# Floating duckweed mitigated ammonia volatilization and increased grain yield and nitrogen use efficiency of rice in biochar amended paddy soils



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#### HIGHLIGHTS

• Biochar (BC) was applied alone or along with floating duckweed (FDW) to two rice paddy soils.

• BC alone significantly increased NH<sub>3</sub> volatilizations by 25.6–43.7%.

• Combination of BC and FDW could reduce the NH<sub>3</sub> losses by 34.2–38.0%.

• Combination of BC + FDW promoted the nitrogen usage efficiency and the rice grain yield.

#### ARTICLE INFO

Article history: Received 20 June 2019 Received in revised form 2 August 2019 Accepted 5 August 2019 Available online 8 August 2019

Handling Editor: Xinde Cao

Keywords: Ammonia volatilization Atmospheric environment Biochar Grain yield Nitrogen use efficiency Urea

### ABSTRACT:

Biochar (BC) potentially accelerates ammonia (NH<sub>3</sub>) volatilization from rice paddy soils. In this regard, however, application the floating duckweed (FDW) to biochar-amended soil to control the NH<sub>3</sub> volatilization is not studied up-to-date. Therefore, the impacts of BC application with and without FDW on the NH<sub>3</sub> and nitrous oxide (N<sub>2</sub>O) emissions, NUE and rice grain yield were evaluated in a soil columns experiment. We repacked soil columns with Hydragric Anthrosol and Haplic Acrisol treated in triplicates with Urea, Urea + BC and Urea + BC + FDW. Total NH<sub>3</sub> losses from Hydragric Anthrosol and Haplic Acrisol were 15.2–33.2 kg N ha<sup>-1</sup> and 19.6–39.7 kg N ha<sup>-1</sup>, respectively. Urea + BC treatment recorded 25.6–43.7% higher (p < 0.05) NH<sub>3</sub> losses than Urea treatment, attributing to higher pH value of floodwater. Floating duckweed decreased soil pH and therefore significantly reduced (p < 0.05) the NH<sub>3</sub> volatilizations from Hydragric Anthrosol and Haplic Acrisol were 1.19–3.42 kg N ha<sup>-1</sup> and 0.67 –2.08 kg N ha<sup>-1</sup>, respectively. Urea + BC treatment. Total N<sub>2</sub>O emissions by 58.8–68.7% and Urea + BC + FDW treatment further increased N<sub>2</sub>O emissions by 58.8–68.7% and Urea + BC + FDW treatment of the topsoil, explained the N<sub>2</sub>O increases in the Urea + BC and Urea + BC + FDW treatments. Urea + BC slightly reduced the rice grain yield and NUE, while the

#### 1. Introduction

Rice (Oryza sativa L.) is one of the major staple crops in Asia, feeding more than half of the world's population. To ensure high grain yield, excessive nitrogen (N) fertilizer is often used, especially in the rice fields of China (Hofmeier et al., 2015). Consequently, large proportion of applied N was lost to the adjacent environment (Xia et al., 2017). Ammonia (NH<sub>3</sub>) volatilization is the main pathway of N losses in rice paddy fields (Zhong et al., 2017; Wang et al., 2018). Total NH<sub>3</sub> volatilized from fertilizer N was estimated to be 2.80–3.55 Tg yr<sup>-1</sup>, with a value of 0.30–0.65 Tg yr<sup>-1</sup> observed in paddy fields in China (Zhang et al., 2017). Emitted NH<sub>3</sub> poses a major threat to environmental quality and ecosystem biodiversity, and also contributes to indirect nitrous oxide (N<sub>2</sub>O) emission through the subsequent nitrification and denitrification processes (Sun et al., 2015; Lam et al., 2017). Meanwhile, N<sub>2</sub>O, being with a global warming potential of approximately 298 times greater than carbon dioxide  $(CO_2)$  with a lifetime of about 150 years, is directly emitted from rice paddy soils (Xia et al., 2017). There were approximately 138–154 Gg N<sub>2</sub>O emitted from Chinese rice fields according to Liang et al. (2013). Therefore, it is imperative to evaluate the synchronous impacts of practically adopted N managements in stable food production on NH<sub>3</sub> volatilization and N<sub>2</sub>O emissions and minimize them from agricultural soils receiving high rate of N fertilizer.

