





## 25 1 Introduction

26 Agriculture accounted for an estimated emission of 4.1 (1.7–4.8) Tg N yr<sup>-1</sup> for N<sub>2</sub>O and 3.7 Tg N yr<sup>-1</sup> for NO,  
27 contributing 60 % and 10 %, respectively, to the total global anthropogenic emissions, largely due to increases of N  
28 fertilizer application in cropland (Ciais, 2013). The concentration of atmospheric N<sub>2</sub>O, a powerful, long-lived,  
29 greenhouse gas, has increased from 270 parts per billion by volume (ppbv) in the pre-industrial era to ~ 324 ppbv (Ussiri  
30 and Lal, 2013); it has 298 times the global warming potential (GWP) of CO<sub>2</sub> on a 100-year horizon (IPCC, 2013) and  
31 also causes depletion of the ozone layer in the atmosphere (Ravishankara et al., 2009). In contrast, NO<sub>x</sub>, which is mainly  
32 emitted as nitric oxide (NO), does not directly affect the earth's radiative balance but catalyzes the production of  
33 tropospheric ozone (O<sub>3</sub>), which is a greenhouse gas associated with detrimental effects on human health (Anenberg et al.,  
34 2012) and crop production (Avnery et al., 2011). Additionally, along with the high nitrate (N) application, ammonia  
35 volatilization is one of the major N loss pathways (Harrison and Webb, 2001) as well, with up to 90% coming from  
36 agricultural activities (Misselbrook et al., 2000; Boyer et al., 2002). As a natural component and a dominant atmospheric  
37 alkaline gas, NH<sub>3</sub> plays an important role in atmospheric chemistry and ambient aerosol formation (Langridge et al.,  
38 2012; Wang et al., 2015b). In addition to nutrient enrichment (eutrophication) of terrestrial and aquatic systems and  
39 global acidification of precipitation, NH<sub>3</sub> has also been shown to be a major factor in the formation of atmospheric  
40 particulate matter and secondary aerosols (Kim et al., 2006; Pinder et al., 2007), leading to potentially adverse effects on  
41 human and ecosystem health such as visibility degradation and threats to biodiversity (Powlson et al., 2008; Behera et al.,  
42 2013). Consequently, the release of various reactive N species results in lower N use efficiency in agricultural systems.

43 In China, vegetable production devotes an area of approximately 24.7 × 10<sup>6</sup> ha, equivalent to 12.4% of the total  
44 available cropping area, and the production represented 52 % of the world vegetable production in 2012 (FAO, 2015).  
45 Intensified vegetable cultivation in China is characterized by high N application rates, high cropping index and frequent  
46 farm practices. Annual nitrogen fertilizer inputs for intensively managed vegetable cultivation in rapidly developing areas  
47 are 3–6 times higher than in cereal grain cultivation in China (Ju et al., 2006; Diao et al., 2013; Wang et al., 2015a). As a  
48 result, great concern exists about excess N fertilizer application, leading to low use efficiency in intensive vegetable  
49 fields in China (Deng et al., 2013; Diao et al., 2013). Meanwhile, intensive vegetable agriculture is considered to be an  
50 important source of N<sub>2</sub>O (Xiong et al., 2006; Jia et al., 2012; Li et al., 2015b; Zhang et al., 2015) and NO production  
51 (Mei et al., 2009). Moreover, ammonia volatilization is another important N pathway in fertilized soil, resulting in large  
52 losses of soil-plant N (Pacholski et al., 2008; Zhang et al., 2011). Therefore, the reduction of reactive N loss becomes a  
53 central environmental challenge to meet the joint challenges of high production and acceptable environmental  
54 consequences in intensive vegetable production (Zhang et al., 2013).



55 Biochar is the dark-colored, carbon (C)-rich residue of pyrolysis or gasification of plant biomass under oxygen  
56 ( $O_2$ )-limited conditions, specifically produced for use as a soil amendment (Sohi, 2012). The amendment of agricultural  
57 ecosystems with biochar has been proposed as an effective countermeasure for climate change (Smith, 2016). These  
58 additions will increase soil carbon storage (Mukherjee and Zimmerman, 2013; Stavi and Lal, 2013), decrease GHG  
59 emissions (Li et al., 2016), and improve soil fertility and crop production (Major et al., 2010; Liu et al., 2013). However,  
60 some recent studies have reported no difference or even an increase in soil  $N_2O$  emissions induced by biochar application  
61 on different soils (Saarnio et al., 2013; Wang et al., 2015a).  $NH_3$  volatilization was enhanced by biochar  
62 application in pasture soil (Clough et al., 2010), vegetable soil (Sun et al., 2014) and paddy soil in the wheat-growing  
63 season (Zhao et al., 2014). Additionally, crop productivity responses to biochar amendments differed among various  
64 biochars (Cayuela et al., 2014). These inconsistent results suggest that current biochar application to soil is not a  
65 “one-size fit-all paradigm” because of the variation in the physical and chemical characteristics of the different biochars,  
66 soil types and crop species (Field et al., 2013; Cayuela et al., 2014). Moreover, limited types of biochar (Spokas and  
67 Reicosky, 2009) and soil (Sun et al., 2014) were involved in the experiments in previous studies. Thus, the evaluation of  
68 the different types of biochar under the typical soils is imperative to gain a comprehensive understanding of potential  
69 interactions before the large-scale application of biochars in intensive vegetable cropping systems in China.

70 Therefore, a greenhouse pot experiment was conducted in an effort to investigate the effects of different types of  
71 biochar on gaseous nitrogen emissions (GNEs), namely,  $N_2O$ , NO and  $NH_3$ , simultaneously in four typical intensively  
72 vegetable soils across main vegetable production areas of mainland China. Overall, the objectives of this research were to  
73 gain a comprehensive insight into the effects of the different types of biochar on the GNEs, vegetable yield and gaseous  
74 nitrogen intensity (GNI) in intensively managed vegetable production in China.

75

## 76 2 Materials and methods

### 77 2.1. Experimental soil and biochar

78 Four typical greenhouse vegetable cultivation sites with a long history (more than 10 years) of conventional  
79 cultivation were selected from Northeast, Northwest, Central and Eastern China (Fig. S1), namely, Phaeozem, Anthrosol,  
80 Acrisol and Cambisol (FAO and ISRIC, 2012) from Jiamusi (46°48' N, 130°12' E), Heilongjiang province (HLJ);  
81 Yangling (34°18' N, 108°2' E), Shanxi province (SX); Changsha (28°32' N, 113°23' E), Hunan province (HN) and  
82 Shouguang (36°56' N, 118°38' E), Shandong province (SD), respectively were collected and represented a range of  
83 differences in physicochemical properties and regions (Table S1). Soil samples were manually collected from the  
84 cultivated layer (0–20 cm) after the local vegetable harvest in April, 2015. The samples were air-dried and passed through



85 a 5 mm stainless steel mesh sieve and homogenized thoroughly. Any visible roots and organic residues were removed  
86 manually before being packed with the necessary amount of soil to achieve the initial field bulk density. Each pot  
87 received 15 kg of 105 °C dry-weight-equivalent fresh soil. For the biochar amendment pots, sieved biochar (2 mm) was  
88 mixed with the soil thoroughly before the experiment, equivalent to a 40 t ha<sup>-1</sup> dose (dry weight). No more biochar was  
89 added later in the experimental period.

