# Biochar reduces yield-scaled emissions of reactive nitrogen gases from vegetable soils across China

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

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

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

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

## Highlights

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

## Abstract

Biochar amendment to soil has been proposed as a strategy for sequestering carbon, mitigating climate change and enhancing crop productivity, but few studies have demonstrated the general effects of different feedstock-derived biochars on the various gaseous reactive nitrogen emissions (GNrEs, $N_2O$, NO and $NH_3$) simultaneously across the typical vegetable soils in China. A greenhouse pot experiment with five consecutive vegetable crops was conducted to investigate the effects of two contrasting biochar, namely, wheat straw biochar (Bw) and swine manure biochar (Bm) on GNrEs, vegetable yield and gaseous reactive nitrogen intensity (GNrI) in four typical vegetable soils from Acrisol (Hunan province), Anthrosol (Shanxi province), Cambisol (Shandong province) and Phaeozem (Heilongjiang province) which are representative of the intensive vegetable ecosystems across mainland China. Results showed that remarkable GNrE mitigation induced by biochar occurred in Anthrosol and Phaeozem, whereas enhancement of yield occurred in Cambisol and Phaeozem. Additionally, both biochars decreased GNrI through reducing $N_2O$ and NO emissions by 36.4–59.1 % and 37.0–49.5 % for Bw (except for Cambisol), respectively, while through improving yield by 13.5–30.5 % for Bm (except for Acrisol and Anthrosol). Biochar amendments generally stimulated the $NH_3$ emissions with greater enhancement from Bm than Bw. We can infer that the biochar's effects on the GNrEs and vegetable yield strongly depend on the attributes of the soil and biochar. Therefore, in order to achieve the maximum benefits under intensive greenhouse vegetable agriculture, both soil type and biochar characteristics should be seriously considered before conducting large-scale biochar applications.

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

## 1 Introduction

Agriculture accounts for an estimated emission of 4.1 (1.7–4.8) Tg N $yr^{-1}$ for nitrous oxide ($N_2O$) and 3.7 Tg N $yr^{-1}$ for nitric oxide (NO), contributing 60 % and 10 %, respectively, to the total global anthropogenic emissions, largely due to increases of nitrogen (N) fertilizer application in cropland (Ciais, 2013). The concentration of atmospheric $N_2O$, a powerful, long-lived, greenhouse gas, has increased from 270 parts per billion by volume (ppbv) in the pre-industrial era to ~ 324 ppbv (Ussiri and Lal, 2013); it has 265 times the global warming potential of carbon dioxide ($CO_2$) on a 100-year horizon (IPCC, 2013) and also causes depletion of the ozone layer in the atmosphere (Ravishankara et al., 2009). In contrast, $NO_x$, which is mainly emitted as NO, does not directly affect the earth's radiative balance but catalyzes the production of tropospheric ozone ($O_3$), which is a greenhouse gas associated with detrimental effects on human health (Anenberg et al., 2012) and crop production (Avnery et al., 2011). Finally, ammonia ($NH_3$) volatilization is one of the major N loss pathways (Harrison and Webb, 2001) as well, with up to 90% coming from agricultural activities (Misselbrook et al., 2000; Boyer et al., 2002). As a natural component and a dominant atmospheric alkaline gas, $NH_3$ plays an important role in atmospheric chemistry and ambient aerosol formation (Langridge et al., 2012; Wang et al., 2015b). In addition to nutrient enrichment (eutrophication) of terrestrial and aquatic systems and global acidification of precipitation, $NH_3$ has also been shown to be a major factor in the formation of atmospheric particulate matter and secondary aerosols (Kim et al., 2006; Pinder et al., 2007), leading to potentially adverse effects on human and ecosystem health such as visibility degradation and threats to biodiversity (Powlson et al., 2008; Behera et al., 2013).