Biochar, a carbon rich material produced by thermal decomposition process named pyrolysis of biomass in absence of oxygen and N environment (Lehmann et al., 2011) has become a promising soil amendment to mitigate greenhouse gas emission (Dong et al., 2013; Deng et al., 2017; Zhou et al., 2017), improve soil fertility (Wang et al., 2014; Li et al., 2018), minimize the bioavailability of potentially toxic elements (Yang et al., 2016, 2017; Lu et al., 2017) and organic pollutants (He et al., 2015, 2018; Qin et al., 2018), and reduce N losses (both gaseous and leaching) (Liu et al., 2011; Dong et al., 2015; Nguyen et al., 2017; Sun et al., 2017). Furthermore, it has been evidenced that biochar addition significantly influenced the N<sub>2</sub>O emission from rice paddy soils (Oomori et al., 2016; Sun et al., 2016a, 2019a). Numerous studies investigated the impact of biochar on N<sub>2</sub>O emission, while the effect of biochar on NH<sub>3</sub> volatilization from rice paddy soil is not well-documented (Feng et al., 2017; Huang et al., 2017). Furthermore, few studies have been conducted to simultaneously evaluate the comprehensive impact of biochar amendment on NH<sub>3</sub> volatilization and N<sub>2</sub>O emission from rice paddy soil (Sun et al., 2016a; Wang et al., 2017).

Volatilization of NH<sub>3</sub> from rice paddy soils is significantly influenced by the ammonium (NH<sup> $\pm$ </sup>) content and the pH of the flooding water after N fertilization. We hypothesize that biochar might retard the NH<sub>3</sub> emitted from surface floodwater/soil due to its adsorption capacity for NH<sup> $\pm$ </sup>/NH<sub>3</sub> (Li et al., 2016; Mandal et al., 2016). On the contrary, the pH value of surface floodwater and topsoil is likely to increase due to the high alkalinity of biochar, which consequently might lead to higher NH<sub>3</sub> volatilization even from the soil after biochar application (Feng et al., 2017; Mandal et al., 2018; Sun et al., 2019b). How biochar influenced NH<sub>3</sub> volatilization from rice paddy soils by aforementioned two courses is yet to be studied. In addition, little is known about whether biochar has consistent impact on NH<sub>3</sub> volatilization from different soil type with diverse ecological factors, especially with different basal pH value. Therefore, the impacts of biochar application on the NH<sub>3</sub> volatilization from different rice paddy soils should be further assessed.

Potentially high NH<sub>3</sub> volatilization from rice paddy soil amended with biochar should be resolved before large-scale application of biochar to agriculture. Floating duckweed (*Lemna minor* L.) is able to grow under a variety of climatic conditions and its presence in flooded rice fields is a very common phenomenon (Liu et al., 2017). Reduction of NH<sub>3</sub> volatilization from inorganic N fertilizer by duckweed in flooded rice fields has been confirmed by Li et al. (2009) and Sun et al. (2016a). Yao et al. (2017) showed that urea combined with floating duckweed reduced the NH<sub>3</sub> volatilization by 36–52% compared to urea alone treatment. Therefore, we hypothesized that floating duckweed inoculation to rice paddy soil can at least balance the NH<sub>3</sub> stimulate effect resulting from biochar amendment or even reduce the NH<sub>3</sub> volatilization to a desired rate.

During the nitrification and the thereafter denitrification processes of  $NH_{4}^{+}$  contained in soil/water, certain amount of  $N_{2}O$  was emitted due to partial denitrification (Sims et al., 2013). Previous works have indicated that nitrification and denitrification processes are the most important mechanisms for N removal in duckweed-based ponds (Lu et al., 2014; Sun et al., 2016b). Wang et al. (2015a) reported that the averaged  $N_{2}O$  emission load was higher in the duckweed rice plots than in the non-duckweed plots. However, Sun et al. (2016a) found that floating duckweed inoculation has no significant influence on  $N_{2}O$  emission from a rice paddy soil irrigated with N-rich wastewater. Up to our best knowledge, the impact of floating duckweed on the NH<sub>3</sub> and N<sub>2</sub>O emissions, NUE, and rice grain yield in different rice soils fertilized with urea and treated with biochar is not studied up-to-date.

Therefore, the objectives of this study were to evaluate the impacts of biochar with and without floating duckweed on the NH<sub>3</sub> volatilization and N<sub>2</sub>O emission from two rice paddy soils, as well as the rice grain yield and the NUE. To achieve these aims, we conducted a soil columns experiment, where biochar was applied alone or along with floating duckweed to two typical rice paddy soils in China receiving N fertilizer (as urea) according to local recommended rate (240 kg N ha<sup>-1</sup>). The results can provide elaborate guidance and practical basis of how biochar should be applied to minimize gaseous N losses from the rice field and to achieve environmental and economic sustainability.

### 2. Material and methods

#### 2.1. Background information and soil column installation

Two typical paddy soils used for repacking to layered soil columns (70 cm of height and 25 cm of inner diameter) were collected from Yixing (31°28'N, 119°59'E), Jiangsu Province, and Yingtan (28°12'N, 117°10'E), Jiangxi Province, China. The soils from two sites were classified as Hydragric Anthrosol and Haplic Acrisol (FAO/ Unesco, 1988), respectively. The soils were collected from the 0–20 cm, 20–40 cm, and 40–60 cm of a profile at six different sites from each type of paddy soil, then air-dried, crushed, passed through a 2-mm sieve and mixed thoroughly before usage. The soil of each layer was repacked to soil columns with the same order and

 Table 1

 Selected physicochemical properties of the studied soils and wheat straw biochar.

