

1 **Biochar can decrease the gaseous reactive nitrogen intensity in**
2 **intensive vegetable soils across mainland China**

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1 **Highlights**

- 2 1. Two contrasting biochars affected GNrI across 4 major vegetable soils in China.
- 3 2. Biochar affects gaseous Nr or yield largely depending on soil types.
- 4 3. Both biochars decreased GNrI with Bw mitigated gaseous Nr whereas Bm improved yield.

1 **Abstract**

2 Biochar amendment to soil has been proposed as a strategy for sequestering carbon, mitigating climate change and
3 enhancing crop productivity, but few studies have demonstrated the general effects of different feedstock-derived
4 biochars on the various gaseous reactive nitrogen emissions (GNrEs, N₂O, NO and NH₃) simultaneously across the
5 typical vegetable soils in China. A greenhouse pot experiment with five consecutive vegetable crops was conducted to
6 investigate the effects of two contrasting biochar, namely, wheat straw biochar (Bw) and swine manure biochar (Bm) on
7 GNrEs, vegetable yield and gaseous reactive nitrogen intensity (GNrI) in four typical vegetable soils from Acrisol
8 (Hunan province), Anthrosol (Shanxi province), Cambisol (Shandong province) and Phaeozem (Heilongjiang province)
9 which are representative of the intensive vegetable ecosystems across mainland China. Results showed that remarkable
10 GNrE mitigation induced by biochar occurred in Anthrosol and Phaeozem, whereas enhancement of yield occurred
11 in Cambisol and Phaeozem. Additionally, both biochars decreased GNrI with Bw performed better than Bm regarding
12 N₂O mitigation, with Bw mitigating N₂O and NO emissions by 21.8–59.1 % and 37.0–49.5 % (except for Cambisol),
13 respectively, while Bm improved yield by 13.5–30.5 % (except for Acrisol and Anthrosol). Biochar amendments
14 generally stimulated the NH₃ emissions with greater enhancement from Bw than Bm. We can infer that the biochar's
15 effects on the GNrEs and vegetable yield strongly depend on the attributes of the soil and biochar. Therefore, both soil
16 type and biochar characteristics should be seriously considered before conducting large-scale application of biochar in
17 order to achieve the maximum benefits under intensive greenhouse vegetable agriculture.

18 **Keyword:** Biochar, Intensive vegetable soil, Gaseous reactive nitrogen emissions (GNrEs), Gaseous reactive
19 nitrogen intensity (GNrI)

1 **1 Introduction**

2 Agriculture accounts for an estimated emission of 4.1 (1.7–4.8) Tg N yr⁻¹ for N₂O and 3.7 Tg N yr⁻¹ for NO,
3 contributing 60 % and 10 %, respectively, to the total global anthropogenic emissions, largely due to increases of N
4 fertilizer application in cropland (Ciais, 2013). The concentration of atmospheric N₂O, a powerful, long-lived,
5 greenhouse gas, has increased from 270 parts per billion by volume (ppbv) in the pre-industrial era to ~ 324 ppbv (Ussiri
6 and Lal, 2013); it has 265 times the global warming potential (GWP) of CO₂ on a 100-year horizon (IPCC, 2013) and
7 also causes depletion of the ozone layer in the atmosphere (Ravishankara et al., 2009). In contrast, NO_x, which is mainly
8 emitted as nitric oxide (NO), does not directly affect the earth's radiative balance but catalyzes the production of
9 tropospheric ozone (O₃), which is a greenhouse gas associated with detrimental effects on human health (Anenberg et al.,
10 2012) and crop production (Avnery et al., 2011). Additionally, along with the high nitrogen (N) application, ammonia
11 volatilization is one of the major N loss pathways (Harrison and Webb, 2001) as well, with up to 90% coming from
12 agricultural activities (Misselbrook et al., 2000; Boyer et al., 2002). As a natural component and a dominant atmospheric
13 alkaline gas, NH₃ plays an important role in atmospheric chemistry and ambient aerosol formation (Langridge et al.,
14 2012; Wang et al., 2015b). In addition to nutrient enrichment (eutrophication) of terrestrial and aquatic systems and
15 global acidification of precipitation, NH₃ has also been shown to be a major factor in the formation of atmospheric
16 particulate matter and secondary aerosols (Kim et al., 2006; Pinder et al., 2007), leading to potentially adverse effects on
17 human and ecosystem health such as visibility degradation and threats to biodiversity (Powelson et al., 2008; Behera et al.,
18 2013). Consequently, the release of various reactive N species results in lower N use efficiency in agricultural systems.

19 In China, vegetable production devotes an area of approximately 24.7×10^6 ha, equivalent to 12.4% of the total
20 available cropping area, and the production represented 52 % of the world vegetable production in 2012 (FAO, 2015).
21 Intensified vegetable cultivation in China is characterized by high N application rates, high cropping index and frequent
22 farm practices. Annual nitrogen fertilizer inputs for intensively managed vegetable cultivation in rapidly developing areas
23 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
24 result, great concern exists about excess N fertilizer application, leading to low use efficiency in intensive vegetable
25 fields in China (Deng et al., 2013; Diao et al., 2013). Meanwhile, intensive vegetable agriculture is considered to be an
26 important source of N₂O (Xiong et al., 2006; Jia et al., 2012; Li et al., 2015b; Zhang et al., 2015) and NO production
27 (Mei et al., 2009). Moreover, ammonia volatilization is another important N pathway in fertilized soil, resulting in large
28 losses of soil-plant N (Pacholski et al., 2008; Zhang et al., 2011). Therefore, the reduction of reactive N loss becomes a
29 central environmental challenge to meet the joint challenges of high production and acceptable environmental
30 consequences in intensive vegetable production (Zhang et al., 2013).

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

16 Therefore, a greenhouse pot experiment was conducted in an effort to investigate the effects of different types of
17 biochar on gaseous reactive nitrogen emissions (GNrEs), namely, N_2O , NO and NH_3 , simultaneously in four typical
18 intensified vegetable soils across main vegetable production areas of mainland China. We hypothesized that: 1) biochar
19 amendment could affect GNrEs, vegetable yield and GNrI in vegetable soils across mainland China, 2) those influences
20 would vary among biochar and soil types. Overall, the objectives of this research were to gain a comprehensive insight
21 into the effects of the different types of biochar on the GNrEs, vegetable yield and gaseous reactive nitrogen intensity
22 (GNrI) in intensively managed vegetable production in China.

1 **2 Materials and methods**

2 *2.1. Experimental soil and biochar*

3 Four typical greenhouse vegetable cultivation sites with a long history (more than 10 years) of conventional
4 cultivation were selected from Northeast, Northwest, Central and Eastern China (Fig. S1), namely, Phaeozem, Anthrosol,
5 Acrisol and Cambisol (FAO and ISRIC, 2012). Those four types of vegetable soil were collected from: (1) Jiamusi
6 (46°48' N, 130°12' E), Heilongjiang province; (2) Yangling (34°18' N, 108°2' E), Shanxi province; (3) Changsha
7 (28°32' N, 113°23' E), Hunan province and (4) Shouguang (36°56' N, 118°38' E), Shandong province, respectively,
8 which represented a range of differences in physicochemical properties and regions (Table S1). Soil samples were
9 manually collected from the cultivated layer (0–20 cm) after the local vegetable harvest in April, 2015. The samples were
10 air-dried and passed through a 5 mm stainless steel mesh sieve and homogenized thoroughly. Any visible roots and
11 organic residues were removed manually before being packed with the necessary amount of soil to achieve the initial
12 field bulk density. Each pot received 15 kg of 105 °C dry-weight-equivalent fresh soil. For each of the biochar
13 amendment pot, 282.6 g pot⁻¹ sieved biochar (2 mm) was mixed with the soil thoroughly before the experiment, which
14 was equivalent to a 40 t ha⁻¹ biochar dose (dry weight). No more biochar was added later in the experimental period.

15 Two types of biochar, derived from two common agricultural wastes in China were used: wheat straw and swine
16 manure, hereafter referred to as Bw and Bm, respectively (Table S1). The Bw was produced at the Sanli New Energy
17 Company in Henan, China, by pyrolysis and thermal decomposition at 400–500 °C. The Bm was produced through
18 thermal decomposition at 400 °C by the State Key Laboratory of Soil Science and Sustainable Agricultural, Institute of
19 Soil Science, Chinese Academy of Sciences. In accordance with Lu (2000), the SOC was measured by wet digestion with
20 H₂SO₄–K₂Cr₂O₇, TN was determined by semi-micro Kjeldahl digestion, and soil texture was determined with the pipette
21 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
22 PHS-3C mv/pH detector (Shanghai Kangyi Inc. China). Biochar content of hydrogen (H) was measured by elemental
23 analysis after dry combustion (Euro EA, Hekatech GmbH, Wegberg, Germany). The oxygen content of biochar was
24 measured with the same device after pyrolysis of the sample at 1000 °C followed by reduction of the evolved O₂ to CO
25 and quantification by GC-TCD. The soil NO₃⁻-N and NH₄⁺-N were measured following the two-wavelength ultraviolet
26 spectrometry and indophenol blue methods, respectively, using an ultraviolet spectrophotometer (HITACHI, UV-2900,
27 Tokyo, Japan). Electric conductivity (EC) was measured by using a Mettler-Toledo instrument (FE30-K, Shanghai, China)
28 at a 1:5 (w:v) soil to water ratio. Cation exchange capacity (CEC) was determined using the CH₃COONH₄ method.
29 Dissolved organic carbon (DOC) was extracted from 5 g of the biochar/soil with an addition of 50 ml deionized water
30 and measured by a TOC analyzer (TOC-2000/3000, Metash Instruments Co., LTD, Shanghai, China). Ash content was

1 measured by heating the biochars at 750 °C for 4 h. The specific surface area of the biochar material was tested using the
2 Brunauer–Emmett–Teller (BET) method, from which the N adsorption–desorption isotherms at 77 K were measured by
3 an automated gas adsorption analyzer ASAP2000 (Micromeritics, Norcross, GA) with + 5% accuracy. Scanning electron
4 microscopy (SEM) imaging analysis was conducted using a HITACHI S-3000N scanning electron microscope.

5 2.2. *Experimental set-up and management*

6 The pot experiments were performed at the greenhouse experimental station of Nanjing Agricultural University,
7 China. Five vegetable crops were grown successively in the four vegetable soils during the experimental period. For each
8 type of soil, three treatments with three replicates were arranged in a random design: urea without biochar (N), urea with
9 wheat straw biochar (N+Bw), urea with swine manure biochar (N+Bm). In addition, phosphate and potassium fertilizers
10 in the form of calcium magnesium phosphate and potassium chloride, together with urea, were broadcasted and mixed
11 with soil thoroughly prior to sowing the vegetables. No topdressing events occurred because of the frequent cultivation
12 and short growth period for the leafy vegetables. Based on the vegetable growth, all pots received equal amounts of water
13 and no precipitation. Detailed information on the pot management practices is provided in Table S2.

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

18 2.3. *Measurement of N₂O, NO and NH₃*

19 The NO and N₂O fluxes were measured simultaneously from each vegetable cultivation using a static opaque
20 chamber method (Zheng et al., 2008; Yao et al., 2009). A square PVC chamber of 35 cm × 35 cm × 40 cm (length ×
21 width × height) was temporarily mounted on the pot for gas flux measurement. The chamber was coated with sponge and
22 aluminum foil outside to prevent solar radiation heating the chamber. Gas samples for flux measurements were collected
23 between 8 and 10 a.m. on each measuring day to minimize the influence of diurnal temperature variation. Gas fluxes
24 were usually measured once a week and every other day for one week following fertilizer application. To measure the
25 N₂O flux, four samples were collected from the headspace chamber using 20 ml polypropylene syringes at 0, 10, 20, and
26 30 min after chamber closure. The gas concentrations in the samples were analyzed within 12 h after sampling using an
27 Agilent 7890A gas chromatograph equipped with an electron capture detector (ECD) for N₂O detection. The carrier gas
28 was argon-methane (50 %) at a flow rate of 40 ml min⁻¹. The column and ECD temperatures were maintained at 40 and
29 300 °C, respectively. The gas chromatography configurations described by Wang et al. (2013) were adopted for the gas
30 concentration analysis. N₂O flux was calculated using the linear increases in gas concentration with time. Sample sets

1 were rejected unless they yielded a linear regression value of $R^2 > 0.90$.

2 For each NO flux measurement, gas samples were collected from the same chamber that was used for the N₂O flux
3 measurements (Yao et al., 2009). Before closing the chamber, an approximately 1.0 L gas sample from the headspace of
4 each chamber was extracted into an evacuated sampling bag (Delin Gas Packing Co., LTD, Dalian, China), and this
5 measurement was regarded as time 0 min for NO analysis. After 30 min under chamber enclosure conditions (i.e., after
6 the N₂O sample collections were completed), another headspace gas sample with the same volume was extracted from
7 each chamber into another evacuated bag. Within 1 h after sampling, NO concentrations were analyzed by a model 42i
8 chemiluminescence NO–NO–NO_x analyzer (Thermo Environmental Instruments Inc., Franklin, MA, USA). The NO
9 fluxes were derived from the concentration differences between the two collected samples. The NO_x analyzer was
10 calibrated by a model 146i dynamic dilution calibrator system at the end of each crop-growing season.

11 The mean flux of N₂O or NO during the experiment period was calculated as the average of all measured fluxes,
12 which were weighted by the interval between the two measurements (Xiong et al., 2006). The cumulative N₂O was
13 calculated as the product of the mean flux and the entire duration.