90 Two types of biochar, derived from two common agricultural wastes in China: wheat straw and swine manure,  
91 hereafter referred to as Bw and Bm, respectively (Table S1). The Bw was produced at the Sanli New Energy Company in  
92 Henan, China, by pyrolysis and thermal decomposition at 400–500 °C. The Bm was produced through thermal  
93 decomposition at 400 °C by the State Key Laboratory of Soil Science and Sustainable Agricultural, Institute of Soil  
94 Science, Chinese Academy of Sciences. In accordance with Lu (2000), the SOC was measured by wet digestion with  
95 H<sub>2</sub>SO<sub>4</sub>–K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, TN was determined by semi-micro Kjeldahl digestion, and soil texture was determined with the pipette  
96 method. The soil pH and biochar pH were measured in deionized water at a volume ratio of 1:2.5 (soil to water) with a  
97 PHS-3C mv/pH detector (Shanghai Kangyi Inc. China). The soil NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N were measured following the  
98 two-wavelength ultraviolet spectrometry and indophenol blue methods, respectively, using an ultraviolet  
99 spectrophotometer (HITACHI, UV-2900, Tokyo, Japan). Electric conductivity (EC) was measured by using a  
100 Mettler-Toledo instrument (FE30-K, Shanghai, China) at a 1:5 (w:v) soil to water ratio. Cation exchange capacity (CEC)  
101 was determined using the CH<sub>3</sub>COONH<sub>4</sub> method. Dissolved organic carbon (DOC) was extracted from 5 g of the  
102 biochar/soil with an addition of 50 ml deionized water and measured by a TOC analyzer (TOC-2000/3000, Metash  
103 Instruments Co., LTD, Shanghai, China). Ash content was measured by heating the biochars at 750 °C for 4 h. The  
104 specific surface area of the biochar material was tested using the Brunauer–Emmett–Teller (BET) method, from which  
105 the N adsorption–desorption isotherms at 77 K were measured by an automated gas adsorption analyzer ASAP2000  
106 (Micromeritics, Norcross, GA) with + 5% accuracy. Scanning electron microscopy (SEM) imaging analysis was  
107 conducted using a HITACHI S-3000N scanning electron microscope.

## 108 2.2. Experimental set-up and management

109 The pot experiments were performed at the greenhouse experimental station of Nanjing Agricultural University,  
110 China. Five vegetable crops were grown successively in the four vegetable soils during the experimental period. For each  
111 type of soil, three treatments with three replicates were arranged in a completely random design: urea without biochar  
112 (N), urea with wheat straw biochar (N+Bw), urea with swine manure biochar (N+Bm). In addition, phosphate and  
113 potassium fertilizers in the form of calcium magnesium phosphate and potassium chloride, together with urea, were  
114 broadcasted and mixed with soil thoroughly prior to sowing the vegetables. No topdressing events occurred because of



115 the frequent cultivation and short growth period for the leafy vegetables. Based on the vegetable growth, all pots received  
116 equal amounts of water and no precipitation. Detailed information on the pot management practices is provided in Table  
117 S2.

118 Each pot consists of a 30 cm × 30 cm (height × diameter) cylinder made of polyvinyl chloride (PVC). The top of  
119 each pot was surrounded by a special water-filled trough collar, which allowed a chamber to sit on the pot and prevent  
120 gas exchange during the gas-sampling period. Small holes (diameter of 1 cm) at the bottom of the pots were designed for  
121 drainage. To prevent soil loss, a fine nylon mesh (< 0.5 mm) was attached to the base of the soil cores before packing.

### 122 2.3. Measurement of $N_2O$ , $NO$ and $NH_3$

123 The  $NO$  and  $N_2O$  fluxes were measured simultaneously from each vegetable cultivation using a static opaque  
124 chamber method (Zheng et al., 2008; Yao et al., 2009). A square PVC chamber of 35 cm × 35 cm × 40 cm (length ×  
125 width × height) was temporarily mounted on the pot for gas flux measurement. The chamber was coated with sponge and  
126 aluminum foil outside to prevent solar radiation heating the chamber. Gas samples for flux measurements were collected  
127 between 8 and 10 a.m. on each measuring day to minimize the influence of diurnal temperature variation. Gas fluxes  
128 were usually measured once a week and every other day for one week following fertilizer application. To measure the  
129  $N_2O$  flux, four samples were collected from the headspace chamber using 20 ml polypropylene syringes at 0, 10, 20, and  
130 30 min after chamber closure. The gas concentrations in the samples were analyzed within 12 h after sampling using an  
131 Agilent 7890A gas chromatograph equipped with an electron capture detector (ECD) for  $N_2O$  detection. The carrier gas  
132 was argon-methane (50 %) at a flow rate of 40 ml min<sup>-1</sup>. The column and ECD temperatures were maintained at 40 and  
133 300 °C, respectively. The gas chromatography configurations described by Wang et al. (2013) were adopted for the gas  
134 concentration analysis.  $N_2O$  flux was calculated using the linear increases in gas concentration with time. Sample sets  
135 were rejected unless they yielded a linear regression value of  $R^2 > 0.90$ .

136 For each  $NO$  flux measurement, gas samples were collected from the same chamber that was used for the  $N_2O$  flux  
137 measurements (Yao et al., 2009). Before closing the chamber, an approximately 1.0 L gas sample from the headspace of  
138 each chamber was extracted into an evacuated sampling bag (Delin Gas Packing Co., LTD, Dalian, China), and this  
139 measurement was regarded as time 0 min for  $NO$  analysis. After 30 min under chamber enclosure conditions (i.e., after  
140 the  $N_2O$  sample collections were completed), another headspace gas sample with the same volume was extracted from  
141 each chamber into another evacuated bag. Within 1 h after sampling,  $NO$  concentrations were analyzed by a model 42i  
142 chemiluminescence  $NO-NO-NO_x$  analyzer (Thermo Environmental Instruments Inc., Franklin, MA, USA). The  $NO$   
143 fluxes were derived from the concentration differences between the two collected samples. The  $NO_x$  analyzer was  
144 calibrated by a model 146i dynamic dilution calibrator system at the end of each crop-growing season.



145 The mean flux of N<sub>2</sub>O or NO during the experiment period was calculated as the average of all measured fluxes,  
 146 which were weighted by the interval between the two measurements (Xiong et al., 2006). The cumulative N<sub>2</sub>O was  
 147 calculated as the product of the mean flux and the entire duration.

148 The NH<sub>3</sub> volatilization was determined using the ventilation method (Zhao et al., 2010). The  
 149 phosphoglycerol-soaked sponge was replaced every day after each fertilization event for approximately one week. The  
 150 phosphoglycerol-soaked sponges used to collect the NH<sub>3</sub> samples were immediately extracted with 300 mL potassium  
 151 chloride (KCl) solution (1 mol L<sup>-1</sup>) for 1 h. The concentration of ammonia nitrogen (NH<sub>4</sub><sup>+</sup>-N) was measured using the  
 152 indophenol blue method at 625 nm (Sororzano, 1969) by ultraviolet spectrophotometry (HITACHI, UV-2900, Tokyo,  
 153 Japan, with 0.005 absorbance of photometric accuracy). The cumulative seasonal NH<sub>3</sub> volatilization was the sum of the  
 154 daily emissions during the measurement period.

#### 155 2.4. Auxiliary measurements

156 Simultaneously with the determination of trace gas fluxes, the air temperature and the soil temperature at a depth of  
 157 5 cm were measured using thermally sensitive probes at each sampling date. Soil water content was also measured using  
 158 a portable water detector (Mode TZS-1K, Zhejiang Top Instrument Corporation Ltd., China) by the frequency domain  
 159 reflectometer method at a depth of 5 cm. Measured soil water contents (v/v) were converted to water filled pore space  
 160 (WFPS) with the following equation:

$$161 \text{ WFPS} = \text{volumetric water content (cm}^3 \text{ cm}^{-3}) / \text{total soil porosity (cm}^3 \text{ cm}^{-3}) \quad (1)$$

162 Here, total soil porosity = [1 - (soil bulk density (g cm<sup>-3</sup>) / 2.65)] with an assumed soil particle density of 2.65 (g cm<sup>-3</sup>).

163 The total soil bulk density was determined with the cutting ring method according to Lu (2000).

164 After each vegetable crop reached physiological maturity, the fresh vegetable yield was measured by weighing the  
 165 whole aboveground and belowground biomass in each pot.


$$166 \text{ GNE} = \text{cumulative N}_2\text{O} + \text{cumulative NO} + \text{cumulative NH}_3 \text{ emissions (kg N ha}^{-1}) \quad (2)$$

$$167 \text{ GNI} = \text{GNE} / \text{vegetable fresh yield (kg N t}^{-1} \text{ yield)} \quad (3)$$

168 After the one-year pot experiment, a soil sample from each pot was blended carefully. One subsample was stored at  
 169 4 °C for determination of microbial biomass carbon (MBC), potential nitrification rate (PNR) and denitrification enzyme  
 170 activity (DEA) within 3 days. Another subsample was air-dried for analysis of SOC, TN, pH and EC. MBC was  
 171 determined by substrate-induced respiration using a gas chromatography (Anderson and Domsch 1978). PNR was  
 172 measured using the chlorate inhibition soil-slurry method as previously described (Kurola et al., 2005) with  
 173 modifications (Hu et al., 2016). DEA was quantified as described by Smith and Tiedje (1979).