In China, vegetable production devotes an area of approximately 24.7 × $10^6$ ha, equivalent to 12.4% of the total available cropping area, and the production represented 52 % of the world vegetable production in 2012 (FAO, 2015). Intensified vegetable cultivation in China is characterized by high N application rates, high cropping index and frequent farm practices. Annual N fertilizer inputs for intensively managed vegetable cultivation in rapidly developing areas 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 result, great concern exists about excess N fertilizer application, leading to low use efficiency in intensive vegetable fields in China (Deng et al., 2013; Diao et al., 2013; Li et al., 2016). Meanwhile, intensive vegetable agriculture is considered to be an important source of $N_2O$ (Xiong et al., 2006; Jia et al., 2012; Li et al., 2015b; Zhang et al., 2015) and NO production (Mei et al., 2009). Moreover, $NH_3$ volatilization is another important N pathway in fertilized soil, resulting in large losses of soil-plant N (Pacholski et al., 2008; Zhang et al., 2011). Therefore, the reduction of reactive N loss is key to meet the joint challenges of high production and acceptable environmental consequences in intensive vegetable production (Zhang et al., 2013).

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

($O_2$)-limited conditions, specifically produced for use as a soil amendment (Sohi, 2012). The amendment of agricultural ecosystems with biochar has been proposed as an effective countermeasure for climate change (Smith, 2016). These additions have been suggested to increase soil carbon storage (Mukherjee and Zimmerman, 2013; Stavi and Lal, 2013), decrease greenhouse gas emissions (Li et al., 2016), and improve soil fertility and crop production (Major et al., 2010; Liu et al., 2013). However, some recent studies have reported no difference or even an increase in soil $N_2O$ emissions induced by biochar application for various soils (Saarnio et al., 2013; Wang et al., 2015a). Besides, $NH_3$ volatilization was enhanced by biochar application in pasture soil (Clough et al., 2010), vegetable soil (Sun et al., 2014) and paddy soil in the wheat-growing season (Zhao et al., 2014). Additionally, crop productivity responses to biochar amendments differed among various biochars (Cayuela et al., 2014). These inconsistent results suggest that current biochar application to soil is not a "one-size fit-all paradigm" because of the variation in the physical and chemical characteristics of the different biochars, soil types and crop species (Field et al., 2013; Cayuela et al., 2014). Moreover, limited types of biochar (Spokas and Reicosky, 2009) and soil (Sun et al., 2014) were involved in the experiments in previous studies. Thus, the evaluation of the different types of biochar under the typical soils is imperative to gain a comprehensive understanding of potential interactions before the large-scale application of biochars.

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

## 2 Materials and methods

### *2.1. Experimental soil and biochar*

Four typical greenhouse vegetable cultivation sites with a long history (more than 10 years) of conventional cultivation were selected from Northeast, Northwest, Central and Eastern China (Fig. S1): 1. a Phaeozem from Jiamusi (46°48′N, 130°12′E) in the Heilongjiang province, 2. an Anthrosol from Yangling (34°18′N, 108°2′E) in the Shanxi province, 3. an Acrisol from Changsha (28°32′N, 113°23′E) in the Hunan province, 4. a Cambisol from Shouguang (36°56′N, 118°38′E) in the Shandong province (FAO and ISRIC, 2012). Those four types of vegetable soil represented a range of differences in physicochemical properties and regions (Table S1). Soil samples were manually collected from the cultivated layer (0–20 cm) after the local vegetable harvest in April, 2015. The samples were air-dried and passed through a 5 mm stainless steel mesh sieve and homogenized thoroughly. Any visible roots and organic residues were removed manually before being packed with the necessary amount of soil to achieve the initial field bulk density. Each pot received 15 kg of 105 ℃ dry-weight-equivalent fresh soil. For each of the biochar amendment pot, 282.6 g $pot^{-1}$ sieved biochar (2 mm) was mixed with the soil thoroughly before the experiment, which was equivalent to a 40 t $ha^{-1}$ biochar dose (dry weight). No more biochar was added later in the experimental period.