14 The NH₃ volatilization was determined using the ventilation method (Zhao et al., 2010). The
15 phosphoglycerol-soaked sponge was replaced every day after each fertilization event for approximately one week. The
16 phosphoglycerol-soaked sponges used to collect the NH₃ samples were immediately extracted with 300 mL potassium
17 chloride (KCl) solution (1 mol L⁻¹) for 1 h. The concentration of ammonia nitrogen (NH₄⁺-N) was measured using the
18 indophenol blue method at 625 nm (Sororzano, 1969) by ultraviolet spectrophotometry (HITACHI, UV-2900, Tokyo,
19 Japan, with 0.005 absorbance of photometric accuracy). The cumulative seasonal NH₃ volatilization was the sum of the
20 daily emissions during the measurement period.

21 *2.4. Auxiliary measurements*

22 Simultaneously with the determination of trace gas fluxes, the air temperature and the soil temperature at a depth of
23 5 cm were measured using thermally sensitive probes at each sampling date. Soil water content was also measured using
24 a portable water detector (Mode TZS-1K, Zhejiang Top Instrument Corporation Ltd., China) by the frequency domain
25 reflectometer method at a depth of 5 cm. Measured soil water contents (v/v) were converted to water filled pore space
26 (WFPS) with the following equation:

$$27 \text{WFPS} = \text{volumetric water content (cm}^3 \text{ cm}^{-3}) / \text{total soil porosity (cm}^3 \text{ cm}^{-3}) \quad (1)$$

28 Here, total soil porosity = $[1 - (\text{soil bulk density (g cm}^{-3}) / 2.65)]$ with an assumed soil particle density of 2.65 (g cm⁻³).

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

30 After each vegetable crop reached physiological maturity, the fresh vegetable yield was measured by weighing the

1 whole aboveground and belowground biomass in each pot.

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

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

4 After the one-year pot experiment, a soil sample from each pot was blended carefully. One subsample was stored at
5 4 °C for determination of microbial biomass carbon (MBC), potential nitrification rate (PNR) and denitrification enzyme
6 activity (DEA) within 3 days. Another subsample was air-dried for analysis of SOC, TN, pH and EC. MBC was
7 determined by substrate-induced respiration using a gas chromatography (Anderson and Domsch 1978). PNR was
8 measured using the chlorate inhibition soil-slurry method as previously described (Kurola et al., 2005) with
9 modifications (Hu et al., 2016). DEA was quantified as described by Smith and Tiedje (1979).

10 *2.5. Data processing and statistics*

11 One-way ANOVA was performed to test the effects of the treatments on cumulative N₂O, NO and NH₃ emissions;
12 GNrE; vegetable yield and GNrI. Two-way ANOVA was used to analyze the effects of the biochar type; soil type; and
13 their interactions on N₂O, NO and NH₃ emissions, vegetable yield, GNrE and GNrI throughout the experimental period.
14 Multiple comparisons among the treatments were further explained using Tukey's HSD test. Significant differences were
15 considered at $P < 0.05$. All statistical analyses were performed using JMP ver. 7.0 (SAS Institute, Cary, NC, USA, 2007).
16 Pearson's correlation analysis was used to determine whether there were significant interrelationships between N₂O/NO
17 and PNR or DEA in each soil, using SPSS window version 18.0 (SPSS Inc., Chicago, USA).

1 **3. Results**

2 *3.1. Soil responses to biochar amendment*

3 Obvious differences in all observed soil properties existed among soil types (Table 1, $p < 0.001$), suggesting the
4 wide variations of soil characters across mainland China. Additionally, biochar amendments had significant influences on
5 all the soil properties (Table 1, $p < 0.05$). Compared with N treatments, biochar amendments increased the SOC, TN and
6 EC by 20.4–135.0 %, 0.5–21.2 % and 2.4–38.1 %, respectively, across all the soils. Compared with Bw, Bm amendment
7 resulted in higher contents of SOC and TN by 5.8–20.5 % and 9.5–14.2 %, respectively, whereas EC values were higher
8 by 3.3–21.5 % induced by Bw than Bm amendment over all soils. Additionally, biochar amendments significantly
9 increased soil pH by 0.27–0.64 and 0.08–0.10 units compared with N treatment in Acrisol and Anthrosol soils ($p < 0.05$),
10 respectively, and Bm performed better than Bw on increasing soil pH in Acrisol. Furthermore, biochar amendments
11 tended to increase MBC in Cambisol and Phaeozem, and Bm performed better in MBC enhancements than Bw in
12 Phaeozem.

13 As shown in Fig. 1, no consensus effects on PNR and DEA were observed with biochar amendments across all soils.
14 Compared with N treatment, biochar amendments significantly increased PNR in Phaeozem while exerted no influences
15 on Cambisol (Fig. 1a). Compared with Bw, Bm amendment significantly increased PNR in Acrisol and Anthrosol.
16 Moreover, compared with N, biochar amendments reduced DEA in most soils, significantly in Anthrosol and Phaeozem
17 by an average of 40.1 and 37.8 % (Fig. 1b, $p < 0.05$), respectively. In comparison with Bw, remarkable enhancements in
18 DEA were observed by 42.5 and 74.4 % with Bm amendment in Acrisol and Anthrosol, respectively ($p < 0.05$).

19 *3.2. Seasonal variations of N₂O and NO emissions*

20 The dynamics of N₂O fluxes from all N-applied treatments in the four vegetable soils were relatively consistent and
21 followed a sporadic and pulse-like pattern that was accompanied with fertilization, tillage and irrigation (Fig. 2). In
22 addition, peak N₂O fluxes varied greatly. Most of the N₂O emissions occurred during the Amaranth and Tung choy
23 growing periods, and there were several small emissions peaks during the Spinach and Coriander herb growing periods
24 due to lower N application rate (Table S2), soil temperature and water content (Fig. S2). The highest peaks of N₂O
25 emissions from Acrisol, Anthrosol, Cambisol and Phaeozem were 4133.7, 1784.0, 432.4 and 1777.2 $\mu\text{g N m}^{-2} \text{h}^{-1}$,
26 respectively. Although biochar (Bw and Bm) application did not significantly alter the seasonal pattern of the N₂O fluxes,
27 they greatly lowered some peaks of N₂O emissions in the Anthrosol and Phaeozem by 8.7–74.4% and 23.6–73.6%,
28 respectively (Fig. 2b and d).

29 Clearly, the NO fluxes demonstrated similar seasonal dynamics to the N₂O fluxes (Fig. 3). Some relatively high
30 peak NO fluxes were still observed in the Spinach and Coriander herb planting seasons even though relatively low

1 temperatures occurred during these periods, primarily due to lower soil moisture which was suitable for NO production.
2 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
3 significantly weakened with the Bw and Bm in the Acrisol (Fig. 3a).

4 3.3. Cumulative N_2O , NO and NH_3 emissions

5 Cumulative N_2O emissions varied greatly among soil types (Table 2, $p < 0.001$), from 1.97 to 31.56 kg N ha^{-1} across
6 all the soils during the vegetable cultivation period (Table 3a). Biochar amendments had significant influences on the
7 cumulative N_2O emissions, reducing N_2O emissions by 13.7–41.6 % (Table 2). In comparison with the N treatment,
8 biochar amendment resulted in no consistent effects on N_2O emissions over all soils (Table 3a), indicating significant
9 interactions between biochar and soil types (Table 2, $p < 0.001$). Additionally, Bw amendment performed better
10 mitigation effects which decreased N_2O emissions by 11.8–38.4 % across all the soils, significantly in Acrisol in relation
11 to Bm (Table 3a, $p < 0.05$). The values of cumulative NO emissions were much smaller than those of N_2O emissions,
12 with a remarkable variation of 0.20–8.99 kg N ha^{-1} across all soils (Table 3b). Though pronounced effects on NO
13 emissions with a reduction by average of 45.8 % (Table 2, $p < 0.05$), biochar amendments had no consensus effects
14 across soils (Table 3b), which suggested significant interactions between biochar and soil types (Table 2, $p < 0.001$).
15 Compared with Bm, Bw amendment significantly reduced NO emissions in Anthrosol and Phaeozem (Table 3b, $p < 0.05$).
16 Moreover, N_2O emissions had positive relationships with DEA both in Anthrosol and Phaeozem, and were affected
17 positively with PNR in Acrisol (Table 4). Additionally, NO emissions had positive correlations with both PNR and DEA
18 in Anthrosol. However, neither N_2O nor NO emissions were influenced significantly by PNR and DEA in Cambisol.

19 As is shown in Table 3c, the cumulative NH_3 emissions fluctuated greatly from 4.72–7.57 kg N ha^{-1} across all the
20 soils. Biochar amendments produced no significant influences on the NH_3 emissions relative to N treatment in most soils
21 (Tables 2 and 3c). A tendency was found for the cumulative NH_3 emissions in N+Bm to be higher than those in the
22 N+Bw treatment, although this difference was not remarkable within each soil. Additionally, stimulation effects were
23 consistently present after the first fertilization event in each type of soil (Fig. 4).

24 3.4. Vegetable yield and gaseous reactive N intensity during the five-vegetable crop rotation

25 The vegetable yields for the five consecutive vegetable crops are presented in Table 3e. Pronounced differences
26 existed among all soils (Table 2, $p < 0.001$). Biochar amendments exerted no significant effects on vegetable yield (Table
27 2). Compared with the N treatment, biochar amendments were prone to increase vegetable yield in Cambisol and
28 Phaeozem against Acrisol and Anthrosol (Tables 3e), denoting pronounced interactions between soil and biochar (Table 2,
29 $p < 0.05$). Compared with Bm, Bw amendment lowered total yield over all the soils (Table 3e), significantly in Acrisol
30 and Cambisol ($p < 0.05$).

1 Table 3f presents the GNrI during the whole experiment period, with a pronounced variation among soils (Table 2, p
2 < 0.001). The GNrI was greatly affected by biochar amendment during the whole experiment period (Table 2, p < 0.01).
3 Compared to N treatment, biochar amendments reduced the GNrI by 4.3–27.8 % across all soils, significantly in
4 Anthrosol and Phaeozem (Table 3f, p < 0.05). Moreover, there were no remarkable differences between Bw and Bm
5 throughout all soils.

1 **4. Discussion**

2 *4.1. Biochar effects on GNRs across different soil types*

3 The effects of biochar amendment on the N₂O and NO emissions may be positive, negative or neutral, largely
4 depending on the soil condition and the inherent characteristics of the biochar (Spokas and Reicosky, 2009; Nelissen et
5 al., 2014). In our study, effects of two biochars on the N₂O and NO emissions did not follow a consensus trend across the
6 four typical vegetable soils (Table 3a, b). In agreement with Cayuela et al. (2014), who reported that the role of biochar in
7 mitigating N₂O emission was maximal in soils close to neutrality, remarkable mitigation effects were observed in
8 Anthrosol and Phaeozem with the biochar amendments (Table 3a). These findings potentially resulted from the effects of
9 the biochars on soil aeration, C/N ratio and pH, which affected the N dynamics and N cycling processes (Zhang et al.,
10 2010; Ameloot et al., 2015). In line with Obia et al. (2015), biochar decreased NO emissions in low-pH Acrisol (Table
11 3b), probably by inducing denitrification enzymes with higher activity, and then resulted in less NO accumulation
12 relative to N₂ production. Moreover, the liming effects of biochar prevented the chemical decomposition of NO₂⁻ to NO
13 (Islam et al., 2008), leaving only enzymatically produced NO to accumulate. However, neither N₂O nor NO emission was
14 significantly influenced by PNR or DEA, suggesting other processes might play vital roles in Cambisol. Besides
15 nitrification and denitrification, nitrifiers denitrification (Wrage et al., 2001) and heterotrophic nitrification (Zhu et al.,
16 2011) can be important processes for producing N₂O/NO as well, especially in vegetable soils with low pH, low
17 carbon content and high N content (Wrage et al., 2001). Ma et al. (2015) speculated that nitrifier denitrification was
18 the main process producing N₂O in the North China Plain (Cambisol within this region). In addition, surplus N input
19 in vegetable systems probably masked the beneficial effects of the biochar addition on the N transformation (Wang et al.,
20 2015a). Therefore, the underlying mechanism of how biochar affect those processes needs to be illustrated in the further
21 research.

22 On the other hand, different biochars may not produce universal influences on N₂O emissions for the same soil due
23 to the distinct properties of the biochar (Spokas and Reicosky, 2009). In the current study, overall, in comparison with
24 Bm, the Bw amendment had more effective mitigation effects on N₂O and NO emissions (Table 3a, b), largely due to the
25 following reasons. First, compared with Bw, the contents of the TN and DOC in Bm were 1.8- and 1.4-fold (Table S1),
26 respectively, which might supply extra N or C source for heterotrophic nitrification in the acidic Acrisol, which made Bm
27 ineffective for reducing the N₂O emissions (Table 3a). This result was in accordance with Li et al. (2015a), who observed
28 that biochar amendment had no significant influence on the cumulative N₂O emissions, and even higher N₂O emissions
29 occurred when biochar was input. Additionally, as shown in Fig.1, Bm was more prone to stimulate PNR and DEA, thus
30 displaying lower mitigation ability than Bw. Second, compared with Bm, the C/N ratio was approximately twofold in Bw

1 (Table S1), presumably leading to more inorganic nitrogen being immobilized in biochar with a higher C/N ratio
2 (Ameloot et al., 2015), decreasing the available N for microorganisms. Last, as presented in Fig. S3 and Table S1, Bw
3 had more pores and surface area, having a better advantage over Bm in absorbing NO accordingly. Others have found
4 that the lower mitigation capacity of high-N biochars (e.g., manures or biosolids) is probably due to the increased N
5 release in the soil from the biochar (Schouten et al., 2012). To our knowledge, very few studies have investigated biochar
6 effects on NO emissions (Nelissen et al., 2014; Obia et al., 2015), and the mechanisms through which biochar influence
7 NO emissions are not elucidated yet. Therefore, more research is needed to clarify the underlying mechanisms of biochar
8 on NO emission.