Soils/biochar	pН	Total N	Total P	Total K	SOC	CEC
		${\rm g}~{\rm kg}^{-1}$				cmol kg <sup>-1</sup>
Hydragric Anthrosol Haplic Acrisol Wheat straw biochar	6.38 5.05 9.51	1.56 1.90 13 3	0.96 1.29 4.40	4.12 4.44 20.9	22.8 18.1 —	15.0 8.89 27 5

SOC: Soil organic carbon; CEC: Cation exchange capacity.

#### bulk density as in the field condition.

Biochar derived from wheat straw was pyrolyzed in a continuous slow pyrolysis system at 500 °C under oxygen-limited condition. The biochar has a BET (Brunauer-Emmett-Teller) surface area of  $51.5 \text{ m}^2 \text{ g}^{-1}$  and contains 174 g ash kg<sup>-1</sup>. The quantitative biochar (20 t ha<sup>-1</sup>) were homogeneously mixed with the surface layer soils during repacking practice. The selected properties of the top layer (0–20 cm) of the soils and the biochar are presented in Table 1.

#### 2.2. Experimental design and management

The three treatments for each type of soil were Urea (receiving urea N-fertilizer), Urea + BC (receiving urea N-fertilizer and biochar), Urea + BC + FDW (receiving urea N-fertilizer, biochar and floating duckweed). Each type of soil included one control treatment (no application of N, biochar and floating duckweed, same P and K fertilizer input with other treatments) for calculation of NUE of rice. Three replicates were maintained for each treatment.

Pre-flooding irrigation for each plot was formed one week prior to rice transplanting. Floodwater was continuously maintained at a depth of 3-5 cm in all soil columns, expect during the mid-season drainage from July 30 to August 6, 2017. Nitrogen fertilizer (urea, in rate of 240 kg N ha<sup>-1</sup>) was homogeneously broadcast to the surface water as a basal fertilization and two supplementary fertilizations with ratio of 30%: 30%: 40% on July 3, July 17, and August 13, 2017, respectively. Phosphorous fertilizer (calcium superphosphate, in rate of 90 kg  $P_2O_5$  ha<sup>-1</sup>) and K fertilizer (potassium chloride, in rate of 120 kg K<sub>2</sub>O ha<sup>-1</sup>) were broadcast as basal fertilizers to all treatments. Floating duckweed was placed in Urea + BC + FDW treatments with rice plant before basal fertilizer (N, P, K) application at an initial density of 200 g fresh-weight  $m^{-2}$  (about 80% coverage of surface water) (Li et al., 2009; Sun et al., 2016a; Supplementary Fig. 1). The floating duckweeds were collected from a ditch near the rice fields and the total N content was measured  $(45.4 \text{ g N kg}^{-1})$ dry weight). The experiment was initiated on July 3, 2017 and ended on Oct 31, 2017.

#### 2.3. Sample and measurement

#### 2.3.1. NH<sub>3</sub> volatilization and N<sub>2</sub>O emission

Ammonia volatilization was monitored by a dynamic chamber method (Sun et al., 2013), which was composed of cylindrical chamber (made from transparent poly-methyl methacrylate, with an inner diameter of 15 cm and a height of 25 cm), a vacuum pump, and an acid solution (80 mL 2% boric acid and mixed with indicator of methyl red, bromocresol, and ethanol) to capture emitted NH<sub>3</sub> gas. Ambient air located at 2.0 m above the surface floodwater was pumped to complement the inner air in the chamber. When collecting NH<sub>3</sub> volatilization, the chamber was inserted into the surface floodwater/soil to a depth of approximately 5 cm. The air flow rate through the chamber was set to 15–20 headspace min<sup>-1</sup> and the NH<sub>3</sub> in the chamber was then trapped in a glass bottle containing NH<sub>3</sub> absorbent. Ammonia volatilization was measured twice per day (7:00–9:00 a.m. and 14:00–16:00 p.m., respectively). After taken back laboratory, the NH<sub>3</sub> absorbent solution was titrated against with 0.01 M H<sub>2</sub>SO<sub>4</sub>. The volatilization of NH<sub>3</sub> was continuously detected (approximately continued one week) until there was no color difference of NH<sub>3</sub> absorbent between treatments with and without urea. The cumulative NH<sub>3</sub> volatilization losses were the sum of the NH<sub>3</sub> volatilization fluxes on sampling days. And the total NH<sub>3</sub> losses from N-fertilized treatments were calculated by subtracting the cumulative NH<sub>3</sub> losses of the control treatment from other N treatments (Sun et al., 2013).