#### 174 2.5. Data processing and statistics






175 One-way ANOVA was performed to test the effects of the treatments on cumulative N<sub>2</sub>O, NO and NH<sub>3</sub> emissions;  
176 GNE; vegetable yield and GNI. Two-way ANOVA was used to analyze the effects of the biochar type; soil type; and their  
177 interactions on N<sub>2</sub>O, NO and NH<sub>3</sub> emissions, vegetable yield, GNE and GNI throughout the experimental period.  
178 Multiple comparisons among the treatments were further ained using Tukey's HSD test. Significant differences were  
179 considered at  $P < 0.05$ . All statistical analyses were performed using JMP ver. 7.0 (SAS Institute, Cary, NC, USA, 2007).  
180 Pearson's correlation analysis was used to determine whether there were significant interrelationships between N<sub>2</sub>O/NO  
181 and PNR or DEA in each soil, using SPSS window version 18.0 (SPSS Inc., Chicago, USA).

182

### 183 3. Results

#### 184 3.1. Soil responses to biochar amendment

185 Obvious differences in all observed soil properties existed among soil types (Table 1,  $p < 0.001$ ), suggesting the  
186 wide variations of soil characters across mainland China. Additionally, biochar amendments had significant influences on  
187 all the soil properties ( $p < 0.05$ ). Compared with N treatments, biochar amendments increased the SOC, TN and EC by  
188 20.4–135.0 %, 0.5–21.2 % and 2.4–38.1 %, respectively, across all the soils. Compared with Bw, Bm amendment  
189 resulted in higher ints of SOC and TN by 5.8–20.5 % and 9.5–14.2 %, respectively, whereas EC values were higher  
190 by 3.3–21.5 % induced by Bw than Bm amendment over all soils. Additionally, biochar amendments significantly  
191 enhanced soil pH by 0.27–0.64 and 0.08–0.10 units compared with N treatment in HN and SX soils ( $p < 0.05$ ),  
192 respectively, and higher values were detected with Bm than Bw amendment in all soils. Furthermore, biochar  
193 amendments tended to increase MBC in SD and HLJ soils, and Bm perfor  better in MBC enhancements than Bw in  
194 all soils.

195 As shown in Fig. 1, no consensus effects on PNR and DEA were observed with biochar amendments across all soils.  
196 Compared with N treatment, biochar amendments significantly increased PNR in HLJ while exerted no influences on SD  
197 soil (Fig. 1a). Compared with Bw, Bm amendment significantly increased PNR in HN and SX soils. Moreover, compared  
198 with N, biochar amendments significantly reduced DEA by an average of 40.1 and 37.8 % in SX and HLJ ( $p < 0.05$ ),  
199 respectively, while producing no influence in SD soils (Fig. 1b). In comparison with Bw, rem le enhancements were  
200 observed by 42.5 and 74.4 % with Bm amendment in HN and SX soils, respectively ( $p < 0.05$ ).

#### 201 3.2. Seasonal variations of N<sub>2</sub>O and NO emissions

202 The dynamics of N<sub>2</sub>O fluxes from all N-applied treatments in the four vegetable soils were relatively consistent and  
203 followed a sporadic and pulse-like pattern that was accompanied with fertilization, tillage and irrigation (Fig. 2). In  
204 addition, peak N<sub>2</sub>O fluxes varied greatly. Most of the N<sub>2</sub>O emissions occurred during the Amaranth and Tung choy





205 growing periods, and there were several small emissions peaks during the Spinach and Coriander herb growing periods  
206 due to lower N application rate (Table S2), soil temperature and water content (Fig. S2). The highest peaks of N<sub>2</sub>O  
207 emissions from HN, SX, SD and HLJ were 4133.7, 1784.0, 432.4 and 1777.2  $\mu\text{g N m}^{-2} \text{h}^{-1}$ , respectively. Although  
208 biochar (Bw and Bm) application did not significantly alter the seasonal pattern of the N<sub>2</sub>O fluxes, they greatly lowered  
209 some peaks of N<sub>2</sub>O emissions in the SX and HLJ vegetable soils (Fig. 2b and d).

210 Clearly, the NO fluxes demonstrated similar seasonal dynamics to the N<sub>2</sub>O fluxes (Fig. 3). Some relatively high  
211 peak NO fluxes were still observed in the Spinach and Coriander herb planting seasons even though relatively low  
212 temperatures occurred during these periods, primarily due to lower soil moisture which was suitable for NO production.  
213 The NO fluxes ranged from -44.6 to 377.6  $\mu\text{g N m}^{-2} \text{h}^{-1}$  across all soil types. Furthermore, some NO peaks were  
214 significantly weakened with the Bw and Bm in the HN soil (Fig. 3a).

### 215 3.3. Cumulative N<sub>2</sub>O, NO and NH<sub>3</sub> emissions

216 Cumulative N<sub>2</sub>O emissions varied greatly among soil types (Table 2,  $p < 0.001$ ), from 1.97 to 31.56 kg N ha<sup>-1</sup> across  
217 all the soils during the vegetable cultivation period (Table 3a). Biochar amendments had significant influences on the  
218 cumulative N<sub>2</sub>O emissions, reducing N<sub>2</sub>O emissions by 13.7–41.6 % (Table 2). In comparison with the N treatment,  
219 biochar amendment decreased N<sub>2</sub>O emissions by an average of 56.4 % and 47.5 % in SX and HLJ (Table 3a,  $p < 0.05$ ),  
220 respectively, with no remarkable influence in SD soil, indicating significant interactions between biochar and soil types  
221 (Table 2,  $p < 0.001$ ). Compared with Bm, Bw amendment performed better mitigation effects which decreased N<sub>2</sub>O  
222 emissions by 11.8–38.4 % across all the soils, significantly in HN soil (Table 3a,  $p < 0.05$ ). In comparison with N<sub>2</sub>O  
223 emission, the cumulative NO emission was much smaller, with a remarkable variation of 0.20–8.99 kg N ha<sup>-1</sup> across all  
224 soils (Table 3b). Though pronounced effects on NO emissions with a reduction by average of 45.8 % (Table 2,  $p < 0.05$ ),  
225 biochar amendment had no consensus effects across soils, reducing NO emissions in HN soil (Table 3b,  $p < 0.05$ ) and  
226 producing no remarkable influence on SD soil, which suggested significant interactions between biochar and soil types  
227 (Table 2,  $p < 0.001$ ). Compared with Bm, Bw amendment significantly reduced NO emissions in SX and HLJ soils  
228 (Table 3b,  $p < 0.05$ ). As shown in Table 4, N<sub>2</sub>O emissions had positive relationships with DEA both in SX and HLJ soils,  
229 and were affected positively by PNR in HN soil. Additionally, NO emissions had positive correlations with both PNR  
230 and DEA in SX soil. However, neither N<sub>2</sub>O nor NO emissions were influenced significantly by PNR and DEA in SD  
231 soils.


232 As is shown in Table 3c, the cumulative NH<sub>3</sub> emissions fluctuated greatly from 4.72–7.57 kg N ha<sup>-1</sup> across all the  
233 soils. Though significantly enhancing NH<sub>3</sub> emissions (Table 2), biochar amendments produced no significant influences  
234 on the NH<sub>3</sub> emissions relative to N treatment in most soils (Table 3c). A tendency was found for the cumulative NH<sub>3</sub>





235 emissions in N+Bm to be higher than those in the N+Bw treatment, although this difference was not remarkable within  
236 each soil. Additionally, stimulation effects were consistently present after the first fertilization event in each type of soil  
237 (Fig. 4).



### 238 3.4. Vegetable yield and gaseous N emissions intensity during the five-vegetable crop rotation

239 The vegetable yields for the five consecutive vegetable crops are presented in Table 3e. Pronounced differences  
240 existed among all soils (Table 2,  $p < 0.001$ ). Biochar amendments exerted no significant effects on vegetable yield (  
241 2). Compared with the N treatment, biochar amendments were prone to increase vegetable yield in SD and HLJ soils  
242 against HN and SX soils (Tables 3e), denoting pronounced interactions between soil and biochar (Table 2,  $p < 0.05$ ).  
243 Compared with Bm, Bw amendment lowered total yield over all the soils (Table 3e), significantly in HN and SD soils ( $p <$   
244 0.05).

