup>-1</sup> )	N <sub>2</sub> O emission (kg ha <sup>-1</sup> )	CO <sub>2</sub> -equiv (tonne ha <sup>-1</sup> )
Control	0.01 <sup>b</sup>	0.003 <sup>a</sup>	0.013 <sup>b</sup>
ARHBP-40%	0.01 <sup>b</sup>	0.002 <sup>b</sup>	0.012 <sup>b</sup>
APBP-40%	0.017 <sup>a</sup>	0.003 <sup>a</sup>	0.020 <sup>a</sup>
F-values	31.5 <sup>***</sup>	8.32 <sup>*</sup>	36.04 <sup>***</sup>
Pr > F	<.001	0.019	<.001

Legend: CO<sub>2</sub> equivalence factors: CH<sub>4</sub>, 21; N<sub>2</sub>O, 310. Note <sup>\*</sup>p < 0.05, <sup>\*\*</sup>p < 0.01, <sup>\*\*\*</sup>p < 0.001. <sup>\*</sup>Mean values followed by different letters, which indicate significant differences (p < 0.05) among treatments with a one-way ANOVA by the mean comparison for all pairs using Duncan's multiple range test for CH<sub>4</sub>, N<sub>2</sub>O, and CO<sub>2</sub>-equiv. emissions.



**Fig. 4.** Effects of the ABPFs application on the cumulative CH<sub>4</sub> and N<sub>2</sub>O emissions in the rice paddy during rice cultivation. The values were average of three replications, and error bars display standard deviation (p < 0.05).

**Table 8**  
Rice growth responses on the application of the ABPFs during cultivation.

Treatments*	Plant height	Number of tillers	Grain yields	Straw yields	Harvest index
	cm		kg 10a <sup>-1</sup>		
Control	84.5 ± 3.3 ns	19.3 ± 2.3 ns	534.8 ± 4.2 ns	819.5 ± 88.1 a	0.65
ARHBP-40%	80.7 ± 0.7 ns	19.6 ± 1.9 ns	513.3 ± 48.0 ns	776.0 ± 149.1 ab	0.66
APBP-40%	80.7 ± 2.0 ns	16.2 ± 1.0 ns	450.9 ± 53.4 ns	589.0 ± 76.8 b	0.77
F-value	2.85	3.19	3.29	3.76	–
Pr > F	0.1350	0.1141	0.1084	0.0873	–

Legend: Mean values followed by different letters, which indicate significant differences ( $p < 0.05$ ) among treatments with a one-way ANOVA by the mean comparison for all pairs using Duncan's multiple range test for plant growth characteristics.

0.002 kg ha<sup>-1</sup> in the ARHBP-40%, while CH<sub>4</sub> emissions did not show a significant difference ( $p > 0.05$ ) between the control and ARHBP-40% treatments during rice cultivation. The experimental results show that the application of the ARHBP-40% reduced CO<sub>2</sub>-equiv. emission to 10 kg ha<sup>-1</sup> compared to the control. This result coincides with another study that biochar amendment can reduce N<sub>2</sub>O emission (Cayuela et al., 2014) in rice paddies applied with nitrogen fertilizer. Shin et al. (2018) reported that the applied rice hull biochar enhanced NH<sub>4</sub>-N adsorption capacity and reduced 60% of the urea application rate in the crop field. Awad et al. (2018) reported that biochar application of 10 tonne ha<sup>-1</sup> showed significant mitigation of CH<sub>4</sub> emissions. However, the applied amount of activated rice hull biochar was only 161.4 kg ha<sup>-1</sup> in the ARHBP-40% treatment in this experiment.

### 3.4. Rice growth responses

Responses of rice growth characteristics on the application of the ABPFs are shown in Table 8. The plant height, tiller number, and grain yields were not significantly different ( $p > 0.05$ ) among the treatments, although the applied nutrient amounts were significantly reduced in the ARHBP-40% compared to the application amounts in the control plot (Table 4). The highest harvest index was 0.77 in the APBP-40%, while there was no significant difference ( $p > 0.05$ ) between the control and the ARHBP-40%, which implies that the rice in the ARHBP-40% showed a higher nitrogen use efficiency than the control plot because nitrogen application is associated with the growth of biomass. The current research shows that the ABPFs functioned as a slow-release fertilizer that can reduce the N requirements of rice while sustaining yields comparable to the control plot. This result lines up with previous studies (Shin et al., 2019).

## 4. Conclusions

This study indicates that the application of the ABPFs during rice cultivation can reduce the agro-environmental impacts. However, two different raw materials of ABPFs showed different effects on the greenhouse gas emissions. For paddy soil, the mineralization and nitrification in all treatments sharply decreased 14 days after transplant. The highest carbon sequestration was 1.23 tonne ha<sup>-1</sup> in the ARHBP-40% during rice cultivation. It was estimated that the lowest N<sub>2</sub>O emission was 0.002 kg ha<sup>-1</sup> in the ARHBP-40%, while CH<sub>4</sub> emissions did not significantly differ ( $p > 0.05$ ) between the control and the ARHBP-40% treatment through rice cultivation. Grain yields were not significantly different ( $p > 0.05$ ) among the treatments. The reduction in the necessary amounts of nitrogen, phosphorous, and manure for rice cultivation using the ARHBP-40% can be adapted for improving nutrient use efficiency, enhancing carbon sequestration, and mitigating GHG emissions without sacrificing crop yields. Further research is needed to investigate

improving the binding material and increasing the surface area of the biochar to enhance nitrogen use efficiency in the field application.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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