The two types of biochar that were used in this experiment are derived from two common agricultural wastes in China: wheat straw and swine manure, hereafter referred to as Bw and Bm, respectively (Table S1). The Bw was produced at the Sanli New Energy Company in Henan, China, by pyrolysis and thermal decomposition at 400–500 ℃. The Bm was produced through thermal decomposition at 400 ℃ by the State Key Laboratory of Soil Science and Sustainable Agricultural, Institute of Soil Science, Chinese Academy of Sciences. In accordance with Lu (2000), soil organic carbon (SOC) was measured by wet digestion with $H_2SO_4$–$K_2Cr_2O_7$, total nitrogen (TN) was determined by semi-micro Kjeldahl digestion, and soil texture was determined with the pipette 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 PHS-3C mv/pH detector (Shanghai Kangyi Inc. China). Biochar content of hydrogen (H) was measured by elemental analysis after dry combustion (Euro EA, Hekatech GmbH, Wegberg, Germany). The oxygen content of biochar was measured with the same device after pyrolysis of the sample at 1000 ℃ followed by reduction of the evolved $O_2$ to CO and quantified by GC-TCD. The soil nitrate ($NO_3^-$–N) and ammonium ($NH_4^+$–N) were measured following the two-wavelength ultraviolet spectrometry and indophenol blue method, respectively, using an ultraviolet spectrophotometer (HITACHI, UV-2900, Tokyo, Japan). Electric conductivity (EC) was measured by using a Mettler-Toledo instrument (FE30-K, Shanghai, China) at a 1:5 (w:v) soil to water ratio. Cation exchange capacity (CEC) was determined using the $CH_3COONH_4$ method. Dissolved organic carbon (DOC) was extracted from 5 g of the biochar/soil with an addition of 50 ml deionized water and measured by a

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

*2.2. Experimental set-up and management*

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

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

*2.3. Measurement of $N_2O$, NO and $NH_3$*

The NO and $N_2O$ fluxes were measured simultaneously from each vegetable cultivation using a static opaque chamber method (Zheng et al., 2008; Yao et al., 2009). A square PVC chamber of 35 cm × 35 cm × 40 cm (length × width × height) was temporarily mounted on the pot for gas flux measurement. The chamber was coated with sponge and aluminum foil outside to prevent solar radiation heating the chamber. Gas samples for flux measurements were collected between 8 and 10 a.m. on each measuring day to minimize the influence of diurnal temperature variation. Gas fluxes were usually measured once a week and every other day for one week following fertilizer application. To measure the $N_2O$ flux, four samples were collected from the headspace chamber using 20 ml polypropylene syringes at 0, 10, 20, and 30 min after chamber closure. The gas concentrations in the samples were analyzed within 12 h after sampling using an Agilent 7890A gas chromatograph equipped with an electron capture detector (ECD) for $N_2O$ detection. Argon-methane (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 and 300 ℃, respectively. The gas chromatography configurations described by Wang et al. (2013) were adopted for the

gas concentration analysis. $N_2O$ flux was calculated using the linear increases in gas concentration with time. Sample sets were rejected unless they yielded a linear regression value of $R^2 > 0.90$.

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

The mean flux of $N_2O$ or NO during the experiment period is the average of all measured fluxes weighted by the interval between two neighboring measurements (Xiong et al., 2006). The cumulative $N_2O$ was calculated as the product of the mean flux and the entire duration.

The $NH_3$ volatilization was determined using the ventilation method (Zhao et al., 2010). The phosphoglycerol-soaked sponge was replaced every day after each fertilization event for approximately one week. The phosphoglycerol-soaked sponges used to collect the $NH_3$ samples were immediately extracted with 300 mL potassium chloride (KCl) solution (1 mol $L^{-1}$) for 1 h. The concentration of $NH_4^+$–N was measured using the indophenol blue method at 625 nm (Sororzano, 1969) by ultraviolet spectrophotometry (HITACHI, UV-2900, Tokyo, Japan, with 0.005 absorbance of photometric accuracy). The cumulative seasonal $NH_3$ volatilization was the sum of the daily emissions during the measurement period.

