

1 **Biochar reduces yield-scaled emissions of reactive nitrogen gases from**
2 **vegetable soils across China**

3 Changhua Fan, Hao Chen, Bo Li, Zhengqin Xiong*

4 Jiangsu Key Laboratory of Low Carbon Agriculture and GHGs Mitigation, College of Resources and Environmental
5 Sciences, Nanjing Agricultural University, Nanjing 210095, China



6 *Corresponding author (Z. Xiong): E-mail: zqxiong@njau.edu.cn;

7 Tel: +86-25-84395148; Fax: +86-25-84395210

1 **Highlights**


- 2 1. We measured the biochar effects on yield and Nr emissions in four Chinese vegetable soils.
- 3 2. Biochar affects gaseous Nr or yield largely depending on soil types.
- 4 3. Straw biochar mainly mitigated gaseous Nr and manure biochar mainly 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. However, few studies have compared the general effect of different feedstock-derived
4 biochars on the various gaseous reactive nitrogen emissions (GNr ₂O, NO and NH₃) simultaneously across the typical
5 vegetable soils in China. A greenhouse pot experiment with five consecutive vegetable crops was conducted to
6 investigate the effects of two contrasting biochar nely, wheat straw biochar (Bw) and swine manure biochar (Bm) on
7 GNrE, vegetable yield and gaseous reactive nitrogen intensity (GNrI) in four typical soils which are representative of the
8 intensive vegetable cropping systems across mainland China: an Acrisol from Hunan province, an Anthrosol from Shanxi
9 province, a Cambisol from Shandong province and a Phaeozem from Heilongjiang province. Results showed that
10 remarkable GNrE mitigation induced by biochar occurred in Anthrosol and Phaeozem, whereas enhancement of
11 yield occurred in Cambisol and Phaeozem. Additionally, both biochars decreased GNrI through reducing N₂O and
12 NO emissions by 36.4–59.1 % and 37.0–49.5 % for Bw (except for Cambisol), respectively, and by improving yield by
13 13.5–30.5 % for Bm (except for Acrisol and Anthrosol). Biochar amendments generally stimulated the NH₃ emissions
14 with greater enhancement from Bm than Bw. We can infer that the biochar's effects on the GNrE and vegetable yield
15 strongly depend on the attributes of the soil and biochar. Therefore, in order to achieve the maximum benefits under
16 intensive greenhouse vegetable agriculture, both soil type and biochar characteristics should be seriously considered
17 before conducting large-scale biochar applications.

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

1 **1 Introduction**

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

18 In China, vegetable production devotes an area of approximately 24.7×10^6 ha, equivalent to 12.4% of the total
19 available cropping area, and the production represented 52 % of the world vegetable production in 2012 (FAO, 2015).
20 Intensified vegetable cultivation in China is characterized by high N application rates, high cropping index and frequent
21 farm practices. Annual N fertilizer inputs for intensively managed vegetable cultivation are 3–6 times higher than in
22 cereal grain cultivation in China (Ju et al., 2006; Diao et al., 2013; Wang et al., 2015a). As a result, great concern exists
23 about excess N fertilizer application  leading to low use efficiency in intensive vegetable fields in China (Deng et al.,
24 2013; Diao et al., 2013; Li et al., 2016). Meanwhile, intensive vegetable agriculture is considered to be an important
25 source of N₂O (Xiong et al., 2006; Jia et al., 2012; Li et al., 2015b; Zhang et al., 2015) and NO production (Mei et al.,
26 2009). Moreover, NH₃ volatilization is another important N pathway in fertilized soil, resulting in large losses of
27 soil-plant N (Pacholski et al., 2008; Zhang et al., 2011). Therefore, the reduction of reactive N loss is key to meet the
28 joint challenges of high production and acceptable environmental consequences from intensive vegetable production
29 (Zhang et al., 2013).

30 Biochar is the dark-colored, carbon (C)-rich residue of pyrolysis or gasification of plant biomass under oxygen

1 (O₂)-limited conditions, specifically produced for use as a soil amendment (Sohi, 2012). The amendment of agricultural
2 ecosystems with biochar has been proposed as an effective countermeasure for climate change (Smith, 2016). These
3 additions have been suggested to increase soil carbon storage (Mukherjee and Zimmerman, 2013; Stavi and Lal, 2013),
4 decrease greenhouse gas emissions (Li et al., 2016), and improve soil fertility and crop production (Major et al., 2010;
5 Liu et al., 2013). However, some recent studies have reported no difference or even an increase in soil N₂O emissions
6 induced by biochar application for various soils (Saarnio et al., 2013; Wang et al., 2015a). Besides, NH₃ volatilization
7 was enhanced by biochar application in pasture soil (Clough et al., 2010), vegetable soil (Sun et al., 2014) and paddy soil
8 in the wheat-growing season (Zhao et al., 2014). Additionally, crop productivity responses to biochar amendments
9 differed among various biochars (Cayuela et al., 2014). These inconsistent results suggest that current biochar application
10 to soil is not a “one-size fit-all paradigm” because of the variation in the physical and chemical characteristics of the
11 different biochars, soil types and crop species (Field et al., 2013; Cayuela et al., 2014). Moreover, limited types of
12 biochar (Spokas and Reicosky, 2009) and soil (Sun et al., 2014) were involved in the experiments in previous studies.
13 Thus, the evaluation of the different types of biochar under the typical soils is imperative to gain a comprehensive
14 understanding of potential interactions before the large-scale application of biochars.