9 Intensive managed soils receiving fertilizer such as urea or anhydrous NH₃ and ruminant urine patches are potential
10 hot spots for NH₃ formation, where the use of biochar is expected to retain NH₃-N in the soil system (Clough and
11 Condron, 2010). Actually, the effects of biochar amendments on NH₃ volatilization largely depend on soil characteristics,
12 biochar types and duration time. Soil texture is an important factor impacting NH₃ transfer and release. More clay
13 contents were present in the Anthrosol (Table S1), which was limited in large soil pores, thus, the addition of porous
14 biochar could enhance the soil aeration, promoting NH₃ volatilization (Sun et al., 2014). Additionally, it was worthy to
15 note that cumulative NH₃ emissions were slightly higher in soils with the Bm than those with the Bw amendment (Fig. 4
16 and Table 3c) and that difference could presumably be attributed to less surface area and the much higher pH of Bm (Fig.
17 S3 and Table S1), resulting in weak adsorption and great liming effects.

18 *4.2. Biochar effects on vegetable yield and GNrI across different soil types*

19 The application of biochar is usually intended to increase crop yields, and evidence suggests this may be successful
20 (Schulz et al., 2013; Li et al., 2016). Due to its liming effect, biochar helps to improve the supply of essential macro- and
21 micronutrients for plant growth (Chan and Xu, 2009; Major et al., 2010). Enhancement of vegetable yield with biochar
22 amendment occurred in Cambisol and Phaeozem (Table 3e). Additionally, the effects of Bm and Bw on vegetable yield
23 were inconsistent, which probably due to the wide diversity of physicochemical characteristics of biochar that translates
24 into variable reactions in soil (Novak et al., 2014). First, compared to Bw, Bm has a higher DOC content (Table S1),
25 through which more nutrients may be directly introduced to the soil (Rajkovich et al., 2012). Secondly, besides their large
26 amount of plant-available nutrients (Hass et al., 2012), biochars produced with manure have been generally considered
27 significant for improving soil fertility by promoting soil structure development (Joseph et al., 2010), with the result that
28 Bm was found superior to Bw in vegetable production enhancement in our case (Table 3e). As biochar effects on
29 vegetable yield were variable, both biochar properties and soil conditions and crop species ought to be taken into account
30 comprehensively before applying biochar to a certain soil condition.

1 However, no promotion of yield was observed with biochar amendments in Acrisol and Anthrosol. This could be
2 attributed to exacerbated soil salinity, which inhibited the uptake of nutrients and water (Ju et al., 2006; Zhou et al., 2010)
3 and the growth of the soil microorganisms (Setia et al., 2011), leading to unsustainable greenhouse vegetable production.
4 Compared with other biochar (Jia et al., 2012), the higher amounts of ash in Bw and Bm may contain high salts causing
5 soil salinity (Hussain et al., 2016). After the addition of the two salt-rich biochars, the EC values of Acrisol and Anthrosol
6 vegetable soils increased and reached the limits to tolerance for the leafy vegetables (Shannon and Grieve, 1998). Here,
7 we assessed two feedstock-derived biochar effects on GNrI in typical cultivated vegetable soils across mainland China.
8 Overall, biochar amendments reduced GNrI over all the soils, with the magnitude largely depending on soil type.
9 Remarkable reduction in GNrI had been detected due to the efficient mitigation induced by biochar in Anthrosol and
10 Phaeozem (Table 3f). However, despite enhanced vegetable yield, no significant decreases in GNrI were observed in
11 Cambisol, mainly because of the absence of mitigation effects on N₂O, NO and NH₃ emissions of biochars (Table 3a, b
12 and c) Overall, Bw was superior to Bm in mitigating the GNrE while Bm performed better in vegetable yield
13 enhancement (Table 3d and e). Therefore, mitigation efficacys on GNrI were not notably different between Bw and Bm
14 amendments across the four soils.

1 **5. Conclusion**

2 The study demonstrated that biochar amendments mostly reduced N₂O and NO emissions and slightly increased the
3 NH₃ emissions, while produced no consensus influences on yield though those effects were largely both biochar- and
4 soil-specific. Additionally, biochar amendments did decrease GNrI in intensive vegetable soils across mainland China.
5 Furthermore, Bw was superior to Bm in mitigating the GNrE whereas the Bm performed better in crop yield throughout
6 all soils. Consequently, both soil type and biochar characteristics need to be seriously considered before large-scale
7 biochar application under certain regions of intensive vegetable production.

1 **Acknowledge**

2 We would like to express our heartfelt gratitude to the anonymous reviewer for the constructive comments that greatly
3 improved the manuscript. This work was jointly supported by the National Natural Science Foundation of China
4 (41471192), Special Fund for Agro-Scientific Research in the Public Interest (201503106) and the Ministry of Science
5 and Technology (2013BAD11B01).

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1 **Table legends**

2 **Table 1**

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

Soil	Treatment	SOC (g kg ⁻¹)	TN (g kg ⁻¹)	pH	EC (ds m ⁻¹)	MBC (mg kg ⁻¹)
Acrisol	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
Anthrosol	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
Cambisol	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
Phaeozem	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.	**

5 Data shown are means ± standard deviations of three replicates. See Fig. 1 for treatments codes. Different letters within
 6 the same column indicate significant differences among treatments within the same soil at $p < 0.05$ level.

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

1 **Table 2**

2 Two-way ANOVA and mean effects of biochar (Bc) and soil (S) types on cumulative N₂O, NO and NH₃ emissions, gaseous reactive nitrogen emission (GNrE), vegetable
 3 yield and gaseous reactive nitrogen intensity (GNrI) during the entire sampling period.

Factors	DF	N ₂ O emission			NO emission			NH ₃ emission			GNrE			Vegetable yield			GNrI		
		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			0.2		
biochar effect (n = 12)																			
N mean		12.01±1.44a			2.86±0.24a			5.63±0.72a			20.50±1.60a			43.81±5.82a			0.57±0.05a		
N+Bw mean		7.01±0.58b			1.55±0.14b			6.37±1.02a			14.94±0.84b			43.53±6.31a			0.45±0.04b		
N+Bm mean		10.37±0.56a			1.55±0.10b			6.68±1.10a			18.60±0.65a			49.53±6.91a			0.49±0.03ab		
Soil effect (n = 9)																			
Acrisol mean		27.20±1.85a			5.80±0.50a			5.31±0.16c			38.04±1.90a			33.06±1.65c			1.15±0.11a		
Anthrosol mean		4.89±0.45b			1.08±0.13b			12.69±0.46a			12.69±0.46b			25.05±1.11d			0.51±0.01b		
Cambisol mean		2.25±0.26c			0.25±0.09c			9.51±0.55b			9.51±0.55c			44.88±0.49b			0.21±0.01c		
Phaeozem mean		4.48±0.68b			0.81±0.04b			11.79±0.71a			11.79±0.71b			79.50±2.41a			0.15±0.01c		

4 SS: the sum of squares.

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

6 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.

7 n.s.: not significant.

8 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

9 among treatments at $p < 0.05$ level.

1 **Table 3**

2 Cumulative gaseous nitrogen (N₂O, NO and NH₃) emissions, gaseous reactive nitrogen emission (GNrE), vegetable yield
 3 and gaseous reactive nitrogen intensity (GNrI) under the different treatments across the four soils.

Treatments	Acrisol	Anthrosol	Cambisol	Phaeozem
(a) Cumulative N ₂ O emissions (kg N ha ⁻¹)				
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) Cumulative NO emissions (kg N ha ⁻¹)				
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
(c) Cumulative NH ₃ emissions (kg N ha ⁻¹)				
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
(d) GNrE (kg N ha ⁻¹)				
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
(e) Vegetable yield (t ha ⁻¹)				
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
(f) GNrI (kg N t ⁻¹ yield)				
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

4 Data shown are means ± standard deviations of the three replicates. See Fig. 1 for treatments codes. Different letters
 5 within the same column indicate significant differences among treatments within the same soil at $p < 0.05$ level.

1 **Table 4**

2 The correlations between N₂O or NO emission and PNR or DEA in each soil.

Item	Acrisol		Anthrosol		Cambisol		Phaeozem	
	PNR	DEA	PNR	DEA	PNR	DEA	PNR	DEA
N ₂ 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

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

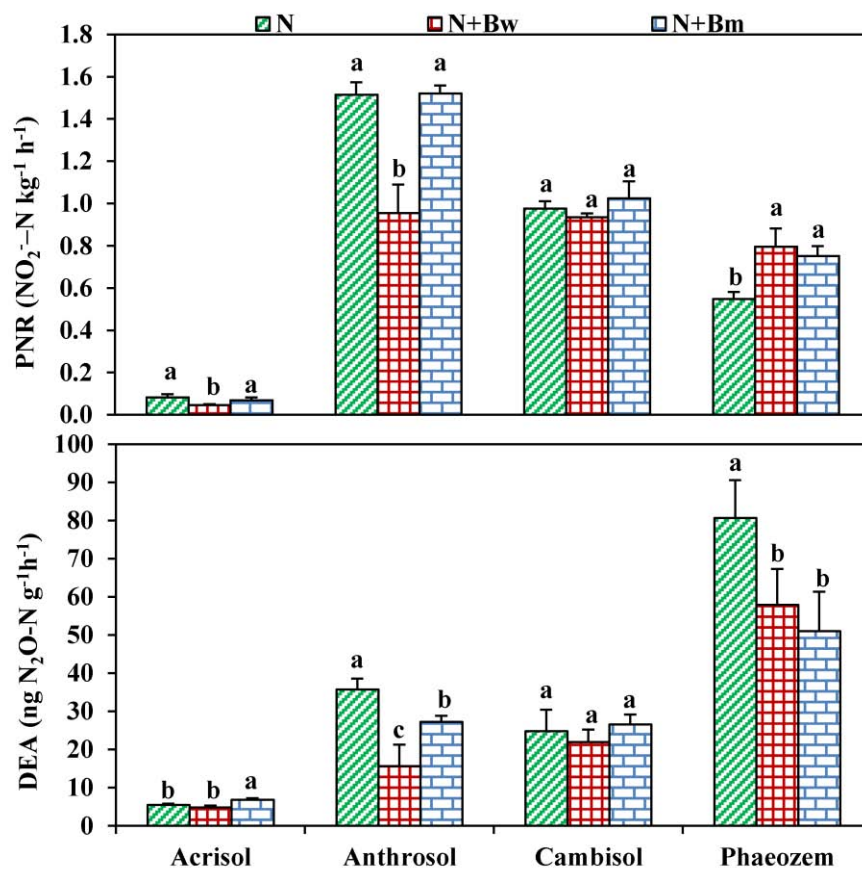
1 **Figure legends**

2 **Fig. 1** Potential nitrification rate (PNR) and Denitrification enzyme activity (DEA) under different treatments in Acrisol,
3 Anthrosol, Cambisol and Phaeozem. The three treatments with each soil were urea without biochar (N), urea with wheat
4 straw biochar (N+Bw) and urea with swine manure biochar (N+Bm). Bars indicate standard deviation (mean + SD, n =
5 3). Different letters above the bars indicate significant differences among the different treatments within the same soil, at
6 $p < 0.05$.

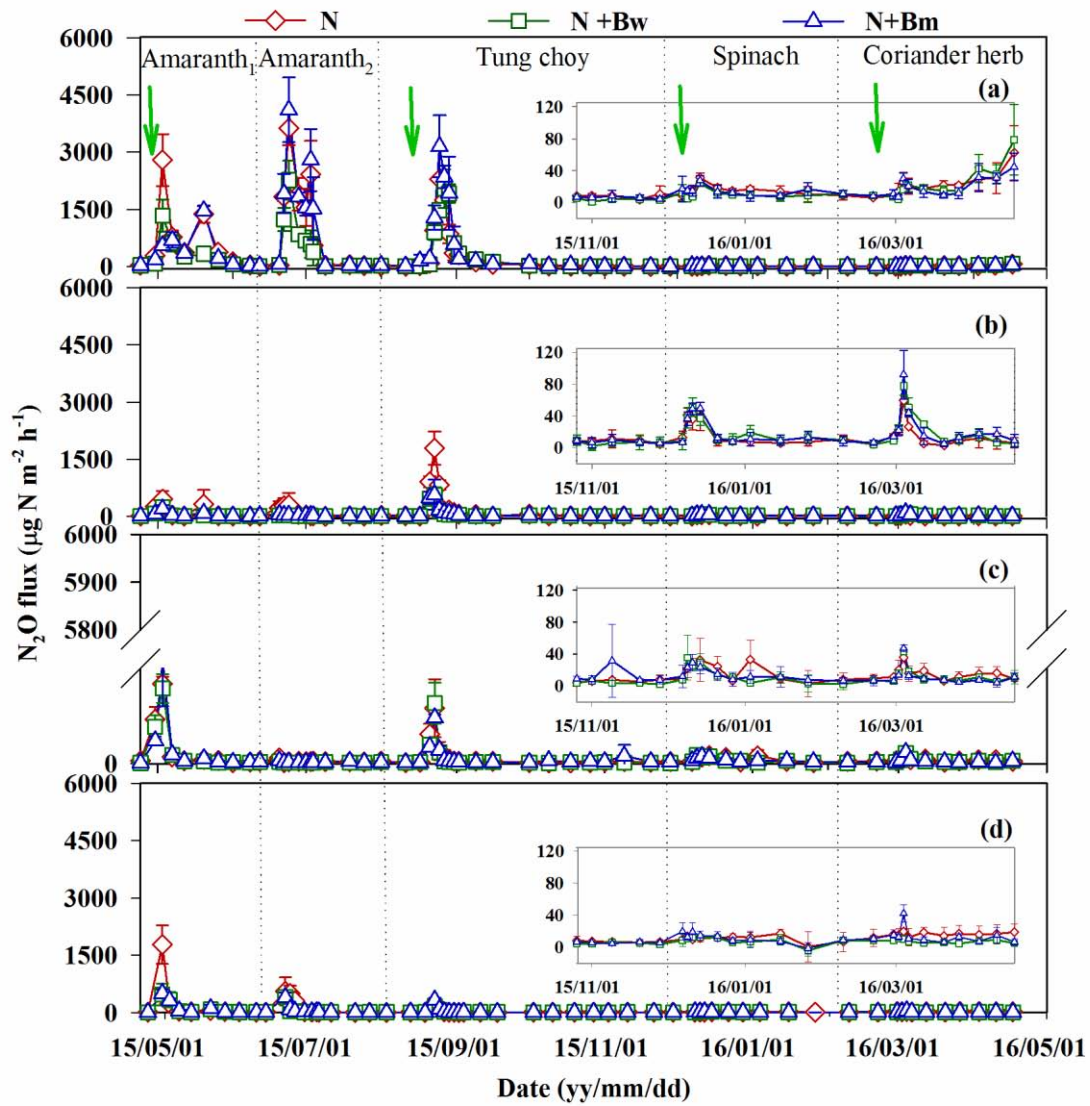
7 **Fig. 2** Temporal dynamics of soil N_2O ($\mu\text{g N m}^{-2} \text{h}^{-1} \pm \text{SD}$, n = 3) fluxes under different treatments in Acrisol (a),
8 Anthrosol (b), Cambisol (c) and Phaeozem (d) vegetable soils with five consecutive vegetable crops. The solid arrows
9 indicate fertilization. See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

10 **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 Acrisol (a),
11 Anthrosol (b), Cambisol (c) and Phaeozem (d) vegetable soils with five consecutive vegetable crops. The solid arrows
12 indicate fertilization. See Fig. 1 for treatments codes.