245 Table 3f presents the GNI during the whole experiment period, with a pronounced variation among soils (Table 2,  $p$   
246  $< 0.001$ ). The GNI was greatly affected by biochar amendment during the whole experiment period (Table 2,  $p < 0.01$ ).  
247 Compared to N treatment, biochar amendments reduced the GNI by 4.3–27.8 % across all soils, significantly in SX and  
248 HLJ soils (Table 3f,  $p < 0.05$ ). Moreover, there were no remarkable differences between Bw and Bm throughout all soils.  
249

## 250 4. Discussion

### 251 4.1. Biochar effects on GNEs across different soil types

252 The effects of biochar amendment on the  $N_2O$  and NO emissions may be positive, negative or neutral, largely  
253 depending on the soil condition and the inherent characteristics of the biochar (Spokas and Reicosky, 2009; Nelissen et  
254 al., 2014). In our study, effects of two biochars on the  $N_2O$  and NO emissions did not follow a consensus trend across the  
255 four typical vegetable soils (Table 3a, b). In agreement with Cayuela et al. (2014), who reported that the role of biochar in  
256 mitigating  $N_2O$  emission was maximal in soils close to neutrality, remarkable mitigation effects were observed in SX and  
257 HLJ with the biochar amendments (Table 3a). These findings potentially resulted from the effects of the biochars on soil  
258 aeration, C/N ratio and pH, which affected the N dynamics and N cycling processes (Zhang et al., 2010; Ameloot et al.,  
259 2015). Moreover, mitigation of  $N_2O$  emissions induced by biochar was probably due to the decreased denitrification in  
260 SX and HLJ soils (Fig.1b and Table 4). In line with Obia et al. (2015), biochar decreased NO emissions in low-pH HN  
261 soil (Table 3b), probably by inducing denitrification enzymes with higher activity, and then resulted in less NO  
262 accumulation relative to  $N_2$  production. Moreover, the liming effects of biochar (  
263  $NO_2^-$  to NO (Islam et al., 2008), leaving only enzymatically produced NO to accumulate. However, neither  $N_2O$  nor NO  
264 emission was significantly influenced by PNR or DEA, suggesting other processes might play vital roles in  soil. In



265 addition, surplus N input in vegetable systems probably masked the beneficial effects of the biochar addition on the N  
266 transformation (Wang et al., 2015a). Therefore, the underlying mechanism of how biochar affect those processes needs to  
267 be illustrated in the further research.


268 On the other hand, different biochars may not produce universal influences on N<sub>2</sub>O emissions for the same soil due  
269 to the distinct properties of the biochar (Spokas and Reicosky, 2009). In the current study, overall, in comparison with  
270 Bm, the Bw amendment had more effective mitigation effects on N<sub>2</sub>O and NO emissions (Table 3a, b), largely due to the  
271 following reasons. First, compared with Bw, the contents of the TN and DOC in Bm were 1.8- and 1.4-fold (Table S1),  
272 respectively, which might supply extra N or C source for heterotrophic nitrification in the acidic HN soil, which made  
273 Bm ineffective for reducing the N<sub>2</sub>O emissions (Table 3a). This result was in accordance with Li et al. (2015a), who  
274 observed that biochar amendment had no significant influence on the cumulative N<sub>2</sub>O emissions, and even higher N<sub>2</sub>O  
275 emissions occurred when biochar was input. Additionally, as shown in Fig.1, Bm was more prone to stimulate PNR and  
276 DEA, thus displaying lower mitigation ability than Bw. Second, compared with Bm, the C/N ratio was approximately  
277 twofold in Bw (Table S1), presumably leading to more inorganic nitrogen being immobilized in biochar with a higher  
278 C/N ratio (Ameloot et al., 2015), decreasing the available N for microorganisms. Last, as presented in Fig. S3 and Table  
279 S1, Bw had more pores and surface area, having a better advantage over Bm in absorbing NO accordingly. Others have  
280 found that the lower mitigation capacity of high-N biochars (e.g., manures or biosolids) is probably due to the increased  
281 N release in the soil from the biochar (Schouten et al., 2012). To our knowledge, very few studies have investigated  
282 biochar effects on NO emissions (Nelissen et al., 2014; Obia et al., 2015), and the mechanisms through which biochar  
283 influence NO emissions are not elucidated yet. Therefore, more research is needed to clarify the underlying mechanisms  
284 of biochar on NO emission.

285 Intermixed managed soils receiving fertilizer such as urea or anhydrous NH<sub>3</sub> and ruminant urine patches are potential  
286 hot spots for NH<sub>3</sub> formation, where the use of biochar is expected to retain NH<sub>3</sub>-N in the soil system (Clough and  
287 Condon, 2010). Actually, the effects of biochar amendments on NH<sub>3</sub> volatilization largely depend on soil characteristics,  
288 biochar types and duration time. Soil texture is an important factor impacting NH<sub>3</sub> transfer and release. More clay  
289 contents were present in the SX soil (Table S1), which was limited in large soil pores, thus, the addition of porous  
290 biochar could enhance the soil aeration, promoting NH<sub>3</sub> volatilization (Sun et al., 2014). Additionally, it was worthy to  
291 note that cumulative NH<sub>3</sub> emissions were slightly higher in soils with the Bm than those with the Bw amendment (Fig. 4  
292 and Table 3c) and that difference could presumably be attributed to less surface area and the much higher pH of Bm (Fig.  
293 S3 and Table S1), resulting in weak adsorption and great liming effects. Overall, compared with previous studies (Ro et  
294 al., 2015; Mandal et al., 2016), no significant reductions were found in cumulative NH<sub>3</sub> volatilizations over the whole



295 observation period when biochar was added to current vegetable soils. In general, freshly produced biochar typically has  
296 very low ability to absorb ammonium (Yao et al., 2012). Over time, biochar surfaces are oxidized and increase adsorption  
297 (Wang et al., 2016). Moreover, the recorded increase in CEC by Cheng et al. (2006) indicated that biochars that are  
298 sufficiently weathered over a period would increase their ability to retain cations such as  $\text{NH}_4^+\text{-N}$ . Further, relatively  
299 long-term experiments are required to elucidate the mechanism and duration of effect.

#### 300 4.2. Biochar effects on vegetable yield and GNI across different soil types

301 The application of biochar is usually intended to increase crop yields, and evidence suggests this may be successful  
302 (Schulz et al., 2013; Li et al., 2016). Due to its liming effect, biochar helps to improve the supply of essential macro- and  
303 micronutrients for plant growth (Chan and Xu, 2009; Major et al., 2010). Enhancement of vegetable yield with biochar  
304 amendment occurred in SD and HLJ soils (Table 3e). However, no promotion of yield was observed with biochar  
305 amendments in HN and SX. This could be attributed to exacerbated soil salinity, which inhibited the uptake of nutrients  
306 and water (Ju et al., 2006; Zhou et al., 2010) and the growth of the soil microorganisms (Setia et al., 2011), leading to  
307 unsustainable greenhouse vegetable production. Compared with other biochar (Jia et al., 2012), the higher amounts of ash  
308 in Bw and Bm may contain high salts causing soil salinity (Hussain et al., 2016). After the addition of the two salt-rich  
309 biochars, the EC values of HN and SX vegetable soils increased and reached the limits to tolerance for the leafy  
310 vegetables (Shannon and Griev  1998).

311 Additionally, the mixed performance of biochars as an amendment is related to the wide diversity of  
312 physicochemical characteristics that translates into variable reactions in soil (Novak et al., 2014). First, compared to Bw,  
313 more DOC content was in the Bm (Table S1), through which more nutrients may be directly introduced to the soil  
314 (Rajkovich et al., 2012). In addition, besides their large amount of plant-available nutrients (Hass et al., 2012), manure  
315 biochars have been generally considered significant for improving soil fertility by promoting soil structure development  
316 (Joseph et al., 2010), with the result that Bm was found superior to Bw in vegetable production enhancement (Table 3e).  
317 As biochar effects on vegetable yield were variable, both biochar properties and soil conditions and crop species ought to  
318 be taken into account comprehensively before applying biochar to a certain soil condition.