15 Therefore, a greenhouse pot experiment was conducted in an effort to investigate the effects of different types of
16 biochar on gaseous reactive nitrogen emissions (GNrE), namely, N₂O, NO and NH₃, simultaneously in four intensively
17 cropped vegetable soils across main vegetable production areas of mainland China. We hypothesized that: 1) biochar
18 amendment could affect GNrE, vegetable yield and yield-scaled gaseous reactive nitrogen emissions, namely, gaseous
19 reactive nitrogen intensity (GNrI) in vegetable soils across mainland China, 2) those influences would vary among
20 biochar and soil types. Overall, the objectives of this research were to gain a comprehensive insight into the effects of
21 two contrasting biochars on the GNrE, vegetable yield and 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): 1. a Phaeozem from Jiamusi
5 (46°48' N, 130°12' E) in the Heilongjiang province, 2. an Anthrosol from Yangling (34°18' N, 108°2' E) in the Shanxi
6 province, 3. an Acrisol from Changsha (28°32' N, 113°23' E) in the Hunan province, 4. a Cambisol from Shouguang
7 (36°56' N, 118°38' E) in the Shandong province (FAO and ISRIC, 2012). Those four types of vegetable soil represented
8 a range of differences in physicochemical properties and regions (Table S1). Soil samples were manually collected from
9 the cultivated layer (0–20 cm) after the local vegetable harvest in April, 2015. The samples were air-dried and passed
10 through a 5 mm stainless steel mesh sieve and homogenized thoroughly. Any visible roots and organic residues were
11 removed manually before being packed with the necessary amount of soil to achieve the initial field bulk density. Each
12 pot received 15 kg of 105 °C dry-weight-equivalent fresh soil. For each of the biochar amendment pot, 282.6 g pot⁻¹
13 sieved biochar (2 mm) was mixed with the soil thoroughly before the experiment, which was equivalent to a 40 t ha⁻¹
14 biochar dose (dry weight). No more biochar was added later in the experimental period.

15 The two types of biochar that were used in this experiment are derived from two common agricultural wastes in
16 China: wheat straw and swine manure, hereafter referred to as Bw and Bm, respectively (Table S1). The Bw was
17 produced at the Sanli New Energy Company in Henan, China, by pyrolysis and thermal decomposition at 400–500 °C.
18 The Bm was produced through thermal decomposition at 400 °C by the State Key Laboratory of Soil Science and
19 Sustainable Agricultural, Institute of Soil Science, Chinese Academy of Sciences. In accordance with Lu (2000), soil
20 organic carbon (SOC) was measured by wet digestion with H₂SO₄–K₂Cr₂O₇, total nitrogen (TN) was determined by
21 semi-micro Kjeldahl digestion, and soil texture was determined with the pipette method. The soil pH and biochar pH
22 were measured in deionized water at a volume ratio of 1:2.5 (soil to water) with a PHS-3C mv/pH detector (Shanghai
23 Kangyi Inc. China). Biochar content of hydrogen (H) was measured by elemental analysis after dry combustion (Euro
24 EA, Hekatech GmbH, Wegberg, Germany). The oxygen content of biochar was measured with the same device after
25 pyrolysis of the sample at 1000 °C followed by reduction of the evolved O₂ to CO and quantified by GC-TCD. The soil
26 nitrate (NO₃⁻-N) and ammonium (NH₄⁺-N) were measured following the two-wavelength ultraviolet spectrometry and
27 indophenol blue method, respectively, using an ultraviolet spectrophotometer (HITACHI, UV-2900, Tokyo, Japan).
28 Electric conductivity (EC) was measured by using a Mettler-Toledo instrument (FE30-K, Shanghai, China) at a 1:5 (w:v)
29 soil to water ratio. Cation exchange capacity (CEC) was determined using the CH₃COONH₄ method. Dissolved organic
30 carbon (DOC) was extracted from 5 g of the biochar/soil with an addition of 50 ml deionized water and measured by a

1 TOC analyzer (TOC-2000/3000, Metash Instruments Co., LTD, Shanghai, China). Ash content was measured by heating
2 the biochars at 750 °C for 4 h. The specific surface area of the biochar material was tested using the Brunauer–Emmett–
3 Teller (BET) method, from which the N adsorption–desorption isotherms at 77 K were measured by an automated gas
4 adsorption analyzer ASAP2000 (Micromeritics, Norcross, GA) with + 5% accuracy. Scanning electron microscopy (SEM)
5 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 random design: urea without biochar (N), urea with
10 wheat straw biochar (N+Bw), urea with swine manure biochar (N+Bm). In addition, phosphate and potassium fertilizers
11 in the form of calcium magnesium phosphate and potassium chloride, together with urea, were broadcasted and mixed
12 with soil thoroughly prior to sowing the vegetables. No topdressing events occurred because of the frequent cultivation
13 and short growth period for the leafy vegetables. Based on the vegetable growth, all pots received equal amounts of water
14 and no precipitation. Detailed information on the pot management practices is provided in Table S2.

