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 NH3 volatilizations by 25.6–41.7%.
- Combination of BC and FDW could reduce the NH3 losses by 34.2–38.0%.
- Combination of BC + FDW promoted the nitrogen usage efficiency and the rice grain yield.

ABSTRACT:

Biochar (BC) potentially accelerates ammonia (NH3) volatilization from rice paddy soils. In this regard, however, application the floating duckweed (FDW) to biochar-amended soil to control the NH3 volatilization is not studied up-to-date. Therefore, the impacts of BC application with and without FDW on the NH3 and nitrous oxide (N2O) 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 NH3 losses from Hydragric Anthrosol and Haplic Acrisol were 15.2–32.2 kg N ha⁻¹ and 19.6–39.7 kg N ha⁻¹, respectively. Urea + BC treatment recorded 25.6–43.7% higher (p < 0.05) NH3 losses than Urea treatment, attributing to higher pH value of floodwater. Floating duckweed decreased soil pH and therefore significantly reduced (p < 0.05) the NH3 volatilizations from the two soils by 50.6–54.2% over Urea + BC and by 34.2–38.0% over Urea treatment. Total N2O emissions from Hydragric Anthrosol and Haplic Acrisol were 1.19–3.42 kg N ha⁻¹ and 68.7% and 0.67–2.08 kg N ha⁻¹, respectively. Urea + BC treatment increased N2O emissions by 58.8–68.7% and Urea + BC + FDW further increased N2O emission by 187.4–210.4% over Urea treatment. Higher ammonium content of the topsoil, explained the N2O increases in the Urea + BC and Urea + BC + FDW treatments. Urea + BC slowly 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 (NH₃) volatilization is the main pathway of N losses in rice paddy fields (Zhong et al., 2017; Wang et al., 2018). Total NH₃ volatilized from fertilizer N was estimated to be 2.80–3.55 Tg yr⁻¹, with a value of 0.30–0.65 Tg yr⁻¹ observed in paddy fields in China (Zhong et al., 2017). Emitted NH₃ poses a major threat to the environmental quality and ecosystem biodiversity, and also contributes to indirect nitrous oxide (N₂O) emission through the subsequent nitrification and denitrification processes (Sun et al., 2015; Lam et al., 2017). Meanwhile, N₂O, being with a global warming potential of approximately 298 times greater than carbon dioxide (CO₂) with a lifetime of about 150 years, is directly emitted from rice paddy soils (Xia et al., 2017). There were approximately 138–154 Gg N₂O emitted from Chinese rice fields according to Liang et al. (2013). Therefore, it is imperative to evaluate the synchronous impacts of practically adopted N management in stable food production on NH₃ volatilization and N₂O 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 amendment process named pyrolysis of biomass in absence of oxygen and N environment (Lehmann et al., 2011) has become a promising approach to mitigate greenhouse gas emissions and minimize them from agricultural soils receiving high rate of N fertilizer. 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

Impacts of biochar application on the NH₃ volatilization from different rice paddy soils should be further assessed. Potentially high NH₃ volatilization from rice paddy soil amended with biochar should be resolved before large-scale application of biochar to agriculture. Floating duckweed (Lemma 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 NH₃ 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 NH₃ 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 NH₃ stimulate effect resulting from biochar amendment or even reduce the NH₃ volatilization to a desired rate. During the nitrification and the thereafter denitrification processes of NH₄⁻ contained in soil/water, certain amount of N₂O was emitted due to partial denitrification (Sim 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 N₂O 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 N₂O emission from a rice paddy soil irrigated with N-rich wastewater. Up to our best knowledge, the impact of floating duckweed on the NH₃ and N₂O 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 NH₃ volatilization and N₂O 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⁻¹). 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.