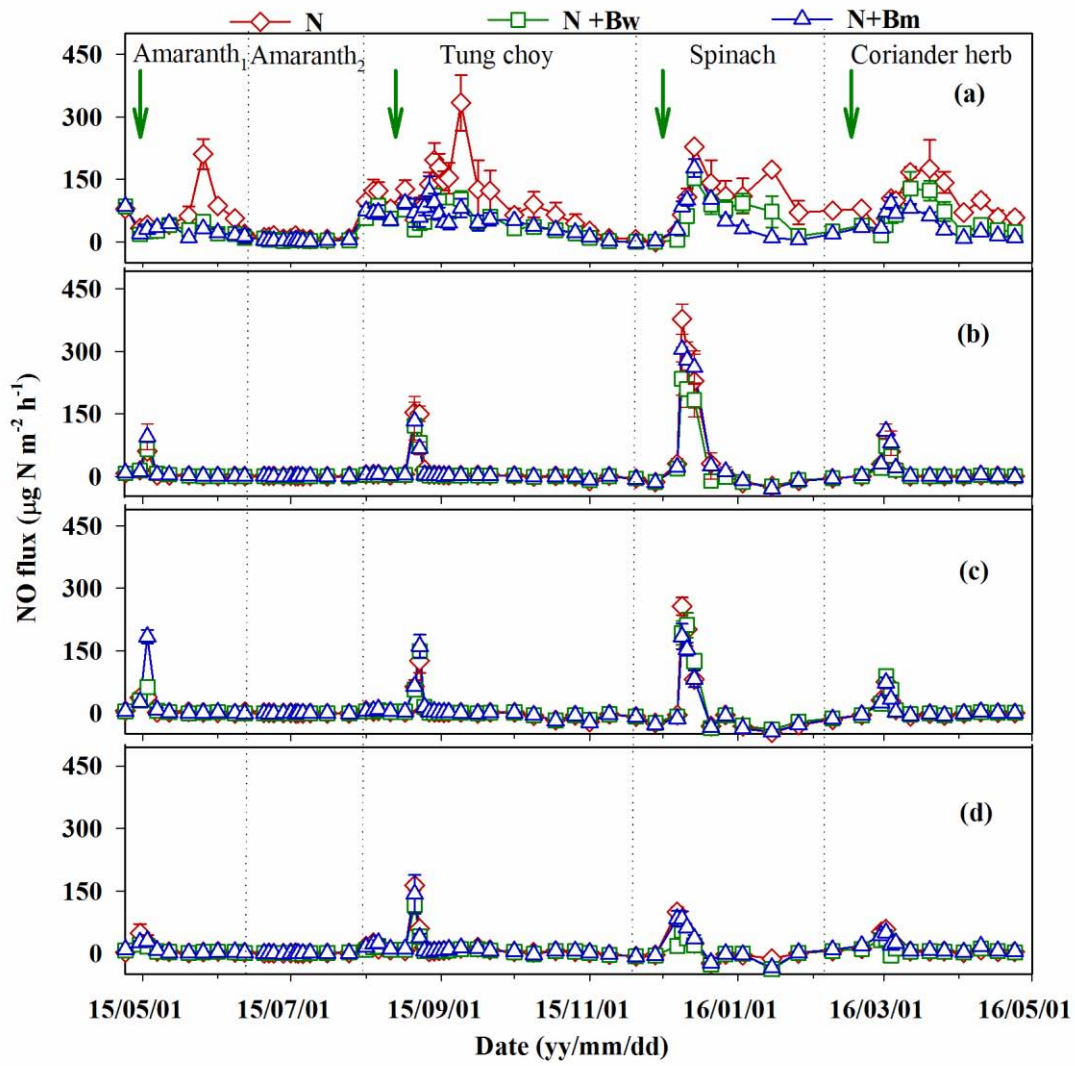
13 **Fig. 4** Cumulative ammonia (NH_3) emissions from the Acrisol (a), Anthrosol (b), Cambisol (c) and Phaeozem (d) soils
14 during the four nitrogen fertilization events F: every N fertilization event. The bars indicate the standard deviation of the
15 mean ($\text{kg N ha}^{-1} \pm \text{SD}$, n = 3) of each treatment for the sum of the four N fertilization events. See Fig. 1 for treatments
16 codes. Different letters above the bars indicate significant differences among the different treatments for each soil, at $p <$
17 0.05.



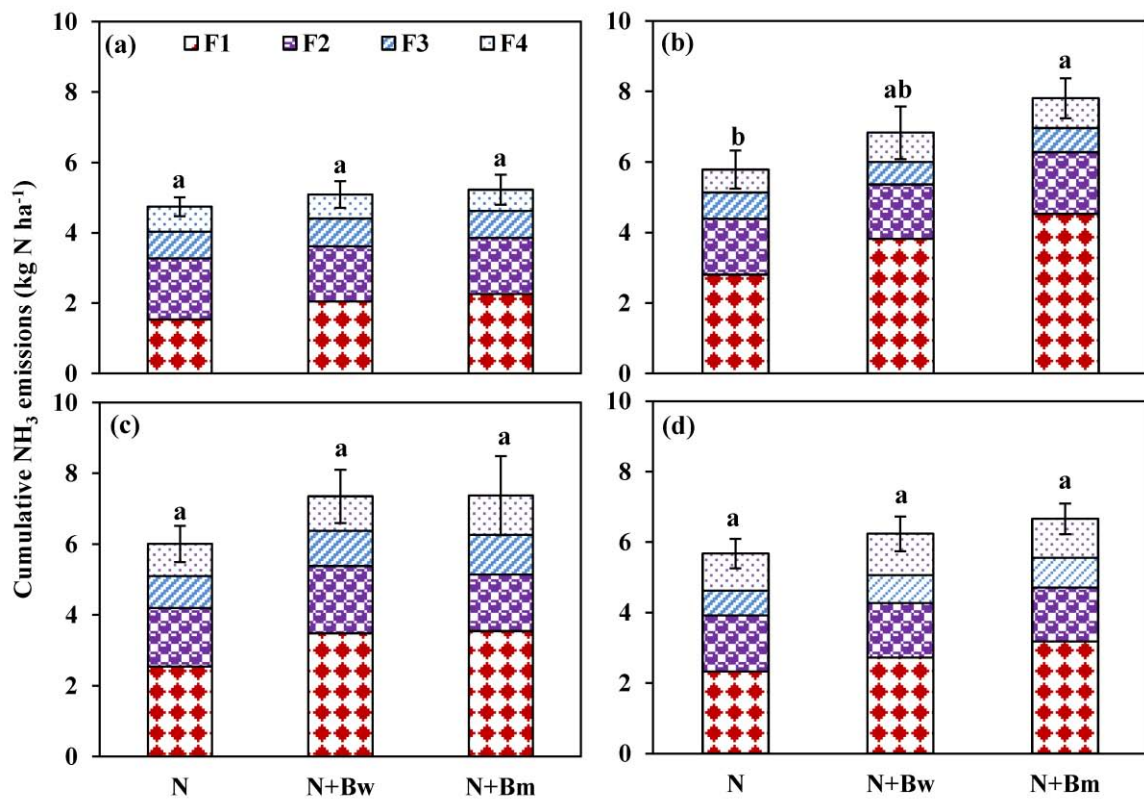
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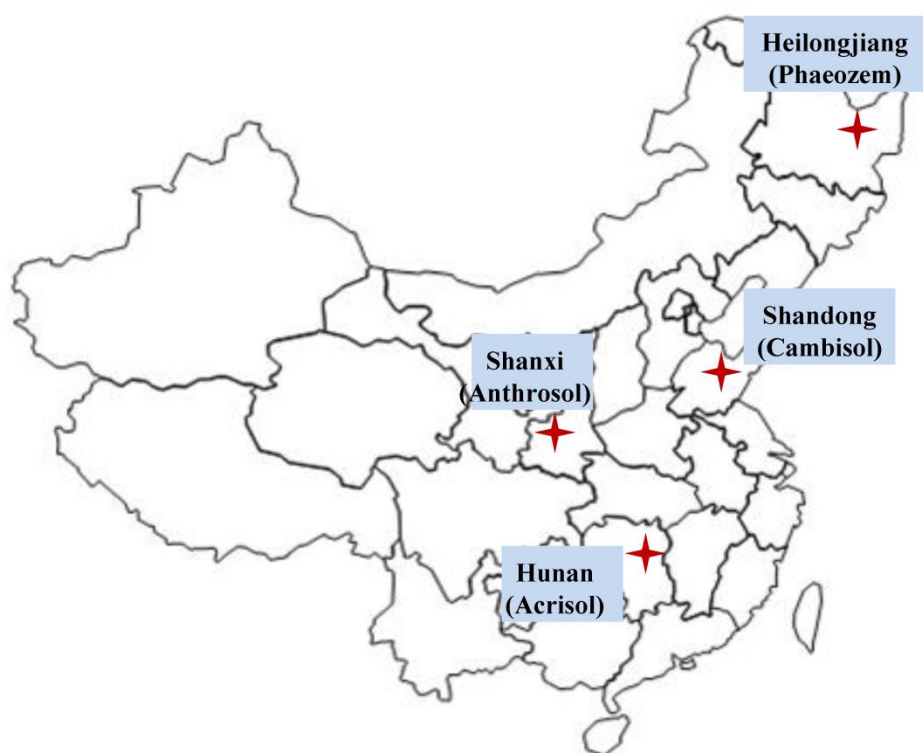
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1 **Supplementary information**

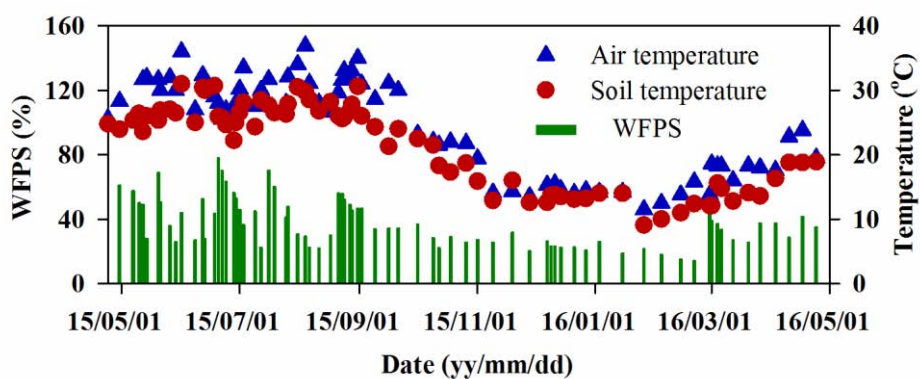
2 **Fig. S1** Map showing the sampling sites in China.

3 **Fig. S2** Dynamics of water filled pore space (WFPS), air temperature and soil temperature during the vegetable
4 cultivation period.