319 Here, we assessed two feedstock-derived biochar effects on GNI in typical cultivated vegetable soils across  
320 mainland China. Overall, biochar amendments reduced GNI over all the soils, with the magnitude largely depending on  
321 soil type. Remarkable reduction in GNI had been detected due to the efficient mitigation induced by biochar in SX and  
322 HLJ (Table 3f). However, despite enhanced vegetable yield, no significant decreases in GNI were observed in SD,  
323 mainly because of the absence of mitigation effects on  $\text{N}_2\text{O}$ , NO and  $\text{NH}_3$  emissions of biochars (Table 3a, b and c)  
324 Additionally, mitigation efficacy on GNI were not notably different between Bw and Bm amendments across the four



325 soils, largely due to the divergent influences on GNE and yield that Bw was superior to Bm in mitigating the GNE while  
326 Bm performed better in vegetable yield (Table 3d and e). Furthermore, from our perspective, economic  
327 effectiveness/feasibility, such as the net ecosystem economic budget, should be considered synchronously in intensive  
328 vegetable production before large-scale biochar application.

329

### 330 **5. Conclusion**

331 The study demonstrated that biochar amendments generally reduced N<sub>2</sub>O and NO emissions without influencing the  
332 NH<sub>3</sub> emissions, while produced no consensus influences on yield though those effects were largely both biochar- and  
333 soil-specific. Additionally, biochar amendments did decrease GNI in intensive vegetable soils across mainland China.  
334 Furthermore, Bw was superior to Bm in mitigating the GNE whereas the Bm performed better in crop yield throughout  
335 all soils. Consequently, both soil type and biochar characteristics need to be seriously considered before large-scale  
336 biochar application under certain regions of intensive vegetable production.

337

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343 **References**

- 344 Ameloot, N., Sleutel, S., Das, K. C., Kanagaratnam, J., and Neve, S. D.: Biochar amendment to soils with contrasting  
345 organic matter level: effects on N mineralization and biological soil properties, *Global Change Biology Bioenergy*, 7,  
346 135–144, 2015.
- 347 Anderson, J. and Domsch, K.: A physiological method for the quantitative measurement of microbial biomass in soils,  
348 *Soil biology and biochemistry*, 10, 215–221, 1978.
- 349 Anenberg, S. C., Schwartz, J., Shindell, D., Amann, M., Faluvegi, G., Klimont, Z., Janssensmaenhout, G., Pozzoli, L.,  
350 Van, D. R., and Vignati, E.: Global Air Quality and Health Co-benefits of Mitigating Near-Term Climate Change  
351 through Methane and Black Carbon Emission Controls, *Environmental Health Perspectives*, 120, 831–839, 2012.
- 352 Avnery, S., Mauzerall, D. L., Liu, J., and Horowitz, L. W.: Global crop yield reductions due to surface ozone exposure: 1.  
353 Year 2000 crop production losses and economic damage, *Atmospheric Environment*, 45, 2284–2296, 2011.
- 354 Behera, S. N., Sharma, M., Aneja, V. P., and Balasubramanian, R.: Ammonia in the atmosphere: a review on emission  
355 sources, atmospheric chemistry and deposition on terrestrial bodies, *Environmental Science and Pollution Research*,  
356 20, 8092–8131, 2013.
- 357 Boyer, E. W., Goodale, C. L., Jaworski, N. A., and Howarth, R. W.: Anthropogenic nitrogen sources and relationships to  
358 riverine nitrogen export in the northeastern USA. In: *The Nitrogen Cycle at Regional to Global Scales*, Springer,  
359 2002.
- 360 Cayuela, M., Van Zwieten, L., Singh, B., Jeffery, S., Roig, A., and Sánchez-Monedero, M.: Biochar's role in mitigating  
361 soil nitrous oxide emissions: A review and meta-analysis, *Agriculture, Ecosystems & Environment*, 191, 5–16, 2014.
- 362 Chan, K. Y. and Xu, Z.: Biochar: nutrient properties and their enhancement, *Biochar for environmental management:*  
363 *science and technology*, 2009. 67–84, 2009.
- 364 Cheng, C.-H., Lehmann, J., Thies, J. E., Burton, S. D., and Engelhard, M. H.: Oxidation of black carbon by biotic and  
365 abiotic processes, *Organic Geochemistry*, 37, 1477–1488, 2006.
- 366 Ciais, P.: Carbon and other biogeochemical cycles: Final draft underlying scientific technical assessment, IPCC  
367 Secretariat, Geneva, 2013. 2013.
- 368 Clough, T. J. and Condon, L. M.: Biochar and the nitrogen cycle: introduction, *Journal of Environmental Quality*,  
369 39, 1218–1223, 2010.
- 370 Clough, T. J., Bertram, J. E., Ray, J. L., Condon, L. M., O'Callaghan, M., Sherlock, R. R., and Wells, N. S.: Unweathered  
371 Wood Biochar Impact on Nitrous Oxide Emissions from a Bovine-Urine-Amended Pasture Soil, *Soil Science*  
372 *Society of America Journal*, 74, 852–860, 2010.



- 373 Deng, J., Zhou, Z., Zheng, X., and Li, C.: Modeling impacts of fertilization alternatives on nitrous oxide and nitric oxide  
374 emissions from conventional vegetable fields in southeastern China, *Atmospheric Environment*, 81, 642–650, 2013.
- 375 Diao, T., Xie, L., Guo, L., Yan, H., Lin, M., Zhang, H., Lin, J., and Lin, E.: Measurements of N<sub>2</sub>O emissions from  
376 different vegetable fields on the North China Plain, *Atmospheric Environment*, 72, 70–76, 2013.
- 377 FAO, IIASA, ISRIC, and ISSCAS: Harmonized World Soil Database Version 1.2, 2012. 2012.
- 378 Field, J. L., Keske, C. M. H., Birch, G. L., Defoort, M. W., and Cotrufo, M. F.: Distributed biochar and bioenergy  
379 coproduction: a regionally specific case study of environmental benefits and economic impacts, *Global Change  
380 Biology Bioenergy*, 5, 177–191, 2013.
- 381 Food and Agriculture Organization (FAO) (2015) FAOSTAT (Food and Agriculture Organization Statistical Data)  
382 Statistical Yearbook Vol. 4. Available at: <http://faostat.fao.org> (accessed 12 August 2015)
- 383 Harrison, R. and Webb, J.: A review of the effect of N fertilizer type on gaseous emissions, *Advances in Agronomy*, 73,  
384 65–108, 2001.
- 385 Hass, A., Gonzalez, J. M., Lima, I. M., Godwin, H. W., Halvorson, J. J., and Boyer, D. G.: Chicken manure biochar as  
386 liming and nutrient source for acid Appalachian soil, *Journal of Environmental Quality*, 41, 1096–1106, 2012.
- 387 Hu, H. W., Macdonald, C. A., Trivedi, P., Anderson, I. C., Zheng, Y., Holmes, B., Bodrossy, L., Wang, J. T., He, J. Z., and  
388 Singh, B. K.: Effects of climate warming and elevated CO<sub>2</sub> on autotrophic nitrification and nitrifiers in dryland  
389 ecosystems, *Soil Biology & Biochemistry*, 92, 1–15, 2016.
- 390 Hussain, M., Farooq, M., Nawaz, A., Al-Sadi, A. M., Solaiman, Z. M., Alghamdi, S. S., Ammara, U., Yong, S. O., and  
391 Siddique, K. H. M.: Biochar for crop production: potential benefits and risks, *Journal of Soils & Sediments*, 2016.  
392 1–32, 2016.
- 393 IPCC, 2013. The Physical Science Basis: Working Group I Contribution to the Fifth Assessment Report of the  
394 Intergovernmental Panel on Climate Change. New York: Cambridge University Press 1, 535–531.
- 395 Islam, A., Chen, D., White, R. E., and Weatherley, A. J.: Chemical decomposition and fixation of nitrite in acidic pasture  
396 soils and implications for measurement of nitrification, *Soil Biology & Biochemistry*, 40, 262–265, 2008.
- 397 Jia, J., Li, B., Chen, Z., Xie, Z., and Xiong, Z.: Effects of biochar application on vegetable production and emissions of  
398 N<sub>2</sub>O and CH<sub>4</sub>, *Soil Science and Plant Nutrition*, 58, 503–509, 2012.
- 399 Joseph, S. D., Camparbestain, M., Lin, Y., Munroe, P., Chia, C. H., Hook, J., Van, Z. L., Kimber, S., Cowie, A., and  
400 Singh, B. P.: An investigation into the reactions of biochar in soil, *Australian Journal of Soil Research*, 48, 501–515,  
401 2010.
- 402 Ju, X. T., Kou, C. L., Zhang, F. S., and Christie, P.: Nitrogen balance and groundwater nitrate contamination: comparison