The N<sub>2</sub>O gas samples were taken using the modified closed method presented by Sun et al. (2013). Gas samples were taken weekly and on the 1st, 3rd, 5th day after drainage started during mid-season drainage phase. At each observation, four gas samples were collected every 15 min after chamber were water-sealed for 5 min. The temperature inside the chamber was recorded at the same time of sampling. The N<sub>2</sub>O concentration of gas sample was analyzed by a gas chromatograph (Agilent 7890 B, USA) equipped with ECD detector. Cumulative N<sub>2</sub>O emissions were calculated from the individual N<sub>2</sub>O fluxes and the interval time. And the total N<sub>2</sub>O losses from N-fertilized treatment were the difference between the cumulative N<sub>2</sub>O losses of the N treatments and the control treatment.

#### 2.3.2. Rice grain yield and NUE

At crop maturity, all of above-ground biomass was handful harvested from each soil column. Straw and grain were separated, air-dried, and weighed to calculate the fresh rice grain weight and NUE. Biomass was oven-dried at 80 °C for 48 h, and then powdered by a grinder for the total N content analyzed by the Kjeldahl method. Rice crop N uptake amount was calculated depending on the total N content and the oven-dried weight. The NUE was calculated as the percentage of applied fertilizer N recovered in above-ground biomass minus that of the control treatment (Sun et al., 2015).

#### 2.3.3. pH value, $NH_4^+$ content of surface floodwater and soil

Along with the NH<sub>3</sub> volatilization measurement, 20 mL surface floodwater samples were taken at 10:00 a.m. every day until the NH<sub>3</sub> volatilization measurement ended. During mid-season anaerobic phase, soil samples (about 200 g) were collected from the top layer (0–15 cm) of each soil column. The soil pH was measured in deionized water at a ratio of 1: 2.5 w/v using combined reference electrodes and a  $\Phi$ 255 pH/temp/mV meter (Coulter Bechman Co., USA). Surface floodwater pH was directly measured following the similar method. Soil NH<sub>4</sub><sup>+</sup> was extracted by 2.0 M KCl, and their contents in KCl-extracted soil solution, together with the filtered surface floodwater samples, were measured by a San<sup>++</sup> Continuous Flow Injection Analyzer (Skalar, Netherlands).

# 2.4. Statistical analysis

The difference among three treatments was analyzed with oneway analysis of variance (ANOVA). All tests of significance were conducted with Duncan's multiple-comparison tests (p < 0.05). Statistical analyses were performed using SPSS 16.0 (SPSS Ver. 16.0 for Windows, Chicago, IL, USA).

# 3. Results

#### 3.1. NH<sub>3</sub> volatilization

The  $NH_3$  volatilization rates from two soils after each N (urea) fertilization, as well as the cumulative  $NH_3$  volatilization of rice growth cycle are summarized in Table 2. The cumulative  $NH_3$ 

Table 2 Impacts of the studied treatments on NH<sub>3</sub> volatilization losses from the studied soils.

Soils	Treatments	Ammonia volatilization losses (kg N ha <sup>-1</sup> )					
		BF	SF1	SF2	Total		
Hydragric Anthrosol	Urea	12.6 ± 0.5 a	$6.0\pm0.6b$	$4.6 \pm 1.3$ b	$23.1\pm1.8b$		
	Urea + BC	11.0 ± 0.9 a	9.0 ± 2.0 a	13.2 ± 4.8 a	33.2 ± 6.4 a		
	Urea + BC + FDW	7.3 ± 1.5 b	3.7 ± 0.9 b	$4.2 \pm 1.4 \text{ b}$	15.2 ± 5.1 c		
Haplic Acrisol	Urea	21.6 ± 1.0 a	$3.3 \pm 0.2 \text{ b}$	6.8 ± 2.3 b	$31.6 \pm 2.9 \text{ b}$		
	Urea + BC	20.1 ± 0.3 a	7.3 ± 2.3 a	12.4 ± 0.7 a	39.7 ± 2.0 a		
	Urea + BC + FDW	$6.6\pm3.3~b$	$5.1\pm0.8b$	$7.9\pm1.4b$	$19.6\pm4.6~c$		

BF: basal fertilizer; SF1: 1st supplementary fertilizer; SF2: 2nd supplementary fertilizer. Data were mean  $\pm$  standard deviation (SD) of the means (n = 3), and the different lowercase letters in the same column indicate a significant difference at p < 0.05.

