



# The effects of rice husk char on ammonium, nitrate and phosphate retention and leaching in loamy soil



Endita Prima Ari Pratiwi<sup>a,b,\*</sup>, Aurelia Karina Hillary<sup>a</sup>, Tetsuro Fukuda<sup>a</sup>, Yoshiyuki Shinogi<sup>a</sup>

<sup>a</sup> Faculty of Agriculture, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, Japan

<sup>b</sup> Department of Civil and Environmental Engineering, Universitas Gadjah Mada, Yogyakarta, Indonesia

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## ABSTRACT

Understanding the nutrient retention and release characteristics of biochar before its application to agricultural soils is crucial to maximize the benefits and minimize the damage that might be posed. In this study, batch sorption experiments were carried out to determine the ability of biochar produced from rice husk to adsorb or release three major nutrient ions: ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ). Column leaching experiments were conducted to investigate the effects of rice husk char (RHC) application on soil nutrient leaching. The results showed that RHC could adsorb ammonium  $4.7 \text{ mg N g}^{-1}$  and nitrate  $2.1 \text{ mg N g}^{-1}$  in solutions with an initial concentration of  $200 \text{ mg N L}^{-1}$ . Almost no phosphate sorption was observed using the RHC. Instead, some phosphate was released into aqueous solution at lower initial concentrations (below  $60 \text{ mg P L}^{-1}$ ). Application of RHC into loamy soils at a rate of 4% (w/w) reduced total ammonium leaching by 11% and total nitrate leaching by 23%, but increased phosphate leaching by 72%, compared with the control soil columns. Total leached phosphate throughout experimental period was  $0.16 \text{ mg P}$  from control soil and  $0.27 \text{ mg P}$  from soil with RHC application. These findings suggest that the application of RHC can be considered a potential strategy for mitigation of nitrogen leaching in loamy soil. The RHC, however, is unsuitable for phosphorus leaching mitigation. Instead, RHC addition is a possible method to increase the availability of phosphorus in a low P index soil.

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## 1. Introduction

Nitrogen (N) and phosphorus (P) are two plant nutrients of major concern for surface and groundwater quality, mainly as a result of agricultural activities (Sparks, 2003). The excessive application of fertilizer has caused the leaching of these nutrients from agricultural soils. Nutrient leaching may pose a great threat to environmental health, leading to either surface and groundwater pollution or eutrophication, depleted soil fertility and rapid soil acidification. One alternative method to increase nutrient retention and reduce nutrient leaching is the application of biochar. Biochar is the carbon-rich material obtained when biomass or organic materials are heated in a closed container either without oxygen or with limited oxygen at a relatively low temperature ( $<700 \text{ }^\circ\text{C}$ ) (Lehmann and Joseph, 2009).

Studies have demonstrated the biochar, attributed to its surface area and surface charge, has the capability to serve as an environmental sorbent (Ahmad et al., 2014, etc). A single type of biochar, however, may not be appropriate to be a sorbent for all substances. The sorption and

release of ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and phosphate ( $\text{PO}_4^{3-}$ ) to and from independent biochar (not mixed into soils) has not been widely studied. Several previous investigations (Hale et al., 2013; Hollister et al., 2013; Yao et al., 2012; Zeng et al., 2013) focusing on  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  have shown that the sorption affinity of biochar varies greatly with biochar characteristics and nutrient types. For example, Yao et al. (2012) found nitrate is most likely adsorbed onto high temperature ( $>600 \text{ }^\circ\text{C}$ ) biochar, whereas CEC of biochar is the most important factor influencing ammonium adsorption. They found, however, no clear trend for phosphate sorption or release.

When biochar is applied to soil, the interaction of the biochar and soil is influenced not only by the biochar characteristics but also by the soil properties, and will determine the nutrient leaching or retention characteristics of the mixture (Mukherjee and Zimmerman, 2013). Chen et al. (2010) reported a reduction of cumulative nitrate leaching by 59% and 12% for bagasse charcoal and biosolids charcoal, respectively. Knowles et al. (2011) also found that biochar application decreased nitrate leaching from biosolid-amended soils to levels at or below that in the control treatments in lysimeter experiments. Uzoma et al. (2011) observed that biochar produced from black locust increased the nutrient retention ability of sandy soil up to 23% for nitrate and up to 37% for phosphate. D. Laird et al. (2010); D.A. Laird et al. (2010) observed a significant decrease in the total N and P leaching from biochar-amended soil columns receiving manure application.