- 403 among three intensive cropping systems on the North China Plain, *Environmental Pollution*, 143, 117–125, 2006.
- 404 Kim, J. Y., Song, C. H., Ghim, Y. S., Won, J. G., Yoon, S. C., Carmichael, G. R., and Woo, J. H.: An investigation on  $\text{NH}_3$   
405 emissions and particulate  $\text{NH}_4^+ - \text{NO}_3^-$  formation in East Asia, *Atmospheric Environment*, 40, 2139–2150, 2006.
- 406 Kurola, J., Salkinoja-Salonen, M., Aarnio, T., Hultman, J., and Romantschuk, M.: Activity, diversity and population size  
407 of ammonia-oxidising bacteria in oil-contaminated landfarming soil, *FEMS Microbiology Letters*, 250, 33–38,  
408 2005.
- 409 Langridge, J. M., Lack, D., Brock, C. A., Bahreini, R., Middlebrook, A. M., Neuman, J. A., Nowak, J. B., Perring, A. E.,  
410 Schwarz, J. P., and Spackman, J. R.: Evolution of aerosol properties impacting visibility and direct climate forcing  
411 in an ammonia-rich urban environment, *Journal of Geophysical Research Atmospheres*, 117, 2240–2260, 2012.
- 412 Li, B., Bi, Z., and Xiong, Z.: Dynamic responses of nitrous oxide emission and nitrogen use efficiency to nitrogen and  
413 biochar amendment in an intensified vegetable field in southeastern China, *Global Change Biology Bioenergy*, 2016,  
414 2016.
- 415 Li, B., Fan, C. H., Xiong, Z. Q., Li, Q. L., and Zhang, M.: The combined effects of nitrification inhibitor and biochar  
416 incorporation on yield-scaled  $\text{N}_2\text{O}$  emissions from an intensively managed vegetable field in southeastern China,  
417 *Biogeosciences*, 12, 15185–15214, 2015a.
- 418 Li, B., Fan, C. H., Zhang, H., Chen, Z. Z., Sun, L. Y., and Xiong, Z. Q.: Combined effects of nitrogen fertilization and  
419 biochar on the net global warming potential, greenhouse gas intensity and net ecosystem economic budget in  
420 intensive vegetable agriculture in southeastern China, *Atmospheric Environment*, 100, 10–19, 2015b.
- 421 Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., Pan, G., and Paz-Ferreiro, J.: Biochar's effect on crop productivity  
422 and the dependence on experimental conditions—a meta-analysis of literature data, *Plant and Soil*, 373, 583–594,  
423 2013.
- 424 Lu, R.: *Methods of soil and agro-chemical analysis*, China Agricultural Science and Technology Press, Beijing, 2000.  
425 127–332, 2000. (in Chinese)
- 426 Major, J., Lehmann, J., Rondon, M., and Goodale, C.: Fate of soil-applied black carbon: downward migration, leaching  
427 and soil respiration, *Global Change Biology*, 16, 1366–1379, 2010.
- 428 Mandal, S., Thangarajan, R., Bolan, N. S., Sarkar, B., Khan, N., Ok, Y. S., and Naidu, R.: Biochar-induced concomitant  
429 decrease in ammonia volatilization and increase in nitrogen use efficiency by wheat, *Chemosphere*, 142, 120–127,  
430 2016.
- 431 Mei, B. L., Zheng, X. H., Xie, B. H., Dong, H. B., Zhou, Z. X., Rui, W., Jia, D., Feng, C., Tong, H. J., and Zhu, J. G.:  
432 Nitric oxide emissions from conventional vegetable fields in southeastern China, *Atmospheric Environment*, 43,





- 433 2762–2769, 2009.
- 434 Misselbrook, T. H., Weerden, T. J. V. D., Pain, B. F., Jarvis, S. C., Chambers, B. J., Smith, K. A., Phillips, V. R., and  
435 Demmers, T. G. M.: Ammonia emission factors for UK agriculture, *Atmospheric Environment*, 34, 871–880(810),  
436 2000.
- 437 Mukherjee, A. and Zimmerman, A. R.: Organic carbon and nutrient release from a range of laboratory-produced biochars  
438 and biochar–soil mixtures, *Geoderma*, s 193–194, 122–130, 2013.
- 439 Nelissen, V.: Effect of different biochar and fertilizer types on N<sub>2</sub>O and NO emissions, *Soil Biology & Biochemistry*, 70,  
440 244–255, 2014.
- 441 Novak, J. M., Spokas, K. A., Cantrell, K. B., Ro, K. S., Watts, D. W., Glaz, B., Busscher, W. J., and Hunt, P. G.: Effects  
442 of biochars and hydrochars produced from lignocellulosic and animal manure on fertility of a Mollisol and Entisol,  
443 *Soil Use and Management*, 30, 175–181, 2014.
- 444 Obia, A., Cornelissen, G., Mulder, J., and Dörsch, P.: Effect of Soil pH Increase by Biochar on NO, N<sub>2</sub>O and N<sub>2</sub>  
445 Production during Denitrification in Acid Soils, *Plos One*, 10, 359–367, 2015.
- 446 Pacholski, A., Cai, G. X., Fan, X. H., Ding, H., Chen, D., Nieder, R., and Roelcke, M.: Comparison of different methods  
447 for the measurement of ammonia volatilization after urea application in Henan Province, China, *Journal of Plant  
448 Nutrition and Soil Science*, 171, 361–369, 2008.
- 449 Pinder, R. W., Adams, P. J., and Pandis, S. N.: Ammonia emission controls as a cost-effective strategy for reducing  
450 atmospheric particulate matter in the Eastern United States, *Environmental Science & Technology*, 41, 380–386,  
451 2007.
- 452 Powlson, D. S., Addiscott, T. M., Benjamin, N., Cassman, K. G., de Kok, T. M., Van, G. H., L'Hirondel, J. L., Avery, A.  
453 A., and Van, K. C.: When does nitrate become a risk for humans?, *Journal of Environmental Quality*, 37, 291–295,  
454 2008.
- 455 Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A. R., and Lehmann, J.: Corn growth and nitrogen  
456 nutrition after additions of biochars with varying properties to a temperate soil, *Biology & Fertility of Soils*, 48,  
457 271–284, 2012.
- 458 Ravishankara, A. R., Daniel, J. S., and Portmann, R. W.: Nitrous oxide (N<sub>2</sub>O): the dominant ozone-depleting substance  
459 emitted in the 21st century, *Science*, 326, 123–125, 2009.
- 460 Ro, K. S., Lima, I. M., Reddy, G. B., Jackson, M. A., and Gao, B.: Removing Gaseous NH<sub>3</sub> Using Biochar as an  
461 Adsorbent, *Agriculture*, 5, 991–1002, 2015.
- 462 Saarnio, S., Heimonen, K., and Kettunen, R.: Biochar addition indirectly affects N<sub>2</sub>O emissions via soil moisture and