volatilization of Urea treatment was  $23.1 \pm 1.8$  kg N ha<sup>-1</sup> for the Hydragric Anthrosol and  $31.6 \pm 2.9$  kg N ha<sup>-1</sup> for the Haplic Acrisol, of which were mainly (54.5%-68.4%) observed after basal N fertilizer applied. For Hydragric Anthrosol, consistent NH<sub>3</sub> volatilization during basal fertilization monitoring period was observed under Urea + BC treatment, compared with Urea treatment, whereas, significantly higher (p < 0.05) NH<sub>3</sub> volatilization rates after 1st and 2nd supplementary fertilizers broadcasted to two soils were recorded (1.5 and 2.9 folds of that under Urea treatment, respectively). In addition, biochar addition to the urea fertilized soils increased significantly the NH<sub>3</sub> volatilization as compared to

the mono urea treatment in the 1st (3.2 folds) and 2nd (1.8 folds) supplementary fertilizations treatments (Table 2). Consequently, total NH<sub>3</sub> volatilization loss of Urea + BC treatment was 43.7% and 25.6% significantly higher (p < 0.05) than that of Urea treatment for Hydragric Anthrosol and Haplic Acrisol, respectively (Table 2).

Urea + BC + FDW treatment significant reduced (p < 0.05) NH<sub>3</sub> volatilization after each time N fertilization as compared to Urea + BC treatment (33.6–68.2% and 30.1–67.6% in the Hydragric Anthrosol and Haplic Acrisol, respectively). Therefore, Urea + BC + FDW treatment effectively reduced the total NH<sub>3</sub> volatilization by 54.2% and 50.6% compared with Urea + BC



Fig. 1. Seasonal dynamics of N<sub>2</sub>O emission flux observed from two paddy soils. BF: basal fertilizer; SF1: 1st supplementary fertilizer; SF2: 2nd supplementary fertilizer. Error bars represent the standard deviation (SD) for three replicates.



**Fig. 2.** Total N<sub>2</sub>O emissions from two rice paddy soils. Error bars represent the standard deviation (SD) for three replicates. Different letters indicate significant differences between each treatment according to Duncan's multiple range test at p < 0.05.

treatment for Hydragric Anthrosol and Haplic Acrisol, respectively. Furthermore, Urea + BC + FDW treatment significantly (p < 0.05) reduced NH<sub>3</sub> loss by 34.2–38.0% as compared to Urea treatment, mainly attributing to the significant decrease of NH<sub>3</sub> volatilization during basal N fertilization period (Table 2).

#### 3.2. N<sub>2</sub>O emissions

During the flooded stage of rice growth, low rate of  $N_2O$  emissions was observed. Mid-season drainage management resulted in dramatic increase of  $N_2O$  production. This  $N_2O$  emission flux pattern was independent with soil type, also the soil managements (Fig. 1).

The total N<sub>2</sub>O emissions of rice growth cycle from two soils receiving urea only were 0.67–1.19 kg N ha<sup>-1</sup> (Fig. 2). They accounted for only 0.28–0.50% of fertilizer N input load during the rice growth season, which were far lower than the cumulative NH<sub>3</sub> volatilizations (section 3.1). Compared with the Urea treatment, Urea + BC treatment increased the N<sub>2</sub>O emissions by 40.7% in Hydragric Anthrosol and by 37.0% in Haplic Acrisol. Interestingly, biochar combined with floating duckweed treatment resulted in

significantly (p < 0.05) higher N<sub>2</sub>O emissions by 44.7 and 39.9% over Urea + BC treatment for Hydragric Anthrosol and Haplic Acrisol, respectively.

#### 3.3. Rice grain yield and NUE

The three tested treatments under Haplic Acrisol harvested same rice grain yields with 10.4–11.1 t ha<sup>-1</sup> (Table 3). However, it was found that biochar application decreased the grain yield of rice planted in Hydragric Anthrosol by 12.6% in compared with urea mono urea treatment (Table 3). On the other hand, grain yield was slightly increased by 0.1–0.3 t ha<sup>-1</sup> under Urea + BC + FDW treatment over Urea treatment in two soils. Biochar amendment lowered the NUE of rice planted in the two soils by 2.9–8.4%, but the differences were not statistically significant. Addition of floating duckweed can conversely promoted the NUE by 11.4–23.2% compared to Urea + BC treatment.

# 4. Discussion

# 4.1. Influence of biochar and floating duckweed inoculation on $NH_3$ volatilization

The cumulative NH<sub>3</sub> losses accounted for 7.5–13.8% of total fertilizer N applied in rice season (values are calculated from the data in Table 2), which is supported by several other studies (Liu et al., 2015; Feng et al., 2017; Yao et al., 2017). For most of treatments, NH<sub>3</sub> volatilization during BF stage is higher than that during two SF stages, which was probably due to the small leaf area of rice growing at BF stage (Chen et al., 2015). Compared with single application of urea fertilizer, biochar application increased the cumulative NH<sub>3</sub> losses by 8.6–17.9% (Wang et al., 2017). Similarly, Feng et al. (2017) and Huang et al. (2017) reported that biochar should be applied at appropriate rates (lower than 3 *wt* % equivalent to 40 t ha<sup>-1</sup>) to minimize gaseous fertilizer-N loss via NH<sub>3</sub> volatilization. Our results suggested that biochar amendments had higher cumulative NH<sub>3</sub> volatilization over mono urea treatments, for both soils (Table 2).