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

19 *2.3. Measurement of N₂O, NO and NH₃*

20 The NO and N₂O fluxes were measured simultaneously from each vegetable cultivation using a static opaque
21 chamber method (Zheng et al., 2008; Yao et al., 2009). A square PVC chamber of 35 cm × 35 cm × 40 cm (length ×
22 width × height) was temporarily mounted on the pot for gas flux measurement. The chamber was coated with sponge and
23 aluminum foil outside to prevent solar radiation heating the chamber. Gas samples for flux measurements were collected
24 between 8 and 10 a.m. on each measuring day to minimize the influence of diurnal temperature variation. Gas fluxes
25 were usually measured once a week and every other day for one week following fertilizer application. To measure the
26 N₂O flux, four samples were collected from the headspace chamber using 20 ml polypropylene syringes at 0, 10, 20, and
27 30 min after chamber closure. The gas concentrations in the samples were analyzed within 12 h after sampling using an
28 Agilent 7890A gas chromatograph equipped with an electron capture detector (ECD) for N₂O detection. Argon-methane
29 (5 %) was used as the carrier gas at a flow rate of 40 ml min⁻¹. The column and ECD temperatures were maintained at 40
30 and 300 °C, respectively. The gas chromatography configurations described by Wang et al. (2013) were adopted for the

1 gas concentration analysis. N₂O flux was calculated using the linear increases in gas concentration with time. Sample sets
2 were rejected unless they yielded a linear regression value of R² > 0.90.

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

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

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

22 Cumulative fluxes of N₂O, NO and NH₃ were added to calculate total gaseous reactive nitrogen gas emissions
23 (GNrE):

$$24 \text{GNrE} = \text{cumulative N}_2\text{O} + \text{cumulative NO} + \text{cumulative NH}_3 \text{ emissions (kg N ha}^{-1}\text{)} \quad (1)$$


25 2.4. Auxiliary measurements

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

1 $WFPS = \text{volumetric water content (cm}^3 \text{ cm}^{-3}) / \text{total soil porosity (cm}^3 \text{ cm}^{-3})$ (2)

2 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).

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

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

6 $GNrI = GNrE / \text{vegetable fresh yield (kg N t}^{-1} \text{ yield)}$ (3)

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

13 *2.5. Data processing and statistics*

14 Two-way ANOVA was used to analyze the effects of the biochar type, soil type, and their interactions on soil
15 properties, N₂O, NO and NH₃ emissions, vegetable yield, GNrE and GNrI throughout the experimental period. Multiple
16 comparisons among the treatments were assessed using Tukey's HSD test. Significant differences were considered at $P <$
17 0.05. All statistical analyses were performed using JMP ver. 7.0 (SAS Institute, Cary, NC, USA, 2007). Pearson's
18 correlation analysis was used to determine whether there were significant interrelationships between N₂O/NO and PNR
19 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 Appreciable differences in all observed soil properties existed among soil types (Table 1), reflecting the wide
4 variations of soil characteristics 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 increased SOC and TN by 5.8–20.5 % and 9.5–14.2 % ($p < 0.05$), respectively, whereas EC values were higher by 3.3–
8 21.5 % induced by Bw than Bm amendment over all soils. Additionally, biochar amendments significantly increased soil
9 pH by 0.27–0.64 and 0.08–0.10 units compared with N treatment in Acrisol and Anthrosol soils ($p < 0.05$), respectively,
10 and Bm performed better than Bw on increasing soil pH in Acrisol. Furthermore, biochar amendments tended to increase
11 MBC in Cambisol and Phaeozem, and Bm increased MBC relative to Bw in all soils.

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

18 *3.2. Seasonal variations of N₂O and NO emissions*

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

28 Clearly, the NO fluxes demonstrated similar seasonal dynamics to the N₂O fluxes (Fig. 3). Some relatively high
29 peak NO fluxes were still observed in the Spinach and Coriander herb planting seasons even though relatively low
30 temperatures occurred during these periods. NO fluxes ranged from -44.6 to 377.6 $\mu\text{g N m}^{-2} \text{h}^{-1}$ across all soil types.