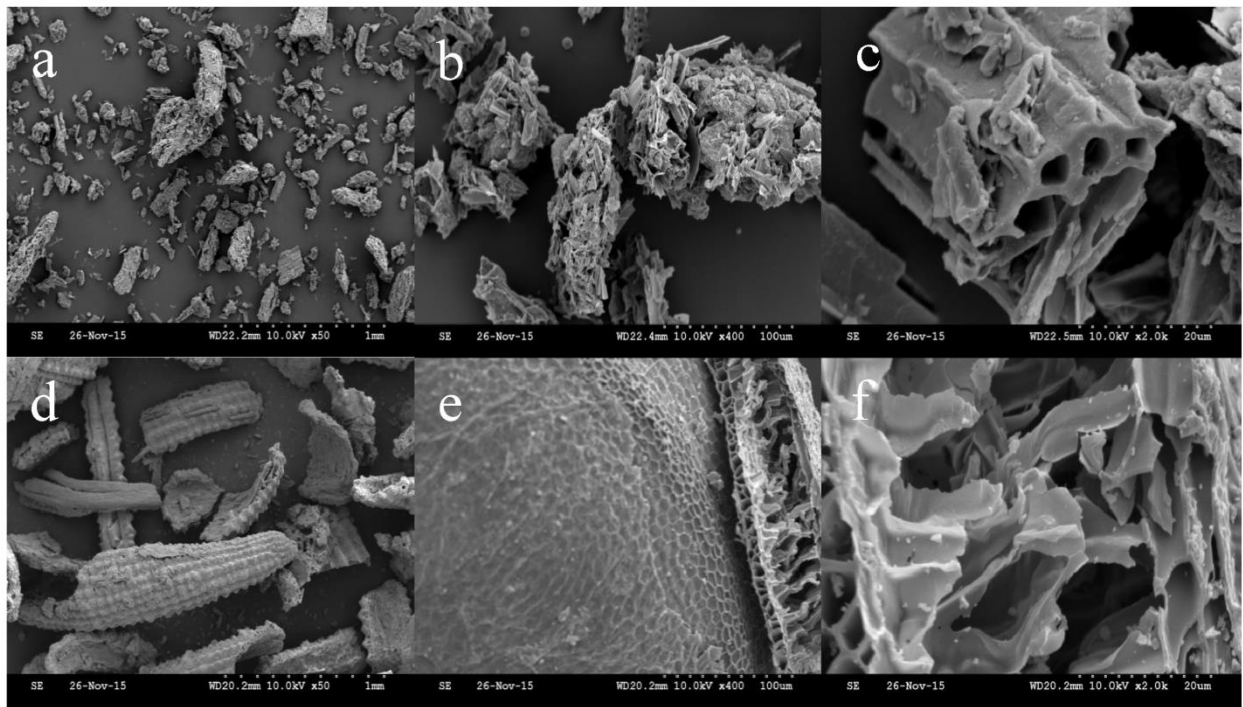
5 **Fig. S3** Scanning electron microscope (SEM) images of the biochars derived from Bw (a, b and c) and Bm (d, e and f).
6 Same magnification for a and d ($\times 50$), b and e ($\times 400$) and c and f ($\times 2000$).



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1 **Table S1**

2 Characteristics of the vegetable soils and biochars used in the experiment.

Item	Vegetable soil				Biochar	
	HN	SX	SD	HLJ	Bw	Bm
Texture	sandy loam	silt (sandy) clay loam	silt (sandy) loam	silt (sandy) loam		
sand, %	47.1	17.7	24.7	31.6		
silt, %	40.0	59.6	60.4	52.8		
clay, %	12.9	22.7	14.9	15.6		
total C (g kg ⁻¹)	7.6	9.8	8.2	26.8	449.1	461.2
total N (g kg ⁻¹)	1.2	1.4	1.0	2.1	6.5	12.0
C/N	6.3	7.0	8.2	12.8	69.1	38.4
H (g kg ⁻¹)					10.5	16.1
O (g kg ⁻¹)					52.4	96.7
H/Corg					0.3	0.4
pH	5.6	7.6	8.2	7.6	9.7	10.0
EC (ds m ⁻¹)	1.8	1.1	0.2	0.2	10.6	3.3
DOC (g kg ⁻¹)	0.5	0.4	0.2	0.7	0.9	1.3
CEC, cmol kg ⁻¹	6.1	13.2	15.3	20.3	22.1	22.7
WHC, %	41.6	50.1	54.4	59.6	362.0	304.1
NH ₄ ⁺ -N (mg kg ⁻¹)	105.3	32.2	28.4	31.6	4.3	4.0
NO ₃ ⁻ -N (mg kg ⁻¹)	415.8	307.6	21.2	30.8	6.1	3.2
Bulk density (g cm ⁻³)	1.2	1.4	1.1	1.1		
Surface area (m ² g ⁻¹)					21.3	9.3
Ash content, %					29.1	38.6

3 EC: electronic conductivity; DOC: dissolved organic carbon; CEC: cation exchange capacity; WHC: water holding capacity

Table S2

Crop rotation, tillage practices, and fertilizer application from April 2015 to April 2016.

Crop	Date	Agricultural activity	Fertilizer N rate (kg N ha ⁻¹)	Fertilizer P rate (kg N ha ⁻¹)	Fertilizer K rate (kg N ha ⁻¹)
Amaranth ₁	04/22/2015	Tillage			
	04/29/2015	Fertilizer application and planting	240	240	240
	06/13/2015	Harvesting			
	06/14/2015	Tillage			
Amaranth ₂	06/19/2015	Fertilizer application and planting	0	0	0
	07/31/2015	Harvesting			
	07/32/2015	Tillage			
Tung choy	08/20/2015	Fertilizer application and planting	200	200	200
	11/27/2015	Harvesting			
	11/28/2015	Tillage			
Spinach	12/06/2015	Fertilizer application and planting	150	150	150
	01/28/2016	Harvesting			
	01/09/2016	Tillage			
Coriander herb	02/28/2016	Fertilizer application and planting	180	180	180
	04/29/2016	Harvesting			
	04/30/2016	Tillage			

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Biochar can decrease the gaseous reactive nitrogen intensity in
intensive vegetable soils across mainland China~~Effects of two-~~
~~contrasting biochars on gaseous nitrogen emissions and intensity in-~~
intensive vegetable soils across mainland China

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1 **Highlights**

- 2 1. Two contrasting biochars affected ~~Gaseous-Nitrogen-Intensity~~ across 4 major vegetable soils in China.
- 3 2. Biochar affects gaseous-~~N_r~~ or yield largely depending on soil types.
- 4 3. Both biochars decreased GN~~r~~I with Bw mitigated gaseous N~~r~~ whereas Bm improved yield.

1 **Abstract**

2 Biochar amendment to soil has been proposed as a strategy for sequestering carbon, mitigating climate change and
3 enhancing crop productivity, but few studies have demonstrated the general effects of different feedstock-derived
4 biochars on the various gaseous reactive nitrogen emissions (GN_rE_s, N₂O, NO and NH₃) simultaneously across the
5 typical vegetable soils in China. A greenhouse pot experiment with five consecutive vegetable crops was conducted to
6 investigate the effects of two contrasting biochar, namely, wheat straw biochar (Bw) and swine manure biochar (Bm) on
7 GN_rE_s, vegetable yield and gaseous reactive nitrogen intensity (GN_rI) in four typical vegetable soils from ~~the main~~
8 ~~vegetable production regions~~ (Acrisol (Hunan province ~~(Acrisol_{HN})~~), Anthrosol (Shanxi province ~~(Anthrosol_{SX})~~),
9 Cambisol (Shandong province ~~(Cambisol_{SD})~~) and Phaeozem (Heilongjiang province ~~(Phaeozem_{HLJ})~~) ~~which~~ ~~that~~ are
10 representative of the intensive vegetable ecosystems across mainland China. Results showed that remarkable GN_rE
11 mitigation induced by biochar occurred in Anthrosol_{SX} and Phaeozem_{HLJ} soils, whereas enhancement of yield
12 occurred in Cambisol_{SD} and Phaeozem_{HLJ} soils. Additionally, both biochars decreased GN_rI with Bw performed
13 better than Bm regarding N₂O mitigation, ~~with Bw mitigating~~ N₂O and NO emissions by 21.8–59.1 % and 37.0–
14 49.5 % (except for Cambisol_{SD}), respectively, while Bm improved yield by ~~4.0~~13.5–30.5 % (except for Acrisol_{HN} and
15 Anthrosol_{SX}). Biochar amendments generally stimulated the NH₃ emissions with greater enhancement from ~~Futhermore~~.
16 Bw performed better than Bm regarding N₂O mitigation by 11.8–38.4 % and Bm promoted yield better than Bw by 11.6–
17 20.2%. We can infer that Biochar amendments stimulated the NH₃ emissions (highest in Anthrosol_{SX}), and Bm resulted
18 in slightly higher NH₃ emissions than Bw did in all types of soils. Since the biochar's effects on the GN_rE_s and vegetable
19 yield strongly depended on the attributes of the soil and biochar. Therefore, both soil type and biochar characteristics
20 should be seriously considered before conducting large-scale application of biochar in order to achieve the maximum
21 benefits under intensive greenhouse vegetable agriculture.

22 **Keyword:** Biochar, Intensive vegetable soil, Gaseous reactive nitrogen emissions (GN_rE_s), Gaseous reactive
23 nitrogen intensity (GN_rI)

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1 **1 Introduction**

2 Agriculture ~~accounted~~-accounts for an estimated emission of 4.1 (1.7–4.8) Tg N yr⁻¹ for N₂O and 3.7 Tg N yr⁻¹ for
3 NO, contributing 60 % and 10 %, respectively, to the total global anthropogenic emissions, largely due to increases of N
4 fertilizer application in cropland (Ciais, 2013). The concentration of atmospheric N₂O, a powerful, long-lived,
5 greenhouse gas, has increased from 270 parts per billion by volume (ppbv) in the pre-industrial era to ~ 324 ppbv (Ussiri
6 and Lal, 2013); it has ~~298-265~~ times the global warming potential (GWP) of CO₂ on a 100-year horizon (IPCC, 2013)
7 and also causes depletion of the ozone layer in the atmosphere (Ravishankara et al., 2009). In contrast, NO_x, which is
8 mainly emitted as nitric oxide (NO), does not directly affect the earth's radiative balance but catalyzes the production of
9 tropospheric ozone (O₃), which is a greenhouse gas associated with detrimental effects on human health (Anenberg et al.,
10 2012) and crop production (Avnery et al., 2011). Additionally, along with the high nitrogen (N) application, ammonia
11 volatilization is one of the major N loss pathways (Harrison and Webb, 2001) as well, with up to 90% coming from
12 agricultural activities (Misselbrook et al., 2000; Boyer et al., 2002). As a natural component and a dominant atmospheric
13 alkaline gas, NH₃ plays an important role in atmospheric chemistry and ambient aerosol formation (Langridge et al.,
14 2012; Wang et al., 2015b). In addition to nutrient enrichment (eutrophication) of terrestrial and aquatic systems and
15 global acidification of precipitation, NH₃ has also been shown to be a major factor in the formation of atmospheric
16 particulate matter and secondary aerosols (Kim et al., 2006; Pinder et al., 2007), leading to potentially adverse effects on
17 human and ecosystem health such as visibility degradation and threats to biodiversity (Powelson et al., 2008; Behera et al.,
18 2013). Consequently, the release of various reactive N species results in lower N use efficiency in agricultural systems.

19 In China, vegetable production devotes an area of approximately 24.7×10^6 ha, equivalent to 12.4% of the total
20 available cropping area, and the production represented 52 % of the world vegetable production in 2012 (FAO, 2015).
21 Intensified vegetable cultivation in China is characterized by high N application rates, high cropping index and frequent
22 farm practices. Annual nitrogen fertilizer inputs for intensively managed vegetable cultivation in rapidly developing areas
23 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
24 result, great concern exists about excess N fertilizer application, leading to low use efficiency in intensive vegetable
25 fields in China (Deng et al., 2013; Diao et al., 2013). Meanwhile, intensive vegetable agriculture is considered to be an
26 important source of N₂O (Xiong et al., 2006; Jia et al., 2012; Li et al., 2015b; Zhang et al., 2015) and NO production
27 (Mei et al., 2009). Moreover, ammonia volatilization is another important N pathway in fertilized soil, resulting in large
28 losses of soil-plant N (Pacholski et al., 2008; Zhang et al., 2011). Therefore, the reduction of reactive N loss becomes a
29 central environmental challenge to meet the joint challenges of high production and acceptable environmental
30 consequences in intensive vegetable production (Zhang et al., 2013).

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

16 Therefore, a greenhouse pot experiment was conducted in an effort to investigate the effects of different types of
17 biochar on gaseous reactive nitrogen emissions ($GNrEs$), namely, N_2O , NO and NH_3 , simultaneously in four typical
18 intensified vegetable soils across main vegetable production areas of mainland China. We hypothesized that: 1) biochar
19 amendment could affect $GNrEs$, vegetable yield and $GNrI$ in vegetable soils across mainland China, 2) those influences
20 would vary among biochar and soil types. Overall, the objectives of this research were to gain a comprehensive insight
21 into the effects of the different types of biochar on the $GNrEs$, vegetable yield and gaseous reactive nitrogen intensity
22 ($GNrI$) in intensively managed vegetable production in China.

1 2 Materials and methods

2 2.1. Experimental soil and biochar

3 Four typical greenhouse vegetable cultivation sites with a long history (more than 10 years) of conventional
4 cultivation were selected from Northeast, Northwest, Central and Eastern China (Fig. S1), namely, Phaeozem, Anthrosol,
5 Acrisol and Cambisol (FAO and ISRIC, 2012). Those four types of vegetable soil were collected from: (1) Jiamusi
6 (46°48'N, 130°12'E), Heilongjiang province-~~(HLJ)~~; (2) Yangling (34°18'N, 108°2'E), Shanxi province-~~(SX)~~; (3)
7 Changsha (28°32'N, 113°23'E), Hunan province-~~(HN)~~ and (4) Shouguang (36°56'N, 118°38'E), Shandong province
8 (SD), respectively, ~~which were collected and~~ represented a range of differences in physicochemical properties and
9 regions (Table S1). Soil samples were manually collected from the cultivated layer (0–20 cm) after the local vegetable
10 harvest in April, 2015. The samples were air-dried and passed through a 5 mm stainless steel mesh sieve and
11 homogenized thoroughly. Any visible roots and organic residues were removed manually before being packed with the
12 necessary amount of soil to achieve the initial field bulk density. Each pot received 15 kg of 105 °C
13 dry-weight-equivalent fresh soil. For each of the biochar amendment pots, 282.6 g pot⁻¹ sieved biochar (2 mm) was
14 mixed with the soil thoroughly before the experiment, which was equivalent to a 40 t ha⁻¹ biochar dose (dry weight). No
15 more biochar was added later in the experimental period.