- 463 plant N uptake, *Soil Biology & Biochemistry*, 58, 99–106, 2013.
- 464 Schouten, S., Groenigen, J. W. V., Oenema, O., and Cayuela, M. L.: Bioenergy from cattle manure? Implications of  
465 anaerobic digestion and subsequent pyrolysis for carbon and nitrogen dynamics in soil, *Global Change Biology*  
466 *Bioenergy*, 4, 751–760, 2012.
- 467 Schulz, H., Dunst, G., and Glaser, B.: Positive effects of composted biochar on plant growth and soil fertility, *Agronomy*  
468 *for Sustainable Development*, 33, 817–827, 2013.
- 469 Setia, R., Marschner, P., Baldock, J., Chittleborough, D., and Verma, V.: Relationships between carbon dioxide emission  
470 and soil properties in salt-affected landscapes, *Soil Biology & Biochemistry*, 43, 667–674, 2011.
- 471 Shannon, M. C. and Grieve, C. M.: Tolerance of vegetable crops to salinity, *Scientia Horticulturae*, 78, 5–38, 1998.
- 472 Smith, M. S. and Tiedje, J. M.: Phases of denitrification following oxygen depletion in soil, *Soil Biology & Biochemistry*,  
473 11, 261–267, 1979.
- 474 Smith, P.: Soil carbon sequestration and biochar as negative emission technologies, *Global Change Biology*, 51, 574–575,  
475 2016.
- 476 Sohi, S. P.: Agriculture. Carbon storage with benefits, *Science*, 338, 1034–1035, 2012.
- 477 Sororzano, L.: Determination of ammonia in natural waters by the phenolhypochlorite method, *Limnol. Oceanogr*, 14,  
478 799–801, 1969.
- 479 Spokas, K. A. and Reicosky, D. C.: Impacts of sixteen different biochars on soil greenhouse gas production, *Ann.*  
480 *Environ. Sci*, 3, 4, 2009.
- 481 Stavi, I. and Lal, R.: Agroforestry and biochar to offset climate change: a review, *Agronomy for Sustainable*  
482 *Development*, 33, 81–96, 2013.
- 483 Sun, L., Li, L., Chen, Z., Wang, J., and Xiong, Z.: Combined effects of nitrogen deposition and biochar application on  
484 emissions of N<sub>2</sub>O, CO<sub>2</sub> and NH<sub>3</sub> from agricultural and forest soils, *Soil science and plant nutrition*, 60, 254–265,  
485 2014.
- 486 Ussiri, D. and Lal, R.: *The Role of Nitrous Oxide on Climate Change*, Springer Netherlands, 2013.
- 487 Wang, B., Lehmann, J., Hanley, K., Hestrin, R., and Enders, A.: Ammonium retention by oxidized biochars produced at  
488 different pyrolysis temperatures and residence times, *Rsc Advances*, 6, 41907–41913, 2016.
- 489 Wang, J., Chen, Z., Ma, Y., Sun, L., Xiong, Z., Huang, Q., and Sheng, Q.: Methane and nitrous oxide emissions as  
490 affected by organic–inorganic mixed fertilizer from a rice paddy in southeast China, *Journal of Soils and Sediments*,  
491 13, 1408–1417, 2013.
- 492 Wang, J., Chen, Z., Xiong, Z., Chen, C., Xu, X., Zhou, Q., and Kuzyakov, Y.: Effects of biochar amendment on



- 493 greenhouse gas emissions, net ecosystem carbon budget and properties of an acidic soil under intensive vegetable  
494 production, *Soil Use and Management*, 31, 375–383, 2015a.
- 495 Wang, S., Nan, J., Shi, C., Fu, Q., Gao, S., Wang, D., Cui, H., Saizlopez, A., and Zhou, B.: Atmospheric ammonia and its  
496 impacts on regional air quality over the megacity of Shanghai, China, *Scientific Reports*, 5, 2015b.
- 497 Xiong, Z., Xie, Y., Xing, G., Zhu, Z., and Butenhoff, C.: Measurements of nitrous oxide emissions from vegetable  
498 production in China, *Atmospheric Environment*, 40, 2225–2234, 2006.
- 499 Yao, Y., Gao, B., Zhang, M., Inyang, M., and Zimmerman, A. R.: Effect of biochar amendment on sorption and leaching  
500 of nitrate, ammonium, and phosphate in a sandy soil, *Chemosphere*, 89, 1467–1471, 2012.
- 501 Yao, Z., Zheng, X., Xie, B., Mei, B., Wang, R., Klaus, B. B., Zhu, J., and Yin, R.: Tillage and crop residue management  
502 significantly affects N-trace gas emissions during the non-rice season of a subtropical rice-wheat rotation, *Soil  
503 Biology & Biochemistry*, 41, 2131–2140, 2009.
- 504 Zhang, A., Cui, L., Pan, G., Li, L., Hussain, Q., Zhang, X., Zheng, J., and Crowley, D.: Effect of biochar amendment on  
505 yield and methane and nitrous oxide emissions from a rice paddy from Tai Lake plain, China, *Agriculture  
506 Ecosystems & Environment*, 139, 469–475, 2010.
- 507 Zhang, F., Chen, X., and Vitousek, P.: Chinese agriculture: An experiment for the world, *Nature*, 497, 33–35, 2013.
- 508 Zhang, M., Fan, C. H., Li, Q. L., Li, B., Zhu, Y. Y., and Xiong, Z. Q.: A 2-yr field assessment of the effects of chemical  
509 and biological nitrification inhibitors on nitrous oxide emissions and nitrogen use efficiency in an intensively  
510 managed vegetable cropping system, *Agriculture Ecosystems & Environment*, 201, 43–50, 2015.
- 511 Zhang, Y., Luan, S., Chen, L., and Shao, M.: Estimating the volatilization of ammonia from synthetic nitrogenous  
512 fertilizers used in China, *Journal of Environmental Management*, 92, 480–493, 2011.
- 513 Zhao, L. M., Wu, L. H., Dong, C. J., and Li, Y. S.: Rice yield, nitrogen utilization and ammonia volatilization as  
514 influenced by modified rice cultivation at varying nitrogen rates, *Agricultural Sciences*, 01, 10–16, 2010.
- 515 Zhao, X., Wang, J., Wang, S., and Xing, G.: Successive straw biochar application as a strategy to sequester carbon and  
516 improve fertility: A pot experiment with two rice/wheat rotations in paddy soil, *Plant and Soil*, 378, 279–294, 2014.
- 517 Zheng, X., Mei, B., Wang, Y., Xie, B., Wang, Y., Dong, H., Xu, H., Chen, G., Cai, Z., and Yue, J.: Quantification of N<sub>2</sub>O  
518 fluxes from soil–plant systems may be biased by the applied gas chromatograph methodology, *Plant and Soil*, 311,  
519 211–234, 2008.
- 520 Zhou, J. B., Chen, Z. J., Liu, X. J., Zhai, B. N., and Powlson, D. S.: Nitrate accumulation in soil profiles under  
521 seasonally open ‘sunlight greenhouses’ in northwest China and potential for leaching loss during summer  
522 fallow, *Soil Use and Management*, 26, 332–339, 2010.

523 **Table legends**524 **Table 1**

525 Soil organic carbon (SOC), soil total nitrogen (TN), soil pH, electric conductivity (EC) and microbial biomass carbon  
 526 (MBC) as affected by different treatments across the four vegetable soils.

Soil	Treatment	SOC (g kg <sup>-1</sup> )	TN (g kg <sup>-1</sup> )	pH	EC (ds m <sup>-1</sup> )	MBC (mg kg <sup>-1</sup> )
HN	N	8.0±0.8c	1.37±0.12b	4.37±0.04c	1.76±0.21b	1353±119a
	N+Bw	15.6±0.5b	1.47±0.07b	4.64±0.04b	2.43±0.31a	1173±49b
	N+Bm	18.8±0.6a	1.64±0.04a	5.01±0.03a	2.00±0.32ab	1234±50ab
SX	N	9.7±0.7c	1.55±0.04b	7.53±0.02b	1.74±0.27b	490±9a
	N+Bw	15.6±0.8b	1.62±0.06b	7.61±0.05a	2.25±0.22a	495±16a
	N+Bm	17.5±1.1a	1.79±0.03a	7.63±0.01a	1.96±0.06ab	504±18a
SD	N	7.9±0.1b	1.13±0.04b	7.70±0.08a	0.85±0.03b	535±13b
	N+Bw	14.2±0.6a	1.20±0.04b	7.66±0.03a	0.92±0.04a	554±10ab
	N+Bm	15.5±1.4a	1.37±0.06a	7.71±0.03a	0.87±0.02ab	573±12a
HLJ	N	29.9±0.5b	2.19±0.04b	6.91±0.05a	0.83±0.03b	921±44b
	N+Bw	36.0±1.5a	2.20±0.03b	6.92±0.06a	0.95±0.03a	988±56b
	N+Bm	38.1±1.8a	2.41±0.01a	6.94±0.04a	0.92±0.06a	1242±196a
ANOVA results						
Biochar		***	***	***	***	*
Soil		***	***	***	***	***
Biochar×Soil		*	n.s.	***	n.s.	**

527 Data shown are means ± standard deviations of three replicates. See Fig. 1 for treatments codes. Different letters within


528 the same column indicate significant differences among treatments within the same soil at  $p < 0.05$  level.

529 \*\*\*Significant at  $p < 0.001$ ; \*\*significant at  $p < 0.01$ ; \*significant at  $p < 0.05$ ; n.s. not significant.