1 Furthermore, some NO peaks were significantly weakened with the Bw and Bm in the Acrisol (Fig. 3a).

2 3.3. Cumulative N₂O, NO and NH₃ emissions

3 Cumulative N₂O emissions varied greatly among soil types (Table 3a, $p < 0.05$), from 1.97 to 31.56 kg N ha⁻¹ ac
4 all the soils during the vegetable cultivation period. Biochar amendments had significant influences on the cumulative
5 N₂O emissions (Table 2, $p < 0.001$). In comparison with the N treatment, bioch
6 effects on N₂O emissions over all soils (Table 3a), indicating significant interactions between biochar and soil types
7 (Table 2, $p < 0.001$). Additionally, Bw amendment decreased N₂O emissions by 11.8–38.4 % across all the soils i
8 relation to Bm, indicating that Bw performed better mitigation effects than Bm across all the soils, significantly in
9 Acrisol (Table 3a, $p < 0.05$). The values of cumulative NO emissions were much smaller than those of N₂O emissions,
10 with a remarkable variation of 0.20–8.99 kg N ha⁻¹ across all soils (Table 3b). Biochar amendments had pronounced
11 effects on NO emissions (Table 2, $p < 0.001$), but their effects differed between vegetable soils (Table 3b), which
12 suggested significant interactions between biochar and soil types (Table 2, $p < 0.001$). Compared with Bm, Bw
13 amendment significantly reduced NO emissions in Anthrosol and Phaeozem (Table 3b, $p < 0.05$). Moreover, N₂O
14 emissions had positive relationships with DEA both in Anthrosol and Phaeozem, and were affected positively with PNR
15 in Acrisol (Table 4). Additionally, NO emissions had positive correlations with both PNR and DEA in Anthrosol.
16 However, neither N₂O nor NO emissions were influenced significantly by PNR and DEA in Cambisol.

17 As is shown in Table 3c, the cumulative NH₃ emissions fluctuated greatly from 4.72–7.57 kg N ha⁻¹ across all the
18 soils. Biochar amendments produced no significant influences on the NH₃ emissions relative to N treatment in most soils
19 (Table 3c). A tendency was found for the cumulative NH₃ emissions in Bm to be higher than those in the Bw treatment,
20 although this difference was not remarkable within each soil. Additionally, stimulation effects were consistently present
21 after the first fertilization event in each type of soil (Fig. 4).

22 3.4. Vegetable yield and gaseous reactive N intensity during the five-vegetable crop rotation

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

29 Table 3f presents the GNrI during the whole experiment period, with a pronounced variation among soils ($p < 0.05$).
30 The GNrI was greatly affected by biochar amendment during the whole experiment period (Table 2, $p < 0.01$). Compared

- 1 to N treatment, biochar amendments reduced the GNrI by 4.3–27.8 % across all soils, significantly in Anthrosol and
- 2 Phaeozem (Table 3f, $p < 0.05$). Moreover, there were no remarkable differences between Bw and Bm throughout all soils.

1 **4. Discussion**

2 *4.1. Biochar effects on G_{NrE} 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 show a consistent 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 pH neutral, 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 stimulating denitrification enzyme activity, which then resulted in less NO accumulation relative to N₂
12 production. Moreover, the liming effects of biochar may have prevented the chemical decomposition of NO₂⁻ to NO
13 (Islam et al., 2008), leaving only enzymatically produced NO to accumulate. However, different from the other soils in
14 our experiment, neither N₂O nor NO emissions from the Cambisol were significantly influenced by PNR or DEA. This
15 finding suggests that processes other than nitrification and denitrification might play vital roles. Besides nitrification and
16 denitrification, nitrifiers denitrification (Wrage et al., 2001) and heterotrophic nitrification (Zhu et al., 2011) can be
17 important processes for producing N₂O/NO as well, especially in vegetable soils with low pH, low carbon content and
18 high N content (Wrage et al., 2001). Ma et al. (2015) speculated that nitrifier denitrification was the main process
19 producing N₂O in the North China Plain (Cambisol within this region). In addition, surplus N input in vegetable systems
20 probably masked the beneficial effects of the biochar addition on the N transformation (Wang et al., 2015a). Therefore,
21 future research needs to study the underlying mechanism of how biochar affects those processes.

22 Different biochars may not produce universal influences on N₂O emissions for the same soil due to the distinct
23 properties of the biochar (Spokas and Reicosky, 2009). In the current study, overall, in comparison with Bm, the Bw
24 amendment had more effective mitigation effects on N₂O and NO emissions (Table 3a, b), largely due to the following
25 reasons. First, compared to Bw, the contents of TN and DOC were 80% and 40% higher in Bm (Table S1), respectively,
26 which might supply extra N or C source for heterotrophic nitrification in the acidic Acrisol, leading Bm to being
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 with biochar addition. 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