Impacts of biochar with and without floating duckweed on the NH₃ volatilization and N₂O 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⁻¹). 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.
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 m² g⁻¹ and contains 174 g ash kg⁻¹. The quantitative biochar (20 t ha⁻¹) 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. 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, except during the mid-season drainage from July 30 to August 6, 2017. Nitrogen fertilizer (urea, in rate of 240 kg N ha⁻¹) 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 P₂O₅ ha⁻¹) and K fertilizer (potassium chloride, in rate of 120 kg K₂O ha⁻¹) were broadcast as soil 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., 2008; 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 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. NH₃ volatilization and N₂O 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 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 NH₃ gas. Ambient air located at 2.0 m above the surface floodwater was pumped to complement the inner air in the chamber. When collecting NH₃ 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⁻¹ and the NH₃ in the chamber was then trapped in a glass bottle containing NH₃ 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 NH₃ absorbent solution was titrated against with 0.01 M H₂SO₄. The volatilization of NH₃ was continuously detected (approximately continued one week) until there was no color difference of NH₃ absorbent between treatments with and without urea. The cumulative NH₃ volatilization losses were the sum of the NH₃ volatilization fluxes on sampling days. And the total NH₃ losses from N-fertilized treatments were calculated by subtracting the cumulative NH₃ losses of the control treatment from other N treatments (Sun et al., 2013).

The N₂O 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 N₂O concentration of gas sample was analyzed by a gas chromatograph (Agilent 7890 B, USA) equipped with ECD detector. Cumulative N₂O emissions were calculated from the individual N₂O fluxes and the interval time. And the total N₂O losses from N-fertilized treatment were the difference between the cumulative N₂O 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 harvested from each soil column. Straw and grain were separated, air-dried, and weighed to determine 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, NH₄⁺ content of surface floodwater and soil

Along with the NH₃ volatilization measurement, 20 mL surface floodwater samples were taken at 10:00 a.m. every day until the NH₃ 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 Φ255 pH/temp/mV meter (Coulter Beckman Co., USA). Surface floodwater pH was directly measured following the similar method. Soil NH₄⁺ 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++ Continuous Flow Injection Analyzer (Skalar, Netherlands).

#### 2.4. Statistical analysis

The difference among three treatments was analyzed with one-way 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. NH₃ volatilization

The NH₃ volatilization rates from two soils after each N (urea) fertilization, as well as the cumulative NH₃ volatilization of rice growth cycle are summarized in Table 2. The cumulative NH₃
volatilization of Urea treatment was 23.1 ± 1.8 kg N ha⁻¹ for the Hydragric Anthrosol and 31.6 ± 2.9 kg N ha⁻¹ for the Haplic Acrisol, of which were mainly (54.5%–68.4%) observed after basal N fertilizer applied. For Hydragric Anthrosol, consistent NH3 volatilization during basal fertilization monitoring period was observed under Urea + BC treatment, compared with Urea treatment, whereas, significantly higher (p < 0.05) NH3 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 NH3 volatilization as compared to the mono urea treatment in the 1st (3.2 folds) and 2nd (1.8 folds) supplementary urea treatments (Table 2). Consequently, total NH3 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 significantly reduced (p < 0.05) NH3 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 NH3 volatilization by 54.2% and 50.6% compared with Urea + BC

Table 2
Impacts of the studied treatments on NH3 volatilization losses from the studied soils.

<table>
<thead>
<tr>
<th>Soils</th>
<th>Treatments</th>
<th>Ammonia volatilization losses (kg N ha⁻¹)</th>
<th>BF</th>
<th>SF1</th>
<th>SF2</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydragric Anthrosol</td>
<td>Urea</td>
<td>12.6 ± 0.5 a</td>
<td>6.0 ± 0.6 b</td>
<td>4.6 ± 1.3 b</td>
<td>23.1 ± 1.8 b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Urea + BC</td>
<td>11.0 ± 0.9 a</td>
<td>9.0 ± 2.0 a</td>
<td>13.2 ± 4.8 a</td>
<td>33.2 ± 6.4 a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Urea + BC + FDW</td>
<td>7.3 ± 1.5 b</td>
<td>3.7 ± 0.9 b</td>
<td>4.2 ± 1.4 b</td>
<td>15.2 ± 5.1 c</td>
<td></td>
</tr>
<tr>
<td>Haplic Acrisol</td>
<td>Urea</td>
<td>21.6 ± 1.0 a</td>
<td>3.3 ± 0.2 b</td>
<td>6.8 ± 2.3 b</td>
<td>31.6 ± 2.9 b</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Urea + BC</td>
<td>20.1 ± 0.3 a</td>
<td>7.3 ± 2.3 a</td>
<td>12.4 ± 0.7 a</td>
<td>39.7 ± 2.0 a</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Urea + BC + FDW</td>
<td>6.6 ± 3.3 b</td>
<td>5.1 ± 0.8 b</td>
<td>7.9 ± 1.4 b</td>
<td>19.6 ± 4.6 c</td>
<td></td>
</tr>
</tbody>
</table>