16 Two types of biochar, derived from two common agricultural wastes in China were used: wheat straw and swine
17 manure, hereafter referred to as Bw and Bm, respectively (Table S1). The Bw was produced at the Sanli New Energy
18 Company in Henan, China, by pyrolysis and thermal decomposition at 400–500 °C. The Bm was produced through
19 thermal decomposition at 400 °C by the State Key Laboratory of Soil Science and Sustainable Agricultural, Institute of
20 Soil Science, Chinese Academy of Sciences. In accordance with Lu (2000), the SOC was measured by wet digestion with
21 H₂SO₄–K₂Cr₂O₇, TN was determined by semi-micro Kjeldahl digestion, and soil texture was determined with the pipette
22 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
23 PHS-3C mv/pH detector (Shanghai Kangyi Inc. China). Biochar content of hydrogen (H) was measured by elemental
24 analysis after dry combustion (Euro EA, Hekatech GmbH, Wegberg, Germany). The oxygen content of biochar was
25 measured with the same device after pyrolysis of the sample at 1000 °C followed by reduction of the evolved O₂ to CO
26 and quantification by GC-TCD. The soil NO₃⁻-N and NH₄⁺-N were measured following the two-wavelength ultraviolet
27 spectrometry and indophenol blue methods, respectively, using an ultraviolet spectrophotometer (HITACHI, UV-2900,
28 Tokyo, Japan). Electric conductivity (EC) was measured by using a Mettler-Toledo instrument (FE30-K, Shanghai, China)
29 at a 1:5 (w:v) soil to water ratio. Cation exchange capacity (CEC) was determined using the CH₃COONH₄ method.
30 Dissolved organic carbon (DOC) was extracted from 5 g of the biochar/soil with an addition of 50 ml deionized water

1 and measured by a TOC analyzer (TOC-2000/3000, Metash Instruments Co., LTD, Shanghai, China). Ash content was
2 measured by heating the biochars at 750 °C for 4 h. The specific surface area of the biochar material was tested using the
3 Brunauer–Emmett–Teller (BET) method, from which the N adsorption–desorption isotherms at 77 K were measured by
4 an automated gas adsorption analyzer ASAP2000 (Micromeritics, Norcross, GA) with + 5% accuracy. Scanning electron
5 microscopy (SEM) imaging analysis was conducted using a HITACHI S-3000N scanning electron microscope.

6 *2.2. Experimental set-up and management*

7 The pot experiments were performed at the greenhouse experimental station of Nanjing Agricultural University,
8 China. Five vegetable crops were grown successively in the four vegetable soils during the experimental period. For each
9 type of soil, three treatments with three replicates were arranged in a ~~completely~~ random design: urea without biochar
10 (N), urea with wheat straw biochar (N+Bw), urea with swine manure biochar (N+Bm). In addition, phosphate and
11 potassium fertilizers in the form of calcium magnesium phosphate and potassium chloride, together with urea, were
12 broadcasted and mixed with soil thoroughly prior to sowing the vegetables. No topdressing events occurred because of
13 the frequent cultivation and short growth period for the leafy vegetables. Based on the vegetable growth, all pots received
14 equal amounts of water and no precipitation. Detailed information on the pot management practices is provided in Table
15 S2.

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

20 *2.3. Measurement of N₂O, NO and NH₃*

21 The NO and N₂O fluxes were measured simultaneously from each vegetable cultivation using a static opaque
22 chamber method (Zheng et al., 2008; Yao et al., 2009). A square PVC chamber of 35 cm × 35 cm × 40 cm (length ×
23 width × height) was temporarily mounted on the pot for gas flux measurement. The chamber was coated with sponge and
24 aluminum foil outside to prevent solar radiation heating the chamber. Gas samples for flux measurements were collected
25 between 8 and 10 a.m. on each measuring day to minimize the influence of diurnal temperature variation. Gas fluxes
26 were usually measured once a week and every other day for one week following fertilizer application. To measure the
27 N₂O flux, four samples were collected from the headspace chamber using 20 ml polypropylene syringes at 0, 10, 20, and
28 30 min after chamber closure. The gas concentrations in the samples were analyzed within 12 h after sampling using an
29 Agilent 7890A gas chromatograph equipped with an electron capture detector (ECD) for N₂O detection. The carrier gas
30 was argon-methane (50 %) at a flow rate of 40 ml min⁻¹. The column and ECD temperatures were maintained at 40 and

1 300 °C, respectively. The gas chromatography configurations described by Wang et al. (2013) were adopted for the gas
2 concentration analysis. N₂O flux was calculated using the linear increases in gas concentration with time. Sample sets
3 were rejected unless they yielded a linear regression value of R² > 0.90.

4 For each NO flux measurement, gas samples were collected from the same chamber that was used for the N₂O flux
5 measurements (Yao et al., 2009). Before closing the chamber, an approximately 1.0 L gas sample from the headspace of
6 each chamber was extracted into an evacuated sampling bag (Delin Gas Packing Co., LTD, Dalian, China), and this
7 measurement was regarded as time 0 min for NO analysis. After 30 min under chamber enclosure conditions (i.e., after
8 the N₂O sample collections were completed), another headspace gas sample with the same volume was extracted from
9 each chamber into another evacuated bag. Within 1 h after sampling, NO concentrations were analyzed by a model 42i
10 chemiluminescence NO–NO–NO_x analyzer (Thermo Environmental Instruments Inc., Franklin, MA, USA). The NO
11 fluxes were derived from the concentration differences between the two collected samples. The NO_x analyzer was
12 calibrated by a model 146i dynamic dilution calibrator system at the end of each crop-growing season.

13 The mean flux of N₂O or NO during the experiment period was calculated as the average of all measured fluxes,
14 which were weighted by the interval between the two measurements (Xiong et al., 2006). The cumulative N₂O was
15 calculated as the product of the mean flux and the entire duration.

16 The NH₃ volatilization was determined using the ventilation method (Zhao et al., 2010). The
17 phosphoglycerol-soaked sponge was replaced every day after each fertilization event for approximately one week. The
18 phosphoglycerol-soaked sponges used to collect the NH₃ samples were immediately extracted with 300 mL potassium
19 chloride (KCl) solution (1 mol L⁻¹) for 1 h. The concentration of ammonia nitrogen (NH₄⁺-N) was measured using the
20 indophenol blue method at 625 nm (Sororzano, 1969) by ultraviolet spectrophotometry (HITACHI, UV-2900, Tokyo,
21 Japan, with 0.005 absorbance of photometric accuracy). The cumulative seasonal NH₃ volatilization was the sum of the
22 daily emissions during the measurement period.

23 2.4. Auxiliary measurements

24 Simultaneously with the determination of trace gas fluxes, the air temperature and the soil temperature at a depth of
25 5 cm were measured using thermally sensitive probes at each sampling date. Soil water content was also measured using
26 a portable water detector (Mode TZS-1K, Zhejiang Top Instrument Corporation Ltd., China) by the frequency domain
27 reflectometer method at a depth of 5 cm. Measured soil water contents (v/v) were converted to water filled pore space
28 (WFPS) with the following equation:

$$29 \text{ WFPS} = \text{volumetric water content (cm}^3 \text{ cm}^{-3}\text{)} / \text{total soil porosity (cm}^3 \text{ cm}^{-3}\text{)} \quad (1)$$

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

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

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

4
$$\text{GNrE} = \text{cumulative N}_2\text{O} + \text{cumulative NO} + \text{cumulative NH}_3 \text{ emissions (kg N ha}^{-1}\text{)} \quad (2)$$

5
$$\text{GNrI} = \text{GNrE} / \text{vegetable fresh yield (kg N t}^{-1} \text{ yield)} \quad -(3)$$

6 After the one-year pot experiment, a soil sample from each pot was blended carefully. One subsample was stored at
7 4 °C for determination of microbial biomass carbon (MBC), potential nitrification rate (PNR) and denitrification enzyme
8 activity (DEA) within 3 days. Another subsample was air-dried for analysis of SOC, TN, pH and EC. MBC was
9 determined by substrate-induced respiration using a gas chromatography (Anderson and Domsch 1978). PNR was
10 measured using the chlorate inhibition soil-slurry method as previously described (Kurola et al., 2005) with
11 modifications (Hu et al., 2016). DEA was quantified as described by Smith and Tiedje (1979).

12 2.5. Data processing and statistics

13 One-way ANOVA was performed to test the effects of the treatments on cumulative N₂O, NO and NH₃ emissions;
14 GNrE; vegetable yield and GNrI. Two-way ANOVA was used to analyze the effects of the biochar type; soil type; and
15 their interactions on N₂O, NO and NH₃ emissions, vegetable yield, GNrE and GNrI throughout the experimental period.
16 Multiple comparisons among the treatments were further explained using Tukey's HSD test. Significant differences were
17 considered at $P < 0.05$. All statistical analyses were performed using JMP ver. 7.0 (SAS Institute, Cary, NC, USA, 2007).
18 Pearson's correlation analysis was used to determine whether there were significant interrelationships between N₂O/NO
19 and PNR or DEA in each soil, using SPSS window version 18.0 (SPSS Inc., Chicago, USA).

1 3. Results

2 3.1. Soil responses to biochar amendment

3 Obvious differences in all observed soil properties existed among soil types (Table 1, $p < 0.001$), suggesting the
4 wide variations of soil characters across mainland China. Additionally, biochar amendments had significant influences on
5 all the soil properties (Table 1, $p < 0.05$). Compared with N treatments, biochar amendments increased the SOC, TN and
6 EC by 20.4–135.0 %, 0.5–21.2 % and 2.4–38.1 %, respectively, across all the soils. Compared with Bw, Bm amendment
7 resulted in higher contents of SOC and TN by 5.8–20.5 % and 9.5–14.2 %, respectively, whereas EC values were higher
8 by 3.3–21.5 % induced by Bw than Bm amendment over all soils. Additionally, biochar amendments significantly
9 ~~increased/enhanced~~ soil pH by 0.27–0.64 and 0.08–0.10 units compared with N treatment in Acrisol^{HN} and Anthrosol^{SX}
10 soils ($p < 0.05$), respectively, and ~~higher values were detected with Bm performed better~~ than Bw ~~on increasing soil pH~~
11 ~~amendment in all soils~~ Acrisol. Furthermore, biochar amendments tended to increase MBC in Cambisol^{SD} and Phaeozem
12 HLJ soils, and Bm performed better in MBC enhancements than Bw in Phaeozem^{all soils}.

13 As shown in Fig. 1, no consensus effects on PNR and DEA were observed with biochar amendments across all soils.
14 Compared with N treatment, biochar amendments significantly increased PNR in Phaeozem^{HLJ} while exerted no
15 influences on Cambisol^{SD} soil (Fig. 1a). Compared with Bw, Bm amendment significantly increased PNR in Acrisol^{HN}
16 and Anthrosol^{SX} soils. Moreover, compared with N, biochar amendments ~~significantly reduced~~ DEA ~~in most soils,~~
17 ~~significantly in Anthrosol and Phaeozem~~ by an average of 40.1 and 37.8 % ~~in SX and HLJ (Fig. 1b, $p < 0.05$),~~
18 ~~respectively, while producing no influence in SD soils (Fig. 1b)~~. In comparison with Bw, remarkable enhancements in
19 DEA were observed by 42.5 and 74.4 % with Bm amendment in Acrisol^{HN} and Anthrosol^{SX} soils, respectively ($p <$
20 0.05).

21 3.2. Seasonal variations of N_2O and NO emissions

22 The dynamics of N_2O fluxes from all N-applied treatments in the four vegetable soils were relatively consistent and
23 followed a sporadic and pulse-like pattern that was accompanied with fertilization, tillage and irrigation (Fig. 2). In
24 addition, peak N_2O fluxes varied greatly. Most of the N_2O emissions occurred during the Amaranth and Tung choy
25 growing periods, and there were several small emissions peaks during the Spinach and Coriander herb growing periods
26 due to lower N application rate (Table S2), soil temperature and water content (Fig. S2). The highest peaks of N_2O
27 emissions from Acrisol^{HN}, Anthrosol^{SX}, Cambisol^{SD} and Phaeozem^{HLJ} were 4133.7, 1784.0, 432.4 and 1777.2 $\mu\text{g N}$
28 $\text{m}^{-2} \text{h}^{-1}$, respectively. Although biochar (Bw and Bm) application did not significantly alter the seasonal pattern of the
29 N_2O fluxes, they greatly lowered some peaks of N_2O emissions in the Anthrosol^{SX} and Phaeozem by 8.7–74.4% and
30 23.6–73.6%, respectively (Fig. 2b and d).

1 Clearly, the NO fluxes demonstrated similar seasonal dynamics to the N₂O fluxes (Fig. 3). Some relatively high
2 peak NO fluxes were still observed in the Spinach and Coriander herb planting seasons even though relatively low
3 temperatures occurred during these periods, primarily due to lower soil moisture which was suitable for NO production.
4 The NO fluxes ranged from -44.6 to 377.6 μg N m⁻² h⁻¹ across all soil types. Furthermore, some NO peaks were
5 significantly weakened with the Bw and Bm in the AcrisolHN soil (Fig. 3a).

6 3.3. Cumulative N₂O, NO and NH₃ emissions

7 Cumulative N₂O emissions varied greatly among soil types (Table 2, $p < 0.001$), from 1.97 to 31.56 kg N ha⁻¹ across
8 all the soils during the vegetable cultivation period (Table 3a). Biochar amendments had significant influences on the
9 cumulative N₂O emissions, reducing N₂O emissions by 13.7–41.6 % (Table 2). In comparison with the N treatment,
10 biochar amendment ~~resulted in no consistent effects on N₂O emissions over all soils~~ decreased N₂O emissions by an
11 average of 56.4 % and 47.5 % in SX and HLJ (Table 3a, $p < 0.05$), ~~respectively, with no remarkable influence in SD soil,~~
12 indicating significant interactions between biochar and soil types (Table 2, $p < 0.001$). ~~Additionally, Compared with Bm,~~
13 Bw amendment performed better mitigation effects which decreased N₂O emissions by 11.8–38.4 % across all the soils,
14 significantly in AcrisolHN soil in relation to Bm (Table 3a, $p < 0.05$). ~~In comparison with N₂O emission, the values of~~
15 ~~cumulative NO emissions~~ was ~~were~~ much smaller than those of N₂O emissions, with a remarkable variation of 0.20–8.99
16 kg N ha⁻¹ across all soils (Table 3b). Though pronounced effects on NO emissions with a reduction by average of 45.8 %
17 (Table 2, $p < 0.05$), biochar amendments had no consensus effects across soils, ~~reducing NO emissions in HN soil~~ (Table
18 ~~3b, $p < 0.05$) and producing no remarkable influence on SD soil,~~ which suggested significant interactions between
19 biochar and soil types (Table 2, $p < 0.001$). Compared with Bm, Bw amendment significantly reduced NO emissions in
20 AnthrosolSX and PhaeozemHLJ soils (Table 3b, $p < 0.05$). ~~Moreover, As shown in Table 4,~~ N₂O emissions had positive
21 relationships with DEA both in AnthrosolSX and PhaeozemHLJ soils, and were affected positively with PNR in
22 AcrisolHN soil (Table 4). Additionally, NO emissions had positive correlations with both PNR and DEA in AnthrosolSX
23 ~~soil~~. However, neither N₂O nor NO emissions were influenced significantly by PNR and DEA in CambisolSD soils.