Biochar's influence in NH<sub>3</sub> volatilization is complex and mainly caused by changes in soil/water pH, NH<sup>4</sup>/NH<sub>3</sub> sorption, as well as microbial community composition (Mandal et al., 2018; Sun et al., 2019b). Previous literature speculated the increased pH resulting from biochar lead to the higher NH<sub>3</sub> volatilization from biochar amended rice paddy soil (Feng et al., 2017; Wang et al., 2017). In the present work, pH value of the floodwater sampled at each day of three N fertilization monitoring periods were summarized in Table 4. It was observed that pH values of the floodwater were increased by 0.91-1.09 and 0.99-1.13 units after biochar application along with urea (Urea + BC treatment) compared to Urea treatment after N fertilized to Hydragric Anthrosol and Haplic Acrisol, respectively.

Besides pH of floodwater,  $NH_4^+$  content of floodwater also influence the  $NH_3$  volatilization from the rice field (Yao et al., 2017).

### Table 3

Impacts of the studied treatments on grain yield and nitrogen usage efficiency of rice.

Soils	Treatments	Grain yield (t ha <sup>-1</sup> )	Nitrogen usage efficiency (%)
Hydragric Anthrosol	Urea	11.1 ± 0.9 a	34.7 ± 4.2 ab
	Urea + BC	9.7 ± 0.5 b	31.8 ± 2.3 b
	Urea + BC + FDW	11.2 ± 0.3 a	39.2 ± 2.7 a
Haplic Acrisol	Urea	10.8 ± 0.5 a	34.2 ± 3.0 a
	Urea + BC	10.4 ± 0.8 a	33.2 ± 2.5 a
	Urea + BC + FDW	11.1 ± 0.3 a	37.0 ± 1.6 a

Data were mean  $\pm$  standard deviation (SD) of the means (n = 3), and the different lowercase letters in the same column indicate a significant difference at p < 0.05.

Soils	Treatments	pH value of the floodwater						
		BF		SF1		SF2		
		Range	Mean	Range	Mean	Range	Mean	
Hydragric Anthrosol	Urea	8.17-8.59	8.34	7.63-8.26	8.04	7.56-8.66	7.99	
	Urea + BC	9.30-9.52	9.43	8.70-9.01	8.98	8.33-9.52	8.90	
	Urea + BC + FDW	7.96-8.20	8.07	7.73-8.14	7.97	7.64-8.94	8.01	
Haplic Acrisol	Urea	7.08-8.25	7.56	7.14-7.84	7.41	7.35-8.68	7.89	
	Urea + BC	8.33-8.89	8.67	8.05-9.08	8.54	8.38-9.07	8.88	
	Urea + BC + FDW	6.63-7.72	7.23	7.32-7.76	7.38	7.40-8.48	7.83	

BF: basal fertilizer; SF1: 1st supplementary fertilizer; SF2: 2nd supplementary fertilizer.

From Table 5, it was observed that after biochar addition the average NH<sup>+</sup><sub>4</sub> content of floodwater were significantly lower than mono Urea at basal fertilization monitoring period by 29.0% in the Hydragric Anthrosol and by 18.4% in the Haplic Acrisol (Table 5). The lower  $NH_4^+$  content of floodwater can be explained by the  $NH_4^+$ adsorption capacity of amended biochar (Kizito et al., 2015; Yang et al., 2015) which decreases the NH<sub>3</sub> volatilization rate. Biochar application potentially enhances the NH<sub>3</sub> volatilization, which might be attributed to the associated increase of soil pH. However, studies found that due to having unique surface characteristics (oxygen-containing functional groups and high surface area) and  $NH_4^+/NH_3$  adsorption capacity, biochar addition can mitigate  $NH_3$ volatilization from soil and rice system (Mandal et al., 2018). In this case, these two capacities (pH and NH<sup>+</sup><sub>4</sub> adsorption capacity of biochar) were offset and resulted in no net effect on NH<sub>3</sub> volatilization at basal fertilization monitoring period. However, data in Table 5 showed that there was nearly no significant difference (p < 0.05) of averaged NH<sub>4</sub><sup>+</sup> content of floodwater at subsequent two supplementary fertilization monitoring periods. This was mainly as the  $NH_{d}^{+}$  capacity of biochar was finite (Kizito et al., 2015) and degraded along with application time (oxidation) (Wang et al., 2015b). Therefore, increased pH value of floodwater indeed result in higher NH<sub>3</sub> volatilization during supplementary fertilization monitoring periods from biochar incorporated rice paddy system. Biochars can have lower pH depending on feedstock, temperature, etc., though they are typically greater than 8 (Li et al., 2018; Sun et al., 2019b). Moreover, Sun et al. (2019a) demonstrated the varied effects of different biochar amendments on soil N<sub>2</sub>O emission. Therefore, impacts of different biochar amendments (biochar type, application rates, etc.) should be further investigated in the future.