1 higher in Bw (Table S1), presumably leading to more inorganic nitrogen being immobilized in biochar with a higher C/N
2 ratio (Ameloot et al., 2015), decreasing the available N for microorganisms. Last, as presented in Fig. S3 and Table S1,
3 Bw 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 Intensively managed soils receiving fertilizer such as urea or anhydrous NH₃ and ruminant urine patches are
10 potential hot spots for NH₃ formation, where the use of biochar is expected to retain NH₃-N in the soil system (Clough
11 and Condron, 2010). Our results show that the effects of biochar amendments on NH₃ volatilization largely depend on
12 soil characteristics and biochar types. Soil texture is an important factor impacting NH₃ transfer and release. High clay
13 contents in the Anthrosol (Table S1) likely limited soil porosity, thus, the addition of porous biochar could enhance the
14 soil aeration, promoting NH₃ volatilization (Sun et al., 2014). Additionally, it was worthy to note that cumulative NH₃
15 emissions were slightly higher in soils with the Bm than those with the Bw amendment (Fig. 4 and Table 3c) and that
16 difference could presumably be attributed to less surface area and the much higher pH of Bm (Fig. S3 and Table S1),
17 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 was probably due to large differences in physicochemical characteristics between the two
24 biochars. First, compared to Bw, Bm has a higher DOC content (Table S1), through which more nutrients may be directly
25 introduced to the soil (Rajkovich et al., 2012). Secondly, besides their large amount of plant-available nutrients (Hass et
26 al., 2012), biochars produced with manure have been generally considered significant for improving soil fertility by
27 promoting soil structure development (Joseph et al., 2010), with the result that Bm was found superior to Bw in vegetable
28 production enhancement in our case (Table 3e). As biochar effects on vegetable yield were variable, both biochar
29 properties and soil conditions and crop species ought to be taken into account comprehensively before applying biochar
30 to a certain soil condition.

1 However, no promotion of yield was observed with biochar amendments in Acrisol and Anthrosol. We speculate that
2 the lack of biochar effects on yield were caused by exacerbated soil salinity, which inhibited the uptake of nutrients and
3 water (Ju et al., 2006; Zhou et al., 2010) and the growth of the soil microorganisms (Setia et al., 2011). Compared with
4 other biochar (Jia et al., 2012), the higher amounts of ash in Bw and Bm may contain high salts, which would result in
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, which might reach the limits to tolerance for the leafy vegetables (Shannon and Grieve, 1998).
7 Here, we assessed two feedstock-derived biochar effects on GNrI in typical cultivated vegetable soils across mainland
8 China. 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). Overall, Bw was superior to Bm in mitigating the GNrE while Bm performed better in vegetable
11 yield enhancement (Table 3d and e). Therefore, the mitigation efficacies on GNrI were not notably different between Bw
12 and Bm 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 from four soils that are representative of vegetable cropping systems across mainland China. In contrast,
4 biochar amendments did not result in consistent effects on yield, with treatment effects that were both biochar- and
5 soil-specific. Additionally, biochar amendments did decrease GNrI in intensive vegetable soils across mainland China.
6 Furthermore, Bw was superior to Bm in mitigating the GNrE and the Bm performed better in crop yield throughout all
7 soils. Consequently, both soil type and biochar characteristics need to be seriously considered before large-scale biochar
8 application under certain regions of intensive vegetable production.

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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 for the effects of biochar (Bc) and soil (S) types on cumulative N₂O, NO and NH₃ emissions, gaseous reactive nitrogen emissions (GNrE), vegetable yield
3 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		

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.

1 **Table 3**

2 Cumulative gaseous nitrogen (N₂O, NO and NH₃) emissions, gaseous reactive nitrogen emissions (GNrE), vegetable
 3 yield 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±3.15aA	7.83±0.60aB	2.52±0.37aC	7.10±1.91aB
N+Bw	19.45±2.43bA	3.20±0.28bB	1.97±0.21aB	3.45±0.86bB
N+Bm	31.56±1.35aA	3.63±0.62bB	2.26±0.58aB	4.01±0.68bB
(b) Cumulative NO emissions (kg N ha ⁻¹)				
N	8.99±1.01aA	1.27±0.15aB	0.20±0.08aC	0.97±0.11aBC
N+Bw	4.54±0.60bA	0.80±0.13bB	0.33±0.19aB	0.52±0.03bB
N+Bm	3.87±0.30bA	1.16±0.17aB	0.21±0.10aC	0.94±0.03aB
(c) Cumulative NH ₃ emissions (kg N ha ⁻¹)				
N	4.72±0.27aB	5.79±0.54bA	6.34±0.51aA	5.67±0.42aA
N+Bw	5.09±0.38aB	6.83±0.74abA	7.35±0.75aA	6.24±0.49aAB
N+Bm	5.32±0.42aB	7.57±0.57aA	7.37±1.11aA	6.48±0.43aAB
(d) GNrE (kg N ha ⁻¹)				
N	44.30±3.13aA	14.89±1.33aB	9.06±0.80aC	13.74±1.67aB
N+Bw	29.08±2.21bA	10.82±1.14bB	9.64±0.88aB	10.21±0.92bB
N+Bm	40.76±1.66aA	12.36±0.74bB	9.84±0.49aC	11.42±0.27bBC
(e) Vegetable yield (t ha ⁻¹)				
N	35.20±2.52aB	25.29±3.90aC	39.09±2.03bB	75.65±5.84bA
N+Bw	29.05±2.35bC	23.57±1.74aC	44.53±3.74bB	76.95±4.04abA
N+Bm	34.93±2.87aC	26.30±2.63aD	51.00±3.18aB	85.89±3.29aA
(f) GNrI (kg N t ⁻¹ yield)				
N	1.27±0.18aA	0.59±0.08aB	0.23±0.02aC	0.18±0.04aC
N+Bw	1.01±0.12aA	0.46±0.05bB	0.22±0.04aC	0.13±0.02bC
N+Bm	1.17±0.15aA	0.47±0.04bB	0.19±0.01aC	0.13±0.01bC