24 As is shown in Table 3c, the cumulative NH₃ emissions fluctuated greatly from 4.72–7.57 kg N ha⁻¹ across all the
25 soils. ~~Though significantly enhancing NH₃ emissions (Table 2), B~~biochar amendments produced no significant influences
26 on the NH₃ emissions relative to N treatment in most soils (Tables 2 and 3c). A tendency was found for the cumulative
27 NH₃ emissions in N+Bm to be higher than those in the N+Bw treatment, although this difference was not remarkable
28 within each soil. Additionally, stimulation effects were consistently present after the first fertilization event in each type
29 of soil (Fig. 4).

30 3.4. Vegetable yield and gaseous reactive N emissions intensity during the five-vegetable crop rotation

1 The vegetable yields for the five consecutive vegetable crops are presented in Table 3e. Pronounced differences
2 existed among all soils (Table 2, $p < 0.001$). Biochar amendments exerted no significant effects on vegetable yield (Table
3 2). Compared with the N treatment, biochar amendments were prone to increase vegetable yield in CambisolSD and
4 PhaeozemHLJ soils against AcrisolHN and AnthrosolSX soils (Tables 3e), denoting pronounced interactions between
5 soil and biochar (Table 2, $p < 0.05$). Compared with Bm, Bw amendment lowered total yield over all the soils (Table 3e),
6 significantly in AcrisolHN and CambisolSD soils ($p < 0.05$).

7 Table 3f presents the GNrI during the whole experiment period, with a pronounced variation among soils (Table 2, p
8 < 0.001). The GNrI was greatly affected by biochar amendment during the whole experiment period (Table 2, $p < 0.01$).
9 Compared to N treatment, biochar amendments reduced the GNrI by 4.3–27.8 % across all soils, significantly in
10 AnthrosolSX and PhaeozemHLJ soils (Table 3f, $p < 0.05$). Moreover, there were no remarkable differences between Bw
11 and Bm throughout all soils.

4. Discussion

4.1. Biochar effects on GNrEs across different soil types

The effects of biochar amendment on the N_2O and NO emissions may be positive, negative or neutral, largely depending on the soil condition and the inherent characteristics of the biochar (Spokas and Reicosky, 2009; Nelissen et al., 2014). In our study, effects of two biochars on the N_2O and NO emissions did not follow a consensus trend across the four typical vegetable soils (Table 3a, b). In agreement with Cayuela et al. (2014), who reported that the role of biochar in mitigating N_2O emission was maximal in soils close to neutrality, remarkable mitigation effects were observed in [Anthrosol_{SX}](#) and [Phaeozem_{HLJ}](#) with the biochar amendments (Table 3a). These findings potentially resulted from the effects of the biochars on soil aeration, C/N ratio and pH, which affected the N dynamics and N cycling processes (Zhang et al., 2010; Ameloot et al., 2015). ~~Moreover, mitigation of N_2O emissions induced by biochar was probably due to the decreased denitrification in [SX](#) and [HLJ](#) soils (Fig.1b and Table 4).~~ In line with Obia et al. (2015), biochar decreased NO emissions in low-pH [Acrisol_{HN} soil](#) (Table 3b), probably by inducing denitrification enzymes with higher activity, and then resulted in less NO accumulation relative to N_2 production. Moreover, the liming effects of biochar prevented the chemical decomposition of NO_2^- to NO (Islam et al., 2008), leaving only enzymatically produced NO to accumulate. However, neither N_2O nor NO emission was significantly influenced by PNR or DEA, suggesting other processes might play vital roles in [Cambisol_{SD} soil](#). Besides nitrification and denitrification, nitrifiers denitrification (Wrage et al., 2001) and heterotrophic nitrification (Zhu et al., 2011) can be important processes for producing $\text{N}_2\text{O}/\text{NO}$ as well, especially in vegetable soils with low pH, low carbon content and high N content (Wrage et al., 2001). Ma et al. (2015) speculated that nitrifier denitrification was the main process producing N_2O in the North China Plain ([Cambisol_{SD} soil](#) within this region). In addition, surplus N input in vegetable systems probably masked the beneficial effects of the biochar addition on the N transformation (Wang et al., 2015a). Therefore, the underlying mechanism of how biochar affect those processes needs to be illustrated in the further research.

On the other hand, different biochars may not produce universal influences on N_2O emissions for the same soil due to the distinct properties of the biochar (Spokas and Reicosky, 2009). In the current study, overall, in comparison with Bm, the Bw amendment had more effective mitigation effects on N_2O and NO emissions (Table 3a, b), largely due to the following reasons. First, compared with Bw, the contents of the TN and DOC in Bm were 1.8- and 1.4-fold (Table S1), respectively, which might supply extra N or C source for heterotrophic nitrification in the acidic [Acrisol_{HN} soil](#), which made Bm ineffective for reducing the N_2O emissions (Table 3a). This result was in accordance with Li et al. (2015a), who observed that biochar amendment had no significant influence on the cumulative N_2O emissions, and even higher N_2O emissions occurred when biochar was input. Additionally, as shown in Fig.1, Bm was more prone to stimulate PNR

1 and DEA, thus displaying lower mitigation ability than Bw. Second, compared with Bm, the C/N ratio was
2 approximately twofold in Bw (Table S1), presumably leading to more inorganic nitrogen being immobilized in biochar
3 with a higher C/N ratio (Ameloot et al., 2015), decreasing the available N for microorganisms. Last, as presented in Fig.
4 S3 and Table S1, Bw had more pores and surface area, having a better advantage over Bm in absorbing NO accordingly.
5 Others have found that the lower mitigation capacity of high-N biochars (e.g., manures or biosolids) is probably due to
6 the increased N release in the soil from the biochar (Schouten et al., 2012). To our knowledge, very few studies have
7 investigated biochar effects on NO emissions (Nelissen et al., 2014; Obia et al., 2015), and the mechanisms through
8 which biochar influence NO emissions are not elucidated yet. Therefore, more research is needed to clarify the
9 underlying mechanisms of biochar on NO emission.

10 Intensive managed soils receiving fertilizer such as urea or anhydrous NH₃ and ruminant urine patches are potential
11 hot spots for NH₃ formation, where the use of biochar is expected to retain NH₃-N in the soil system (Clough and
12 Condon, 2010). Actually, the effects of biochar amendments on NH₃ volatilization largely depend on soil characteristics,
13 biochar types and duration time. Soil texture is an important factor impacting NH₃ transfer and release. More clay
14 contents were present in the ~~Anthrosol SX soil~~ (Table S1), which was limited in large soil pores, thus, the addition of
15 porous biochar could enhance the soil aeration, promoting NH₃ volatilization (Sun et al., 2014). Additionally, it was
16 worthy to note that cumulative NH₃ emissions were slightly higher in soils with the Bm than those with the Bw
17 amendment (Fig. 4 and Table 3c) and that difference could presumably be attributed to less surface area and the much
18 higher pH of Bm (Fig. S3 and Table S1), resulting in weak adsorption and great liming effects. ~~Overall, compared with
19 previous studies (Ro et al., 2015; Mandal et al., 2016), no significant reductions were found in cumulative NH₃
20 volatilizations over the whole observation period when biochar was added to current vegetable soils. In general, freshly
21 produced biochar typically has very low ability to absorb ammonium (Yao et al., 2012). Over time, biochar surfaces are
22 oxidized and increase adsorption (Wang et al., 2016). Moreover, the recorded increase in CEC by Cheng et al. (2006)
23 indicated that biochars that are sufficiently weathered over a period would increase their ability to retain cations such as
24 NH₄⁺-N. Further, relatively long term experiments are required to elucidate the mechanism and duration of effect.~~

25 4.2. Biochar effects on vegetable yield and *GNrI* across different soil types

26 The application of biochar is usually intended to increase crop yields, and evidence suggests this may be successful
27 (Schulz et al., 2013; Li et al., 2016). Due to its liming effect, biochar helps to improve the supply of essential macro- and
28 micronutrients for plant growth (Chan and Xu, 2009; Major et al., 2010). Enhancement of vegetable yield with biochar
29 amendment occurred in ~~CambisolSD~~ and ~~PhaeozemHLJ soils~~ (Table 3e). ~~Additionally, the effects of Bm and Bw on
30 vegetable yield was were mixed inconsistent, which probably due to performance of biochars as an amendment is related~~

1 ~~to the wide diversity of physicochemical characteristics of biochar that translates into variable reactions in soil (Novak et~~
2 ~~al., 2014). First, compared to Bw, more DOC content was in the Bm has a higher DOC content (Table S1), through which~~
3 ~~more nutrients may be directly introduced to the soil (Rajkovich et al., 2012). In addition, besides their large~~
4 ~~amount of plant-available nutrients (Hass et al., 2012), manure-biochars produced with manure have been generally~~
5 ~~considered significant for improving soil fertility by promoting soil structure development (Joseph et al., 2010), with the~~
6 ~~result that Bm was found superior to Bw in vegetable production enhancement in our case (Table 3e). As biochar effects~~
7 ~~on vegetable yield were variable, both biochar properties and soil conditions and crop species ought to be taken into~~
8 ~~account comprehensively before applying biochar to a certain soil condition.~~

9 However, no promotion of yield was observed with biochar amendments in ~~AcrisolHN~~ and ~~AnthrosolSX~~. This
10 could be attributed to exacerbated soil salinity, which inhibited the uptake of nutrients and water (Ju et al., 2006; Zhou et
11 al., 2010) and the growth of the soil microorganisms (Setia et al., 2011), leading to unsustainable greenhouse vegetable
12 production. Compared with other biochar (Jia et al., 2012), the higher amounts of ash in Bw and Bm may contain high
13 salts causing soil salinity (Hussain et al., 2016). After the addition of the two salt-rich biochars, the EC values of
14 ~~AcrisolHN~~ and ~~AnthrosolSX~~ vegetable soils increased and reached the limits to tolerance for the leafy vegetables
15 (Shannon and Grieve, 1998). ~~Additionally, the mixed performance of biochars as an amendment is related to the wide~~
16 ~~diversity of physicochemical characteristics that translates into variable reactions in soil (Novak et al., 2014). First,~~
17 ~~compared to Bw, more DOC content was in the Bm (Table S1), through which more nutrients may be directly introduced~~
18 ~~to the soil (Rajkovich et al., 2012). In addition, besides their large amount of plant available nutrients (Hass et al., 2012),~~
19 ~~manure biochars have been generally considered significant for improving soil fertility by promoting soil structure~~
20 ~~development (Joseph et al., 2010), with the result that Bm was found superior to Bw in vegetable production~~
21 ~~enhancement (Table 3e). As biochar effects on vegetable yield were variable, both biochar properties and soil conditions~~
22 ~~and crop species ought to be taken into account comprehensively before applying biochar to a certain soil condition.~~

23 Here, we assessed two feedstock-derived biochar effects on GN_rI in typical cultivated vegetable soils across
24 mainland China. Overall, biochar amendments reduced GN_rI over all the soils, with the magnitude largely depending on
25 soil type. Remarkable reduction in GN_rI had been detected due to the efficient mitigation induced by biochar in
26 ~~AnthrosolSX~~ and ~~PhaeozemHLJ~~ (Table 3f). However, despite enhanced vegetable yield, no significant decreases in GN_rI
27 were observed in ~~CambisolSD~~, mainly because of the absence of mitigation effects on N₂O, NO and NH₃ emissions of
28 biochars (Table 3a, b and c). ~~Additionally, Overall, divergent influences on GNE and yield were determined with different~~
29 ~~biochars that Bw was superior to Bm in mitigating the GN_rE while Bm performed better in vegetable yield enhancement~~
30 ~~(Table 3d and e). Therefore, mitigation efficacy on GN_rI were not notably different between Bw and Bm amendments~~

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

1 **5. Conclusion**

2 The study demonstrated that biochar amendments ~~mostly generally~~ reduced N₂O and NO emissions ~~(except for~~
3 ~~CambisolSD soil) without influencing and slightly increased~~ the NH₃ emissions, while produced no consensus influences
4 on yield though those effects were largely both biochar- and soil-specific. Additionally, biochar amendments did decrease
5 GNrI in intensive vegetable soils across mainland China. Furthermore, Bw was superior to Bm in mitigating the GNrE
6 whereas the Bm performed better in crop yield throughout all soils. Consequently, both soil type and biochar
7 characteristics need to be seriously considered before large-scale biochar application under certain regions of intensive
8 vegetable production.

1 **Acknowledge**

2 [We would like to express our heartfelt gratitude to the anonymous reviewer for the constructive comments that greatly](#)
3 [improved the manuscript.](#) This work was jointly supported by the National Natural Science Foundation of China
4 (41471192), Special Fund for Agro-Scientific Research in the Public Interest (201503106) and the Ministry of Science
5 and Technology (2013BAD11B01).