530 **Table 2**

531 Two-way ANOVA and mean effects of biochar (Bc) and soil (S) types on cumulative gaseous nitrogen (N<sub>2</sub>O, NO and NH<sub>3</sub>) emissions, gaseous nitrogen emission (GNE),  
 532 vegetable yield and gaseous nitrogen intensity (GNI) during the entire sampling period.

Factors	DF	N <sub>2</sub> O emission			NO emission			NH <sub>3</sub> emission			GNE			Vegetable yield			GNI		
		SS	F	P	SS	F	P	SS	F	P	SS	F	P	SS	F	P	SS	F	P
Bc	2	271.9	65.1	***	46.4	174.7	***	0.5	0.8	n.s.	380.5	86.4	***	76.2	3.2	n.s.	0.1	7.9	**
S	3	1429.9	228.1	***	152.2	382.1	***	4.1	3.8	*	2322.6	351.5	***	4316.9	123.3	***	2.3	110.3	***
Bc×S	6	179.3	14.3	***	33.4	41.9	***	1.4	0.7	n.s.	234.5	17.7	***	230.4	3.3	*	0.1	1.6	n.s.
Model	11	4009.7	174.5	***	225.3	154.3	***	29.1	7.5	***	5290	218.3	***	15962.0	124.4	***	5.8	77.0	***
Error	24	50.1			3.2			8.5			52.9			280.0					
biochar effect (  )																			
N mean			12.01±1.44a			2.86±0.24a			5.92±0.24b			43.81±1.25b			20.50±1.60a				0.49±0.05a
N+Bw mean			7.01±0.58b			1.55±0.14b			6.65±0.27a			43.53±1.67b			14.84b				0.49±0.04b
N+Bm mean			10.37±0.56a			1.55±0.10b			7.01±0.25a			49.53±1.11a			18.60±0.65a				0.49±0.03ab
Soil effect (n = 9)																			
HN mean			27.20±1.85a			5.80±0.50a			5.31±0.16c			33.06±1.65c			38.04±1.90a				1.15±0.11a
SX mean			4.89±0.45b			1.08±0.13b			12.69±0.46a			25.05±1.11d			12.69±0.46b				0.51±0.01b
SD mean			2.25±0.26c			0.25±0.09c			9.51±0.55b			44.88±0.49b			9.51±0.55c				0.21±0.01c
HLLJ mean			4.48±0.68b			0.81±0.04b			11.79±0.71a			79.50±2.41a			11.79±0.71b				0.15±0.01c

533 SS: the sum of squares.

534 F value: the ratio of mean squares of two independents samples.

535 P value: the index of differences between the control group and the experimental group. \*, \*\* and \*\*\* indicate significance at  $p < 0.05$ ,  $p < 0.01$  and  $p < 0.001$ , respectively.

536 n.s.: not significant.

537 Data shown are means ± standard deviations of the nine replicates. See Fig. 1 for treatments codes. Different letters within the same column indicate significant differences

538 among treatments at  $p < 0.05$  level.

539 **Table 3**

540 Cumulative gaseous nitrogen (N<sub>2</sub>O, NO and NH<sub>3</sub>) emissions, gaseous nitrogen emission (GNE), vegetable yield and  
 541 gaseous nitrogen intensity (GNI) under the different treatments across the four soils.

Treatments	HN	SX	SD	HLJ
<b>(a) Cumulative N<sub>2</sub>O emissions (kg N ha<sup>-1</sup>)</b>				
N	30.59±3.15a	7.83±0.60a	2.52±0.37a	7.10±1.91a
N+Bw	19.45±2.43b	3.20±0.28b	1.97±0.21a	3.45±0.86b
N+Bm	31.56±1.35a	3.63±0.62b	2.26±0.58a	4.01±0.68b
<b>(b) Cumulative NO emissions (kg N ha<sup>-1</sup>)</b>				
N	8.99±1.01a	1.27±0.15a	0.20±0.08a	0.97±0.11a
N+Bw	4.54±0.60b	0.80±0.13b	0.33±0.19a	0.52±0.03b
N+Bm	3.87±0.30b	1.16±0.17a	0.21±0.10a	0.94±0.03a
<b>(c) Cumulative NH<sub>3</sub> emissions (kg N ha<sup>-1</sup>)</b>				
N	4.72±0.27a	5.79±0.54b	6.34±0.51a	5.67±0.42a
N+Bw	5.09±0.38a	6.83±0.74ab	7.35±0.75a	6.24±0.49a
N+Bm	5.32±0.42a	7.57±0.57a	7.37±1.11a	6.48±0.43a
<b>(d) GNE (kg N ha<sup>-1</sup>)</b>				
N	44.30±3.13a	14.89±1.33a	9.06±0.80a	13.74±1.67a
N+Bw	29.08±2.21b	10.82±1.14b	9.64±0.88a	10.21±0.92b
N+Bm	40.76±1.66a	12.36±0.74b	9.84±0.49a	11.42±0.27b
<b>(e) Vegetable yield (t ha<sup>-1</sup>)</b>				
N	35.20±2.52a	25.29±3.90a	39.09±2.03b	75.65±5.84b
N+Bw	29.05±2.35b	23.57±1.74a	44.53±3.74b	76.95±4.04ab
N+Bm	34.93±2.87a	26.30±2.63a	51.00±3.18a	85.89±3.29a
<b>(f) GNI (kg N t<sup>-1</sup> yield)</b>				
N	1.27±0.18a	0.59±0.08a	0.23±0.02a	0.18±0.04a
N+Bw	1.01±0.12a	0.46±0.05b	0.22±0.04a	0.13±0.02b
N+Bm	1.17±0.15a	0.47±0.04b	0.19±0.01a	0.13±0.01b

542 Data shown are means ± standard deviations of the three replicates. See Fig. 1 for treatments codes. Different letters

543 within the same column indicate significant differences among treatments within the same soil at  $p < 0.05$  level.



**Table 4**

The correlations between N<sub>2</sub>O or NO emission and PNR or DEA in each soil.

Item	HN		SX		SD		HLJ	
	PNR	DEA	PNR	DEA	PNR	DEA	PNR	DEA
N <sub>2</sub> O	0.75*	0.66	0.49	0.76*	-0.10	0.16	-0.82**	0.70*
NO	0.62	-0.29	0.79*	0.69*	-0.54	0.01	-0.63	0.22

Asterisks indicated 0.05 level significances (\* $p < 0.05$ ) and 0.01 level significances (\*\* $p < 0.01$ ),  $n = 9$ .





### Figure legends

**Fig. 1** Potential nitrification rate (PNR) and Denitrification enzyme activity (DEA) under different treatments in HN, SX, SD and HLJ soils. The three treatments with each soil were urea without biochar (N), urea with wheat straw biochar (N+Bw) and urea with swine manure biochar (N+Bm). Bars indicate standard deviation (mean + SD,  $n = 3$ ). Different letters above the bars indicate significant differences among the different treatments within the same soil, at  $p < 0.05$ .

**Fig. 2** Temporal dynamics of soil  $N_2O$  ( $\mu\text{g N m}^{-2}\text{h}^{-1} \pm \text{SD}$ ,  $n = 3$ ) fluxes under different treatments in HN (a), SX (b), SD (c) and HLJ (d) vegetable soils with five consecutive vegetable crops. The solid arrows indicate fertilization. See Fig. 1 for treatments codes.

**Fig. 3** Temporal dynamics of soil  $NO$  ( $\mu\text{g N m}^{-2}\text{h}^{-1} \pm \text{SD}$ ,  $n = 3$ ) fluxes under different treatments in HN (a), SX (b), SD (c) and HLJ (d) vegetable soils with five consecutive vegetable crops. The solid arrows indicate fertilization. See Fig. 1 for treatments codes.

**Fig. 4** Cumulative ammonia ( $NH_3$ ) emissions from the HN (a), SX (b), SD (c) and HLJ (d) soils during the four nitrogen fertilization events F: every N fertilization event. The bars indicate the standard deviation of the mean ( $\text{kg N ha}^{-1} \pm \text{SD}$ ,  $n = 3$ ) of each treatment for the sum of the four N fertilization events. See Fig. 1 for treatments codes. Different letters above the bars indicate significant differences among the different treatments for each soil, at  $p < 0.05$ .