*2.4. Auxiliary measurements*

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

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

Here, total soil porosity = [1 — (soil bulk density (g $\text{cm}^{-3}$) / 2.65)] with an assumed soil particle density of 2.65 (g $\text{cm}^{-3}$). The total soil bulk density was determined with the cutting ring method according to Lu (2000).

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

GNrE = cumulative $N_2O$ + cumulative NO + cumulative $NH_3$ emissions (kg N $ha^{-1}$) (2)

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

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

*2.5. Data processing and statistics*

Two-way ANOVA was used to analyze the effects of the biochar type, soil type, and their interactions on soil properties, $N_2O$, NO and $NH_3$ emissions, vegetable yield, GNrE and GNrI throughout the experimental period. Multiple comparisons among the treatments were assessed using Tukey's HSD test. Significant differences were considered at $P < 0.05$. All statistical analyses were performed using JMP ver. 7.0 (SAS Institute, Cary, NC, USA, 2007). Pearson's correlation analysis was used to determine whether there were significant interrelationships between $N_2O$/NO and PNR or DEA in each soil, using SPSS window version 18.0 (SPSS Inc., Chicago, USA).

## 3. Results

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

Appreciable differences in all observed soil properties existed among soil types (Table 1), suggesting the wide variations of soil characters across mainland China. Additionally, biochar amendments had significant influences on all the soil properties (Table 1, $p < 0.05$). Compared with N treatments, biochar amendments increased the SOC, TN and 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 increased SOC and TN by 5.8–20.5 % and 9.5–14.2 % ($p < 0.05$), respectively, whereas EC values were higher by 3.3–21.5 % induced by Bw than Bm amendment over all soils. Additionally, biochar amendments significantly increased soil pH by 0.27–0.64 and 0.08–0.10 units compared with N treatment in Acrisol and Anthrosol soils ($p < 0.05$), respectively, and Bm performed better than Bw on increasing soil pH in Acrisol. Furthermore, biochar amendments tended to increase MBC in Cambisol and Phaeozem, and Bm increased MBC relative to Bw in all soils.

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

### *3.2. Seasonal variations of $N_2O$ and NO emissions*

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

Clearly, the NO fluxes demonstrated similar seasonal dynamics to the $N_2O$ fluxes (Fig. 3). Some relatively high peak NO fluxes were still observed in the Spinach and Coriander herb planting seasons even though relatively low temperatures occurred during these periods, primarily due to lower soil moisture which was suitable for NO production.

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 significantly weakened with the Bw and Bm in the Acrisol (Fig. 3a).

*3.3. Cumulative $N_2O$, NO and $NH_3$ emissions*

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

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 soils. Biochar amendments produced no significant influences on the $NH_3$ emissions relative to N treatment in most soils (Table 3c). A tendency was found for the cumulative $NH_3$ emissions in N+Bm to be higher than those in the N+Bw treatment, although this difference was not remarkable within each soil. Additionally, stimulation effects were consistently present after the first fertilization event in each type of soil (Fig. 4).

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

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

Table 3f presents the GNrI during the whole experiment period, with a pronounced variation among soils ($p < 0.05$).