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1 **Table legends**

2 **Table 1**

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

Soil	Treatment	SOC (g kg ⁻¹)	TN (g kg ⁻¹)	pH	EC (ds m ⁻¹)	MBC (mg kg ⁻¹)
<u>AcrisolHN</u>	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
<u>AnthrosolSX</u>	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
<u>CambisolSD</u>	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
<u>PhaeozemHLJ</u>	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.	**

5 Data shown are means ± standard deviations of three replicates. See Fig. 1 for treatments codes. Different letters within
 6 the same column indicate significant differences among treatments within the same soil at $p < 0.05$ level.
 7 ***Significant at $p < 0.001$; **significant at $p < 0.01$; *significant at $p < 0.05$; n.s. not significant.

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1 **Table 2**

2 Two-way ANOVA and mean effects of biochar (Bc) and soil (S) types on cumulative ~~gaseous nitrogen~~ (N₂O, NO and NH₃) emissions, gaseous reactive nitrogen emission
 3 (GN_rE), vegetable yield and gaseous reactive nitrogen intensity (GN_rI) during the entire sampling period.

Factors	DF	N ₂ O emission			NO emission			NH ₃ emission			GN _r E			Vegetable yield			GN _r I		
		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			0.2		
biochar effect (n = 12)																			
N mean		12.01±1.44a			2.86±0.24a			5.925.63 ±0.24 72a			20.50±1.60a			43.81±5.82a			0.57±0.05a		
N+Bw mean		7.01±0.58b			1.55±0.14b			6.6.3765 ±0.27 1.02a			14.94±0.84b			43.53±6.31a			0.45±0.04b		
N+Bm mean		10.37±0.56a			1.55±0.10b			7.046.68 ±0.25 1.10a			18.60±0.65a			49.53±6.91a			0.49±0.03ab		
Soil effect (n = 9)																			
AcrisolHN mean		27.20±1.85a			5.80±0.50a			5.31±0.16c			38.04±1.90a			33.06±1.65c			1.15±0.11a		
AnthrosolSX mean		4.89±0.45b			1.08±0.13b			12.69±0.46a			12.69±0.46b			25.05±1.11d			0.51±0.01b		
CambisolSD mean		2.25±0.26c			0.25±0.09c			9.51±0.55b			9.51±0.55c			44.88±0.49b			0.21±0.01c		
PhaeozemHLJ mean		4.48±0.68b			0.81±0.04b			11.79±0.71a			11.79±0.71b			79.50±2.41a			0.15±0.01c		

4 SS: the sum of squares.

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

6 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.

7 n.s.: not significant.

8 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
 9 among treatments at $p < 0.05$ level.

1 **Table 3**

2 Cumulative gaseous nitrogen (N₂O, NO and NH₃) emissions, gaseous reactive nitrogen emission (GN_rE), vegetable yield
 3 and gaseous reactive nitrogen intensity (GN_rI) under the different treatments across the four soils.

Treatments	<u>AcrisolHN</u>	<u>AnthrosolSX</u>	<u>CambisolSD</u>	<u>PhaeozemHLJ</u>
(a) Cumulative N ₂ O emissions (kg N ha ⁻¹)				
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) Cumulative NO emissions (kg N ha ⁻¹)				
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
(c) Cumulative NH ₃ emissions (kg N ha ⁻¹)				
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
(d) GN _r E (kg N ha ⁻¹)				
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
(e) Vegetable yield (t ha ⁻¹)				
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
(f) GN _r I (kg N t ⁻¹ yield)				
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

4 Data shown are means ± standard deviations of the three replicates. See Fig. 1 for treatments codes. Different letters
 5 within the same column indicate significant differences among treatments within the same soil at $p < 0.05$ level.

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1 **Table 4**

2 The correlations between N₂O or NO emission and PNR or DEA in each soil.

Item	<u>AcrisolHN</u>		<u>AnthrosolSX</u>		<u>CambisolSD</u>		<u>PhaeozemHLJ</u>	
	PNR	DEA	PNR	DEA	PNR	DEA	PNR	DEA
N ₂ 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

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

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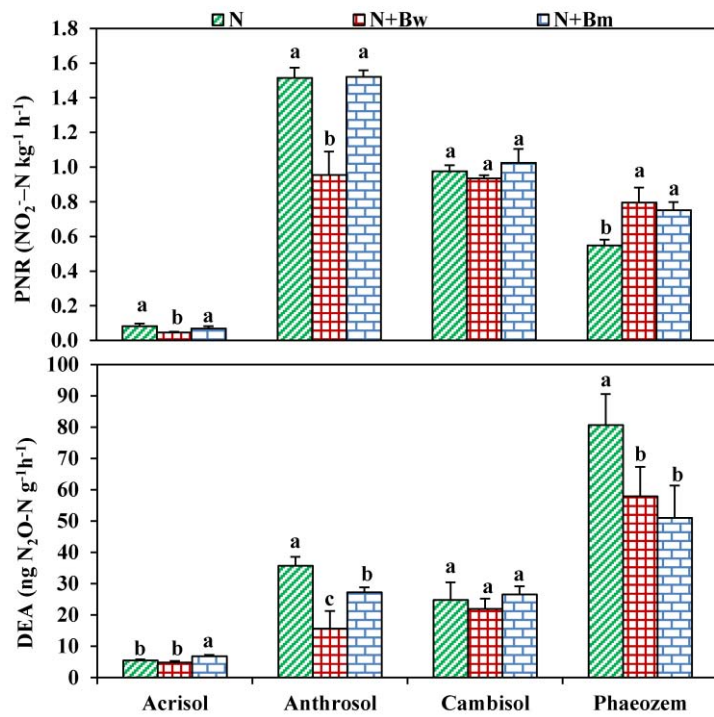
1 **Figure legends**

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

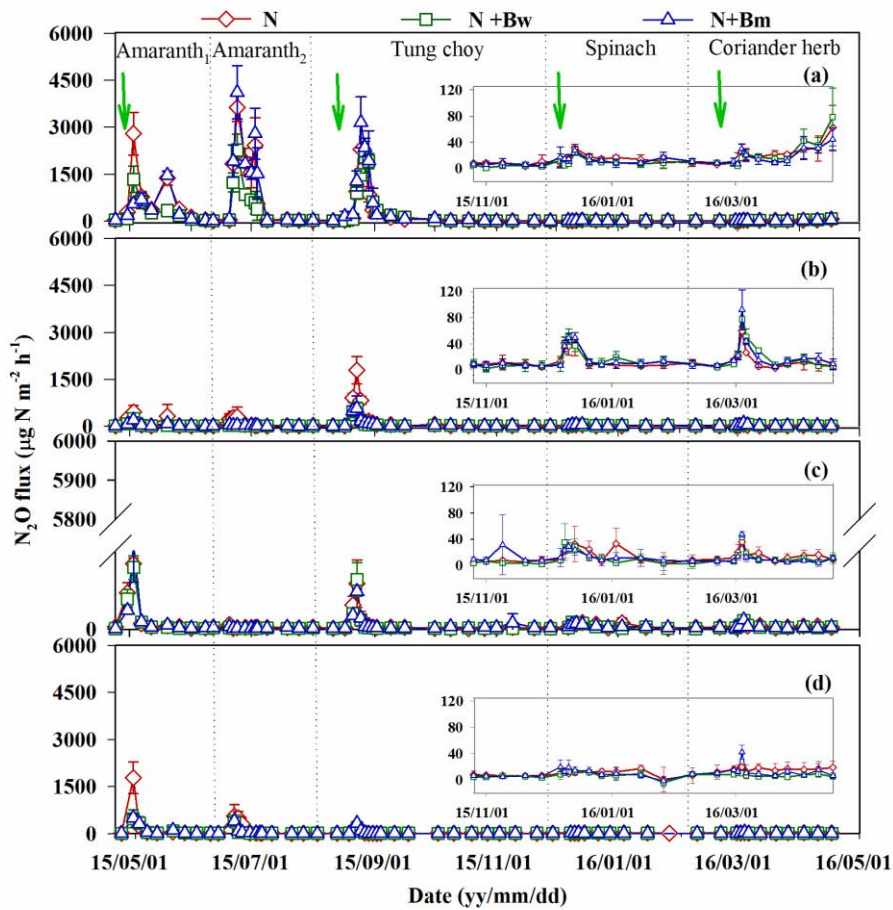
7 **Fig. 2** Temporal dynamics of soil N_2O ($\mu\text{g N m}^{-2} \text{h}^{-1} \pm \text{SD}$, n = 3) fluxes under different treatments in AcrisolHN (a),
8 AnthrosolSX (b), CambisolSD (c) and PhaeozemHLJ (d) vegetable soils with five consecutive vegetable crops. The solid
9 arrows indicate fertilization.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

10 **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 AcrisolHN (a),
11 AnthrosolSX (b), CambisolSD (c) and Phaeozem HLJ (d) vegetable soils with five consecutive vegetable crops. The
12 solid arrows indicate fertilization. See Fig. 1 for treatments codes.

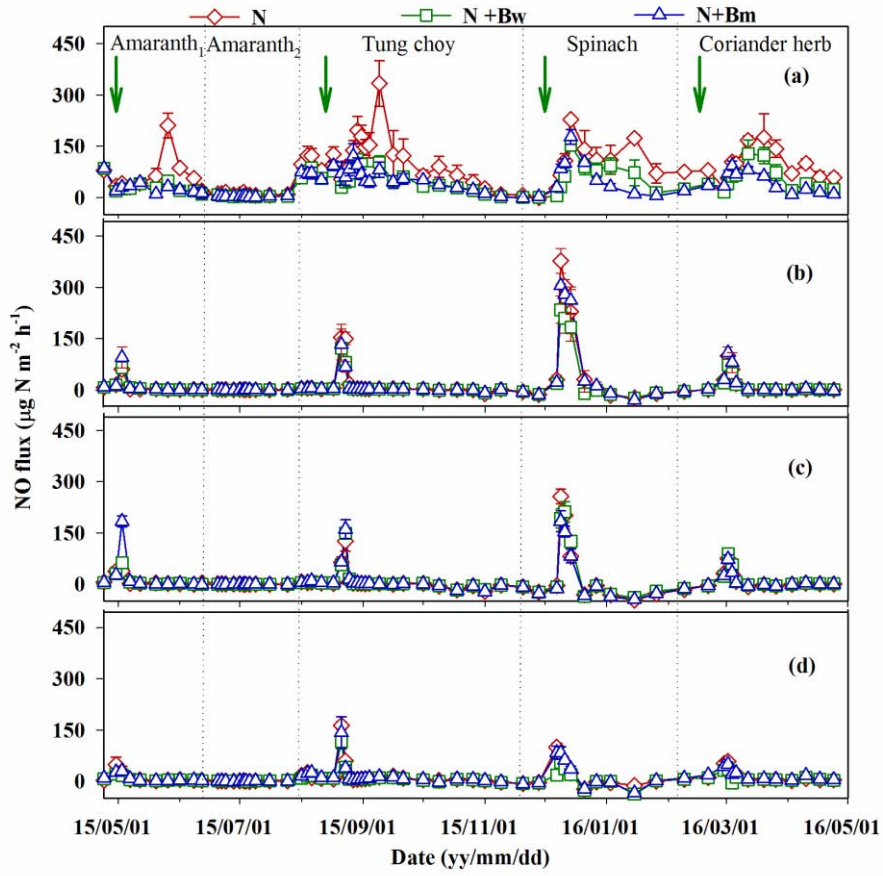
13 **Fig. 4** Cumulative ammonia (NH_3) emissions from the AcrisolHN (a), AnthrosolSX (b), CambisolSD (c) and
14 PhaeozemHLJ (d) soils during the four nitrogen fertilization events F: every N fertilization event. The bars indicate the
15 standard deviation of the mean ($\text{kg N ha}^{-1} \pm \text{SD}$,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



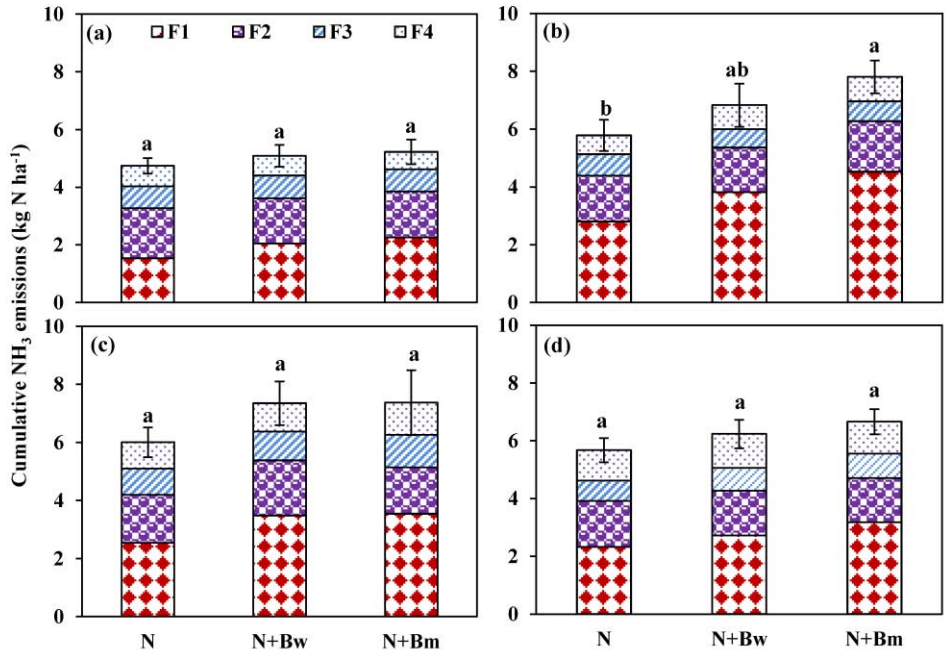
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