\* Corresponding author at: Laboratory of Irrigation and Water Management, Faculty of Agriculture 2nd Bldg, 3rd Floor, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

E-mail address: [enditaprima@gmail.com](mailto:enditaprima@gmail.com) (E.P.A. Pratiwi).

Some studies oppositely showed increases in nutrient leaching with biochar application. Major et al. (2012) found that wood biochar application at the rate of 20 t ha<sup>-1</sup> to a Colombian Savanna Oxisol soil resulted in significant increases in the concentration of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in the soil solution and, in consequence, a greater nutrient leaching. Applying nutrient rich biochars to soils is problematic as it may increase the risk of nutrient leaching. Troy et al. (2014) assigned high water-extractable P contents to the larger P leaching from soil treated with pig manure biochar compared to control soil. At the same experiment, they also found that addition of wood biochar had no effect on P leaching. The effect of biochar on nutrient leaching and retention is inconsistent, and the underlying mechanism has not been fully understood. It is, therefore, suggested that the influence of any single type of biochar should be studied before it is applied on a large scale.

Rice is a staple food in most Asian countries. In paddy field systems, an enormous amount of rice husk is inevitably produced every year. Supposing global rice production is roughly 700 million tons per year (FAO, 2015), 20% of rice production, i.e. 140 million tons, becomes rice husks (<http://knowledgebank.irri.org>). The char yield from rice husk is approximately 35% of feedstock material (Shackley et al., 2012). Converting rice husk waste into rice husk biochar (RHC) and applying it back to the paddy field system as char can be an effective solution for safe and beneficial disposal. However, studies on the sorption affinity for nutrients of RHC alone and RHC effect on nutrient leaching when applied to soil are very limited. Kizito et al. (2015) and Zhu et al. (2012) conducted research on ammonium adsorption onto the RHC surface by a batch sorption experiment. Both studies found that the RHC had a significant ability to adsorb ammonium from aqueous solution. The application of RHC has been reported to have capability to decrease nitrate leaching, but had no effect on ammonium leaching and increase phosphate leaching (Altland and Locke, 2013a; Yoo et al., 2014). Nevertheless, we did not find any study on nitrate or phosphate sorption using RHC as a sorbent in addition to considering phosphate leaching from soils as affected by RHC application.

The objectives of this study were (i) to determine the status of three major nutrient ions (ammonium, nitrate, and phosphate) in the RHC, (ii) to determine the ability of RHC to adsorb or release those nutrients, and (iii) to investigate the effects of the RHC application on soil nutrient leaching. Batch sorption and soil column experiments were carried out to achieve the objectives of this study. We hypothesized that the RHC could adsorb ammonium, nitrate and phosphate from aqueous solution and its application to soil could reduce the leaching of these nutrients from soil columns.

## 2. Materials and methods

### 2.1. Biochar and soil sample

Loamy soil (sand 43%, silt 37%, and clay 20%) was collected from the surface layer (0–0.2 m depth) of a paddy field of Kyushu University experimental farm in the Kasuya district (33°36'N, 130°27'E), Fukuoka, Japan. Biochar used in this study was a commercial charcoal (Midori Sangyou, Japan) derived from rice husk. The characterization methods of soil and RHC have been described elsewhere in Pratiwi and Shinogi (2016a). Concentration of elemental carbon (C), hydrogen (H) and nitrogen (N) were analyzed using elemental analyzer (Yanaco CHN Corder MT-5). Ash content was measured by heating the samples at 900 °C for 4 h and expressed as a percentage by weight. The bulk density of biochar was determined by measuring the weight of compacted biochar in 100 cm<sup>3</sup> stainless steel column. Specific surface area (SSA) of biochar was analyzed using ethylene glycol monoethyl ether (EGME) method. Table 1 shows the main physicochemical properties of the soil and the RHC. The particular production temperature of RHC is unknown; however, considering the diminished aliphatic and hydroxyl group (Fourier Transform Infra Red spectrometer (FTIR) images not shown), the RHC was presumably produced at high temperatures (>600 °C) (Pratiwi