4 Data shown are means ± standard deviations of the three replicates. See Fig. 1 for treatments codes. Different lowercase
 5 letters within the same column indicate significant differences among treatments within the same soil at $p < 0.05$ level.
 6 Different capital letters within the same row indicate significant differences among soil types within the same treatment
 7 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.

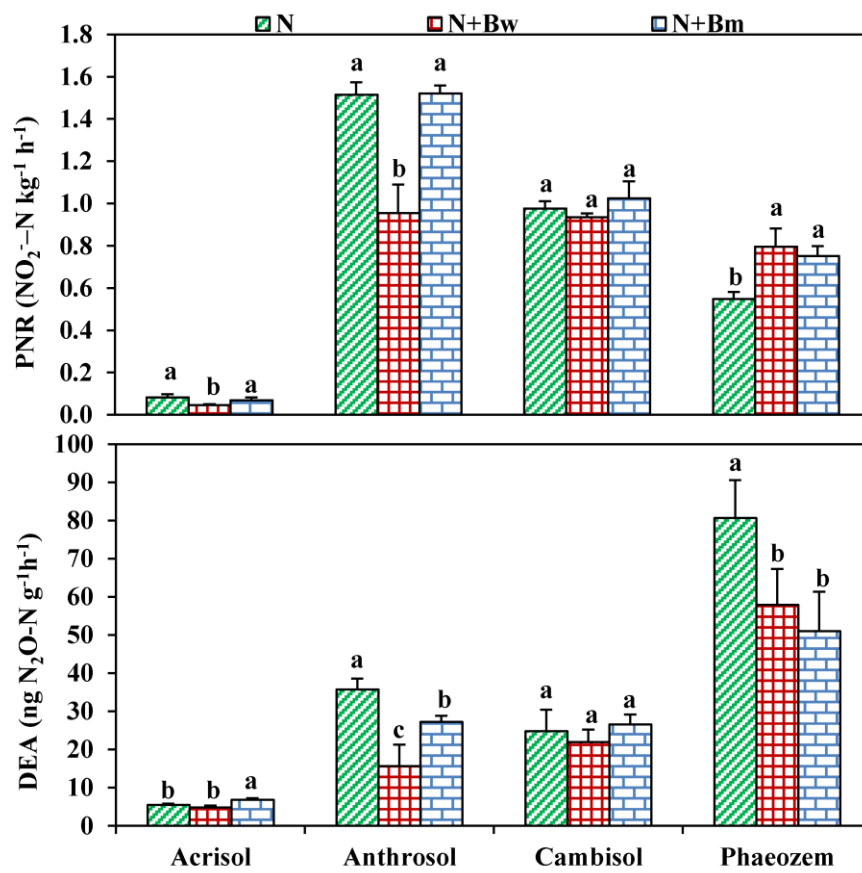
1 **Figure legends**

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 $p < 0.05$.