The GNrI was greatly affected by biochar amendment during the whole experiment period (Table 2, $p < 0.01$). Compared to N treatment, biochar amendments reduced the GNrI by 4.3–27.8 % across all soils, significantly in Anthrosol and Phaeozem (Table 3f, $p < 0.05$). Moreover, there were no remarkable differences between Bw 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 pH neutral, remarkable mitigation effects were observed in Anthrosol and Phaeozem 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). In line with Obia et al. (2015), biochar decreased NO emissions in low-pH Acrisol (Table 3b), probably by stimulating denitrification enzyme activity, and then resulted in less NO accumulation relative to $N_2$ production. Moreover, the liming effects of biochar may have prevented the chemical decomposition of $NO_2^-$ to NO (Islam et al., 2008), leaving only enzymatically produced NO to accumulate. However, different from the rest soils, neither $N_2O$ nor NO emission was significantly influenced by PNR or DEA, suggesting other processes might play vital roles in Cambisol. Besides nitrification and denitrification, nitrifiers denitrification (Wrage et al., 2001) and heterotrophic nitrification (Zhu et al., 2011) can be important processes for producing $N_2O$/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 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, Bm had more the contents of the TN and DOC by 80% and 40% (Table S1), respectively, which might supply extra N or C source for heterotrophic nitrification in the acidic Acrisol, leading Bm to being 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 and DEA, thus displaying lower mitigation ability than Bw. Second, compared with Bm, the C/N ratio was approximately

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

Intensively managed soils receiving fertilizer such as urea or anhydrous $NH_3$ and ruminant urine patches are potential hot spots for $NH_3$ formation, where the use of biochar is expected to retain $NH_3$–N in the soil system (Clough and Condron, 2010). Actually, the effects of biochar amendments on $NH_3$ volatilization largely depend on soil characteristics, biochar types. Soil texture is an important factor impacting $NH_3$ transfer and release. More clay contents were present in the Anthrosol (Table S1), which was limited in large soil pores, thus, the addition of porous biochar could enhance the soil aeration, promoting $NH_3$ volatilization (Sun et al., 2014). Additionally, it was worthy to note that cumulative $NH_3$ emissions were slightly higher in soils with the Bm than those with the Bw amendment (Fig. 4 and Table 3c) and that difference could presumably be attributed to less surface area and the much higher pH of Bm (Fig. S3 and Table S1), resulting in weak adsorption and great liming effects.

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

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

However, no promotion of yield was observed with biochar amendments in Acrisol and Anthrosol. This could be attributed to exacerbated soil salinity, which inhibited the uptake of nutrients and water (Ju et al., 2006; Zhou et al., 2010) and the growth of the soil microorganisms (Setia et al., 2011), leading to unsustainable greenhouse vegetable production. Compared with other biochar (Jia et al., 2012), the higher amounts of ash in Bw and Bm may contain high salts, which would result in soil salinity (Hussain et al., 2016). After the addition of the two salt-rich biochars, the EC values of Acrisol and Anthrosol vegetable soils increased, which might reach the limits to tolerance for the leafy vegetables (Shannon and Grieve, 1998). Here, we assessed two feedstock-derived biochar effects on GNrI in typical cultivated vegetable soils across mainland China. Overall, biochar amendments reduced GNrI over all the soils, with the magnitude largely depending on soil type. Remarkable reduction in GNrI had been detected due to the efficient mitigation induced by biochar in Anthrosol and Phaeozem (Table 3f). However, despite enhanced vegetable yield, no significant decreases in GNrI were observed in Cambisol, mainly because of the absence of mitigation effects on $N_2O$, NO and $NH_3$ emissions of biochars (Table 3a, b and c) Overall, Bw was superior to Bm in mitigating the GNrE while Bm performed better in vegetable yield enhancement (Table 3d and e). Therefore, the mitigation efficacies on GNrI were not notably different between Bw and Bm amendments across the four soils.

## 5. Conclusion

The study demonstrated that biochar amendments mostly reduced $N_2O$ and NO emissions and slightly increased the $NH_3$ emissions, while produced no consensus influences on yield though those effects were largely both biochar- and soil-specific. Additionally, biochar amendments did decrease GNrI in intensive vegetable soils across mainland China. Furthermore, Bw was superior to Bm in mitigating the GNrE whereas the Bm performed better in crop yield throughout all soils. Consequently, both soil type and biochar characteristics need to be seriously considered before large-scale biochar application under certain regions of intensive vegetable production.