It was interestingly observed that the biochar inclusive with floating duckweed not only had 54.2% lower NH<sub>3</sub> losses than that of the Urea + BC treatment, but also had 34.2% lower NH<sub>3</sub> losses than that of the Urea treatment for Hydragric Anthrosol (Table 2). Similar for Haplic Acrisol, the corresponding NH<sub>3</sub> mitigating efficiencies of Urea + BC + FDW treatment were 54.6% and 38.0%, respectively (Table 2). An apparent drop in pH near the duckweed surface mat

The NH<sup>+</sup><sub>4</sub> concentration of the floodwater of three N fertilization monitoring periods.

weed ponds (Chaiprapat et al., 2003). The pH values from Table 4 shows that the pH of floodwater in Urea + BC + FDW treatment for both two soils were significantly lower (p < 0.05) among three treatments those were receiving N. These results indicated that the combination of biochar and floating duckweed can effectively reduce the NH<sub>3</sub> volatilization from rice paddy soils. Furthermore,  $NH_4^+$  contents of floodwater sampled from Urea + BC + FDW treatment were relatively lower than that from Urea treatment of both two soils (Table 5). Present work evidenced that lower pH and NH<sub>4</sub><sup>+</sup> content due to floating duckweed treatment explains the lower NH<sub>3</sub> volatilization observed (Sun et al., 2016a). Other potential mechanisms of how floating duckweed reduce NH<sub>3</sub> loss were that duckweed would uptake N and decrease the floodwater temperature or provide a physical barrier to hinder NH<sub>3</sub> volatilization as reported by Zimmo et al. (2004) and Li et al. (2009). Last publication demonstrated that different duckweed exerted no consistent effect on N metabolism in wastewater treatment systems (latrou et al., 2019), which indicating that the duckweed variety might influence its effects on gaseous N emissions from flooded rice systems. Moreover, the interaction mechanism between BC and FDW should be studied in the future.

was observed that explain low rates of NH<sub>3</sub> emission from duck-

# 4.2. $N_2O$ emissions were increased by whether BC alone or along with FDW

In this study, maximum N<sub>2</sub>O emissions in all three treatments were detected during the drainage period, while small N<sub>2</sub>O flux were observed when rice paddy plots were waterlogged (Fig. 1), which pattern was supported by previous works (Ji et al., 2013; Sun et al., 2013). Our data demonstrated that biochar application significantly increased (p < 0.05) the total N<sub>2</sub>O emissions from the two rice paddy soils (Fig. 2). Consistently, Liu et al. (2014) and Shen et al. (2014) reported that biochar addition stimulated the N<sub>2</sub>O emissions, which was possibly due to increased availability of soil NH<sup>4</sup><sub>4</sub> in the biochar treatments. In our work, the NH<sup>4</sup><sub>4</sub> concentrations of soils sampled at drainage stage in Urea + BC treatment

Soil type	Treatments	$NH_4^+$ concentration of the floodwater (mg L <sup>-1</sup> )					
		BF		SF1		SF2	
		Range	Mean	Range	Mean	Range	Mean
Hydragric Anthrosol	Urea	18.97-43.37	29.51	3.07-33.13	12.08	0.68-23.80	9.34
	Urea + BC	7.33-34.70	20.95	1.18-39.80	14.47	0.57-29.20	10.66
	Urea + BC + FDW	5.97-42.10	20.08	7.65-34.53	13.92	0.68-42.47	12.77
Haplic Acrisol	Urea	35.97-132.60	72.65	3.66-68.80	30.13	1.13-37.67	15.91
	Urea + BC	31.50-116.53	59.27	1.32-59.27	24.68	1.07-43.53	15.26
	Urea + BC + FDW	16.03-104.73	54.28	3.97-67.40	32.08	0.57-43.20	16.76

BF: basal fertilizer; SF1: 1st supplementary fertilizer; SF2: 2nd supplementary fertilizer.

#### Table 5



**Fig. 3.** The NH<sub>4</sub><sup>+</sup>-N concentration of the top (0-20 cm) soil during drainage period. Error bars represent the standard deviation (SD) for three replicates. Columns denoted by different letters indicate significant differences between each other according to Duncan's multiple range test at p < 0.05.

were 42.7 and 67.5% higher than that of the Urea treatment for Hydragric Anthrosol and Haplic Acrisol, respectively (Fig. 3). The presence of high soil NH<sup>+</sup><sub>4</sub> provides sufficient N source directly for the nitrification processes of microbes and thereby generate more N<sub>2</sub>O gas under biochar amended treatments (Fig. 4). Similar mechanism has been reported by Yan et al. (2000).