BF: basal fertilizer; SF1: 1st supplementary fertilizer; SF2: 2nd supplementary fertilizer. Data were mean ± 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.

Fig. 1. Seasonal dynamics of N2O 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.
treatment for Hydragric Anthrosol and Haplic Acrisol, respectively. Furthermore, Urea + BC + FDW treatment significantly (p < 0.05) reduced NH3 loss by 34.2–38.0% as compared to Urea treatment, mainly attributing to the significant decrease of NH3 volatilization during basal N fertilization period (Table 2).

3.2. N2O emissions

During the flooded stage of rice growth, low rate of N2O emissions was observed. Mid-season drainage management resulted in dramatic increase of N2O production. This N2O emission flux pattern was independent with soil type, also the soil managements (Fig. 1).

The total N2O emissions of rice growth cycle from two soils receiving urea only were 0.67–1.19 kg N ha⁻¹ (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 NH3 volatilizations (section 3.1). Compared with the Urea treatment, Urea + BC treatment increased the N2O 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 N2O 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⁻¹ (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⁻¹ 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 NH3 volatilization

The cumulative NH3 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, NH3 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 NH3 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⁻¹) to minimize gaseous fertilizer-N loss via NH3 volatilization. Our results suggested that biochar amendments had higher cumulative NH3 volatilization over mono urea treatments, for both soils (Table 2).

Biochar’s influence in NH3 volatilization is complex and mainly caused by changes in soil/water pH, NH4+/NH3 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 NH3 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, NH4⁺ content of floodwater also influence the NH3 volatilization from the rice field (Yao et al., 2017).

Table 3

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

Data were mean ± 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.
From Table 5, it was observed that after biochar addition the average NH₄⁺ content of floodwater were significantly lower than mono Urea at basal fertilization monitoring period by 29.0% in the Hydric Anthrosol and by 18.4% in the Haplic Acrisol (Table 5). The lower NH₄⁺ content of floodwater can be explained by the NH₄⁺ adsorption capacity of amended biochar (Kizito et al., 2015; Yang et al., 2015) which decreases the NH₄⁺ volatilization rate. Biochar application potentially enhances the NH₃ 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 NH₄⁺/NH₃ adsorption capacity, biochar addition can mitigate NH₃ volatilization from soil and rice system (Mandal et al., 2018). In this case, these two capacities (pH and NH₄⁺ adsorption capacity of biochar) were offset and resulted in no net effect on NH₃ volatilization at basal fertilization monitoring period. However, data in Table 5 showed that there was nearly no significant difference (p < 0.05) of averaged NH₄⁺ content of floodwater at subsequent two supplementary fertilization monitoring periods. This was mainly as the NH₄⁺ 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 NH₃ 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 N₂O 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 NH₃ losses than that of the Urea + BC treatment, but also had 34.2% lower NH₃ losses than that of the Urea treatment for Hydric Anthrosol (Table 2). Similar for Haplic Acrisol, the corresponding NH₃ 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 was observed that explain low rates of NH₃ emission from duckweed 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 NH₃ volatilization from rice paddy soils. Furthermore, NH₃ 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 NH₃ content due to floating duckweed treatment explains the lower NH₃ volatilization observed (Sun et al., 2016a). Other potential mechanisms of how floating duckweed reduce NH₃ loss were that duckweed would uptake N and decrease the floodwater temperature or provide a physical barrier to hinder NH₃ 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 (Iatrou 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.