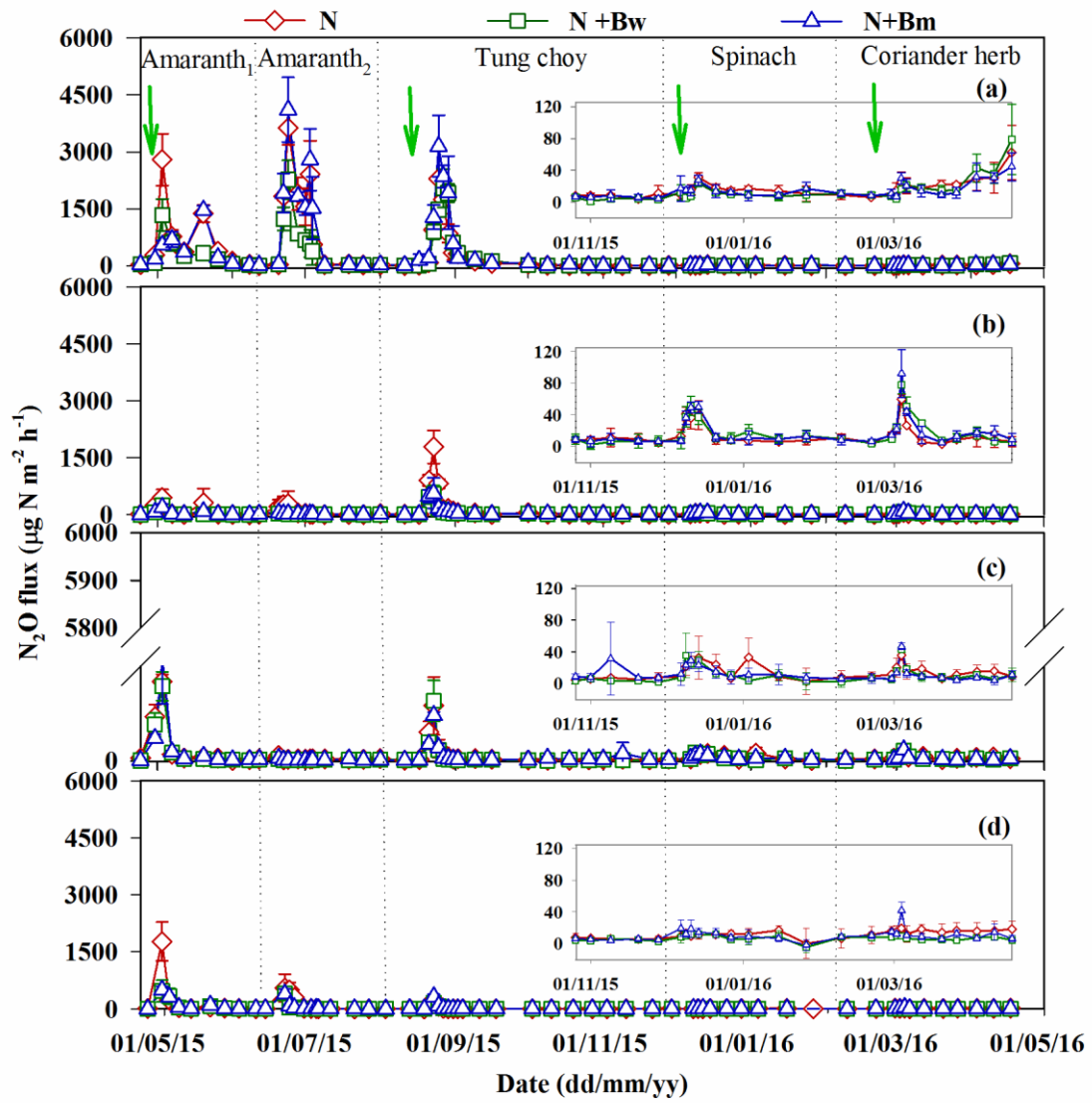
7 **Fig. 2** Temporal dynamics of soil N_2O ($\mu\text{g N m}^{-2} \text{h}^{-1} \pm \text{SD}$, n = 3) fluxes under different treatments in Acrisol (a),
8 Anthrosol (b), Cambisol (c) and Phaeozem (d) with five consecutive vegetable crops. The inserted panels describe the
9 N_2O fluxes during the last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

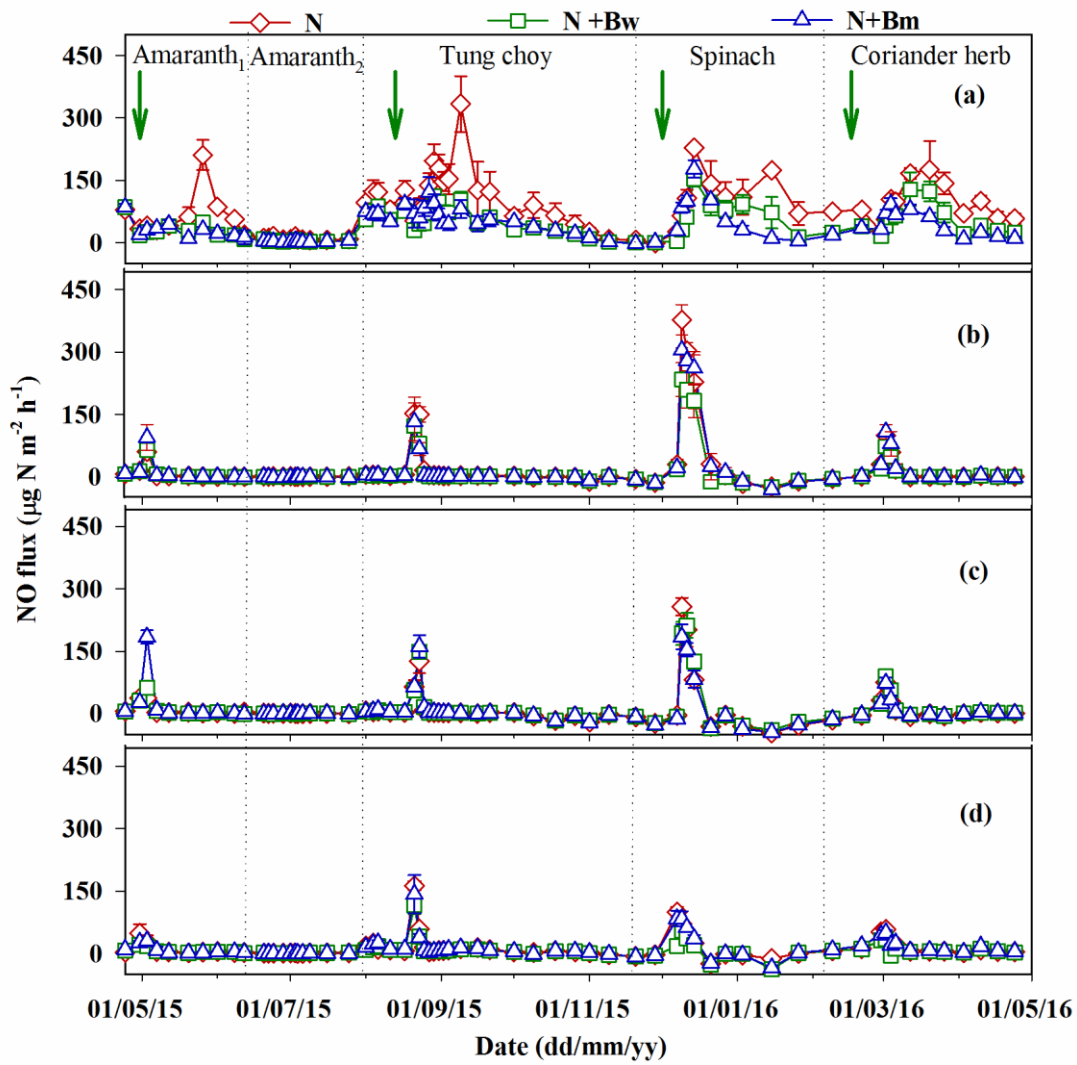
13 **Fig. 4** Cumulative ammonia (NH_3) emissions from the Acrisol (a), Anthrosol (b), Cambisol (c) and Phaeozem (d) during
14 the four nitrogen fertilization events F: every N fertilization event. The bars indicate the standard deviation of the mean
15 ($\text{kg N ha}^{-1} \pm \text{SD}$, n = 3) of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