Rice paddy soil inoculated with floating duckweed potentially have more NH<sup>+</sup><sub>4</sub> staying in the system due to having lower NH<sub>3</sub> volatilization loss. In addition, raising N concentrations in the surface soil was observed with the duckweed life cycle in previous study (Xie et al., 2004). Thus, significantly 33.7-41.7% higher (p < 0.05) soil NH<sub>4</sub><sup>+</sup> concentrations were recorded under Urea + BC + FDW treatments in comparison to the Urea + BC treatment (Fig. 3), which contributes to higher  $N_2O$  emissions observed in Urea + BC + FDW treatment (Fig. 1). We here hypothesized that the presence of duckweed increases N<sub>2</sub>O flux probably as a result of higher and more optimal soil Eh arising from the photosynthetic activity of duckweed for the maximum production and minimum consumption of N<sub>2</sub>O, which was supported by Yuan et al. (2009) and Wang et al. (2015a). In duckweed-based systems, nitrification and denitrification are the most important mechanisms for N removal (Zimmo et al., 2003; Peng et al., 2007), which may result in higher N<sub>2</sub>O emissions flux during flooded period in rice growth system. Overall, our work evidenced that biochar addition along with urea increased N<sub>2</sub>O emissions and the presence of floating duckweed further enhanced the N<sub>2</sub>O emissions from rice paddy soils, which should be considered for controlling in the future.



Fig. 4. Correlation between  $N\mathrm{H}_4^+\mathrm{-N}$  concentration of soil sampled at mid-season drainage period and  $N_2O$  emissions from two rice paddy soils.

# 4.3. Rice grain yield in biochar amend soil can be guaranteed by floating duckweed

Biochar amendment improves crop productivity mainly by increasing nutrient use efficiency, nutrient retention capacity, and water holding capacity of soil. A review of Hussain et al. (2017) suggested that the improvements to crop production are often recorded in highly degraded and nutrient-poor soils, while biochar's application to fertile and healthy soils does not always increase crop or grain yield. The soils used for this study were on a fertile and healthy status according to data listed in Table 1. Therefore, biochar amendment had no positive influence on rice grain yield in our study. Comparatively lower rice grain productions were recorded under two exclusive biochar treatments. Especially, this effect was significant for Hydragric Anthrosol compared to Haplic Acrisol (Table 3). High gaseous N losses (NH<sub>3</sub> volatilization and N<sub>2</sub>O emission) occurred in rice paddy soils possibly decreased the NUE of rice plant. From Table 3 it was found that the two exclusive biochar treatments being with 3.0-8.4% lower NUE over Urea treatments, though the differences were not statistically significant (p < 0.05). Consequently, no increased rice production was found after the exclusive biochar application in the present work.

Floating duckweed could increase rice grain yields, mainly

attributing to its function of reducing NH<sub>3</sub> volatilization and improving NUE (Li et al., 2009; Yao et al., 2017). Consistently, Table 3 suggested that the NUE was enhanced under Urea + BC + FDW treatment, relative to Urea treatment. Therefore, Urea + BC + FDW treatment achieved slightly higher rice grain yield in comparison to Urea treatment. Therefore, exclusive biochar application may not be a good practice for maintaining soil fertility over a long period. Instead, combination of biochar and floating duckweed maybe an optimal practice to ensure food security, while decreasing NH<sub>3</sub> volatilization losses from rice paddy soils. However, the N<sub>2</sub>O emission was higher with this treatment compared to other two. Therefore, further studies are highly recommended to understand the mechanism.

### 5. Conclusions

Application of wheat straw alkaline biochar increased the NH<sub>3</sub> volatilizations and N<sub>2</sub>O emissions from two acidic rice soils fertilized with urea. This effect was mainly attributed to the higher pH value of surface floodwater as results of biochar addition to the rice system. Interestingly, the co-application of biochar together with floating duckweed effectively reduced NH<sub>3</sub> volatilization and increased the grain yield and NUE of rice more than urea either alone and/or mixed with biochar. In conclusion, combined application of biochar and floating duckweed might be recommended as its functions of reducing NH<sub>3</sub> volatilization and promoting N uptake by rice plant and thereby enhancing the rice grain yield. However, the production of N<sub>2</sub>O from floating duckweed applied rice system should be mitigated at the same time. Furthermore, a verification of the gained results under field conditions is required.

#### Acknowledgements

This work was supported by the National Key Research and Development Program of China (2018YFD0800204), the Research Fund Program of Guangdong Provincial Key Laboratory of Environmental Pollution Control and Remediation Technology (2018K22), the National Natural Science Foundation of China (31601832, 21876027, 41877090), the Natural Science Foundation of Jiangsu Province (BK20160931), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and the High-Level Talent Start-Up Research Project of Foshan University (GG07030). We also thank Dr. Huihua Min for analyzing biochar's properties.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124532.

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