**Table 1**  
Physicochemical characteristics and nutrient contents of soil and rice husk biochar.<sup>a</sup>

Properties	Biochar	Soil
C (%)	40.97	1.71
H (%)	1.72	0.67
N (%)	0.47	0.17
C/N ratio	109.0	12.6
Ash content (%)	48.2	n.d. <sup>b</sup>
Bulk density (g cm <sup>-3</sup> )	0.18	1.29
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	179	86

<sup>a</sup> All data are previously published in Pratiwi and Shinogi (2016a).

<sup>b</sup> Not observed.

and Shinogi, 2016a). The concentrations of Total P and major cations in RHC were determined using an X-Ray Fluorescence (XRF) spectrometer (Shimadzu EDX 800, Japan) as follows: P: 8.6 g kg<sup>-1</sup>, K: 113.5 g kg<sup>-1</sup>, Ca: 28.7 g kg<sup>-1</sup>, Al: 7.5 g kg<sup>-1</sup>, Fe: 5.12 g kg<sup>-1</sup>, and Mg: not detected.

### 2.2. Nutrient sorption experiment

Batch sorption experiments were conducted to determine ammonium, nitrate and phosphate sorption abilities for both RHC and soil. RHC was sieved in the size range of 0.25 to 1-mm mesh and air-dried soil was passed through a 2-mm sieve prior to the experiment. For analysis, 0.5 g RHC or 2.5 g soil was placed into a 100-ml bottle and suspended in 50 ml of 0.01 M KCl solution containing different types and concentrations of nutrients. For ammonium (or nitrate) sorption, nutrients were added as NH<sub>4</sub>Cl (or KNO<sub>3</sub>) with initial concentrations 0, 5, 10, 20, 50, 100 and 200 mg L<sup>-1</sup> N. For phosphate sorption, nutrients were added as KH<sub>2</sub>PO<sub>4</sub> with initial concentrations of 0, 3.5, 7, 14, 35, 70 and 140 mg L<sup>-1</sup> P. Three replicates were conducted for each concentration and each nutrient type. The samples were then shaken on a horizontal shaker at ambient temperature for 24 h to reach equilibrium. After equilibration, the suspensions were filtered (Advantec No. 6, equal to Whatman No. 42) to separate the supernatant. The pH value and ion concentrations in the solutions after equilibration were measured immediately (within 24 h).

The amount of adsorbed nutrient was calculated using the following equation:

$$Q_e = \frac{(C_0 - C_e) \times v}{w}, \quad (1)$$

where  $Q_e$  is the amount of nutrient adsorbed by biochar or soil at equilibrium (mg g<sup>-1</sup> N or P),  $C_0$  is the initial nutrient concentration in the solution (mg L<sup>-1</sup> N or P),  $C_e$  is the remaining concentration of nutrient in the solution at equilibrium (mg L<sup>-1</sup> N or P),  $v$  is the volume of the solution (ml), and  $w$  is the weight of biochar or soil (g). A negative value of  $Q_e$  denotes desorption or release of nutrients from biochar or soil into the aqueous solution. The Freundlich isotherm model (Eq. (2)) was used for approximating the relationship of  $C_e$  and  $Q_e$  for the data in which sorption occurred:

$$Q_e = K_f \times C_e^{1/n}, \quad (2)$$

where  $K_f$  (L g<sup>-1</sup>) and  $n$  (–) are experimentally derived adsorption constants.

### 2.3. Soil column experiment

Soil column experiments were carried out to investigate the effect of RHC applications on nutrient leaching from the soil. Columns were made of acrylic cylinders with dimensions of 20 cm length and 2.54 cm inner diameter. The bottom of each column was covered with nylon cloth and a stainless steel mesh to prevent soil loss. Soil and

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