### 4.2. N₂O emissions were increased by whether BC alone or along with FDW

In this study, maximum N₂O emissions in all three treatments were detected during the drainage period, while small N₂O 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 N₂O 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 N₂O emissions, which was possibly due to increased availability of soil NH₄⁺ in the biochar treatments. In our work, the NH₄⁺ concentrations of soils sampled at drainage stage in Urea + BC treatment

### Table 4

*The pH value of the floodwater of three N fertilization monitoring periods.*

<table>
<thead>
<tr>
<th>Soils</th>
<th>Treatments</th>
<th>pH value of the floodwater</th>
<th>BF</th>
<th>SF1</th>
<th>SF2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td></td>
<td>Urea + BC + FDW</td>
<td>7.96–8.20</td>
<td>8.07</td>
<td>7.73–8.14</td>
<td>7.97</td>
</tr>
<tr>
<td>Haplic Acrisol</td>
<td>Urea</td>
<td>7.08–8.25</td>
<td>7.56</td>
<td>7.14–7.84</td>
<td>7.41</td>
</tr>
<tr>
<td></td>
<td>Urea + BC</td>
<td>8.33–8.89</td>
<td>8.67</td>
<td>8.05–9.08</td>
<td>8.54</td>
</tr>
</tbody>
</table>

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

### Table 5

*The NH₄⁺ concentration of the floodwater of three N fertilization monitoring periods.*

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Treatments</th>
<th>NH₄⁺ concentration of the floodwater (mg L⁻¹)</th>
<th>BF</th>
<th>SF1</th>
<th>SF2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Range</td>
<td>Mean</td>
<td>Range</td>
<td>Mean</td>
</tr>
<tr>
<td>Hydratic Anthrosol</td>
<td>Urea</td>
<td>18.97–43.37</td>
<td>29.51</td>
<td>3.07–33.13</td>
<td>12.08</td>
</tr>
<tr>
<td></td>
<td>Urea + BC</td>
<td>7.33–44.70</td>
<td>20.95</td>
<td>1.18–39.80</td>
<td>14.47</td>
</tr>
<tr>
<td></td>
<td>Urea + BC + FDW</td>
<td>5.97–42.10</td>
<td>20.08</td>
<td>7.65–34.53</td>
<td>13.92</td>
</tr>
<tr>
<td>Haplic Acrisol</td>
<td>Urea</td>
<td>35.97–132.60</td>
<td>72.65</td>
<td>3.66–68.80</td>
<td>30.13</td>
</tr>
<tr>
<td></td>
<td>Urea + BC</td>
<td>31.50–136.53</td>
<td>59.27</td>
<td>1.32–59.27</td>
<td>24.68</td>
</tr>
<tr>
<td></td>
<td>Urea + BC + FDW</td>
<td>16.03–104.73</td>
<td>54.28</td>
<td>3.97–67.40</td>
<td>32.08</td>
</tr>
</tbody>
</table>

BF: basal fertilizer; SF1: 1st supplementary fertilizer; SF2: 2nd supplementary fertilizer.
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$_4^+$ provides sufficient N source directly for the nitrification processes of microbes and thereby generate more N$_2$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$_4^+$ staying in the system due to having lower NH$_3$ 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$_4^+$ concentrations were recorded under Urea + BC + FDW treatments in comparison to the Urea + BC treatment (Fig. 3), which contributes to higher N$_2$O emissions observed in Urea + BC + FDW treatment (Fig. 1). We here hypothesized that the presence of duckweed increases N$_2$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$_2$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$_2$O emissions flux during flooded period in rice growth system. Overall, our work evidenced that biochar addition along with urea increased N$_2$O emissions and the presence of floating duckweed further enhanced the N$_2$O emissions from rice paddy soils, which should be considered for controlling in the future.

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$_3$ volatilization and N$_2$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 NH₃ 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 biocar application may not be a good practice for maintaining soil fertility over a long period. Instead, combination of biochar and floating duckweed may be an optimal practice to ensure food security, while decreasing NH₃ volatilization losses from rice paddy soils. However, the N₂O 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 biocar increased the NH₃ volatilizations and N₂O 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 biocar addition to the rice system. Interestingly, the co-application of biochar together with floating duckweed effectively reduced NH₃ 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 NH₃ volatilization and promoting N uptake by rice plant and thereby enhancing the rice grain yield. However, the production of N₂O 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.

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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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