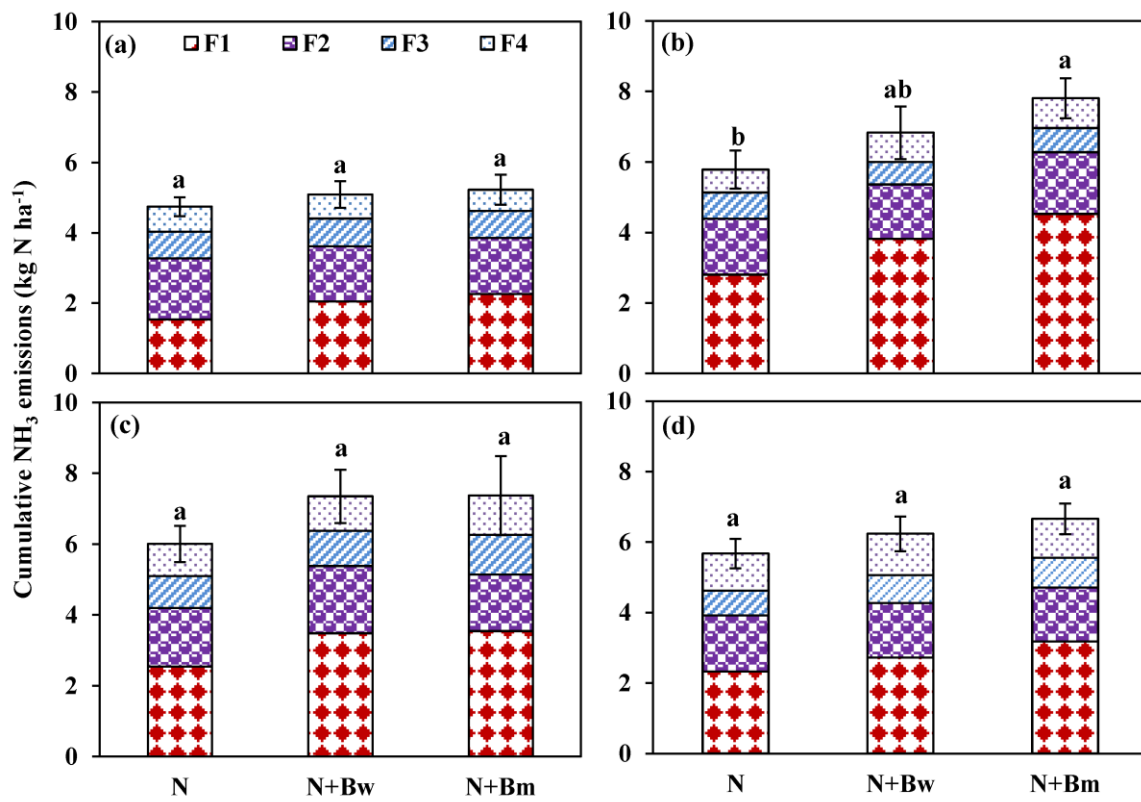
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