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**Table legends**

**Table 1**

Soil organic carbon (SOC), soil total nitrogen (TN), soil pH, electric conductivity (EC) and microbial biomass carbon (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. | ** |

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

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

**Table 2**

Two-way ANOVA for the effects of biochar (Bc) and soil (S) types on cumulative $N_2O$, NO and $NH_3$ emissions, gaseous reactive nitrogen emission (GNrE), vegetable yield and gaseous reactive nitrogen intensity (GNrI) during the entire sampling period.

| Factors | DF | $N_2O$ 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 | | |

SS: the sum of squares.

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

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.

n.s.: not significant.

**Table 3**

Cumulative gaseous nitrogen ($N_2O$, NO and $NH_3$) emissions, gaseous reactive nitrogen emission (GNrE), vegetable yield and gaseous reactive nitrogen intensity (GNrI) under the different treatments across the four soils.

| Treatments | Acrisol | Anthrosol | Cambisol | Phaeozem |
|---|---|---|---|---|
| (a) Cumulative $N_2O$ 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 |

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

**Table 4**

The correlations between $N_2O$ or NO emission and PNR or DEA in each soil.

| Item | Acrisol | | Anthrosol | | Cambisol | | Phaeozem | |
|---|---|---|---|---|---|---|---|---|
| | PNR | DEA | PNR | DEA | PNR | DEA | PNR | DEA |
| $N_2O$ | 0.75* | 0.66 | 0.49 | 0.76* | -0.10 | 0.16 | -0.82** | 0.70* |
| NO | 0.62 | -0.29 | 0.79* | 0.69* | -0.54 | 0.01 | -0.63 | 0.22 |

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

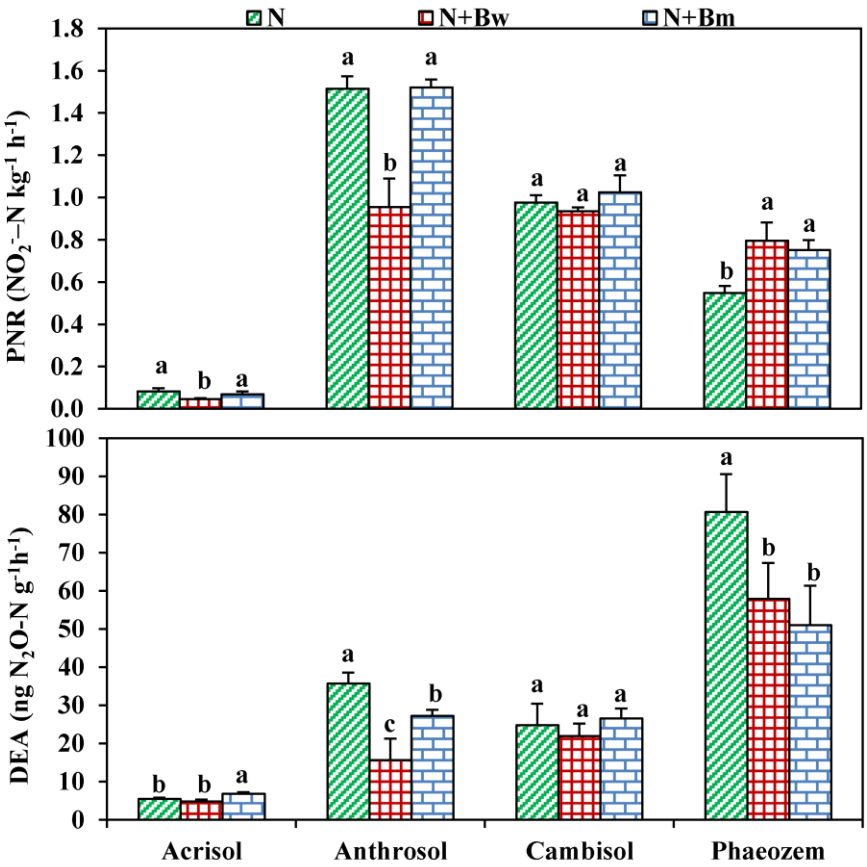
**Figure legends**

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

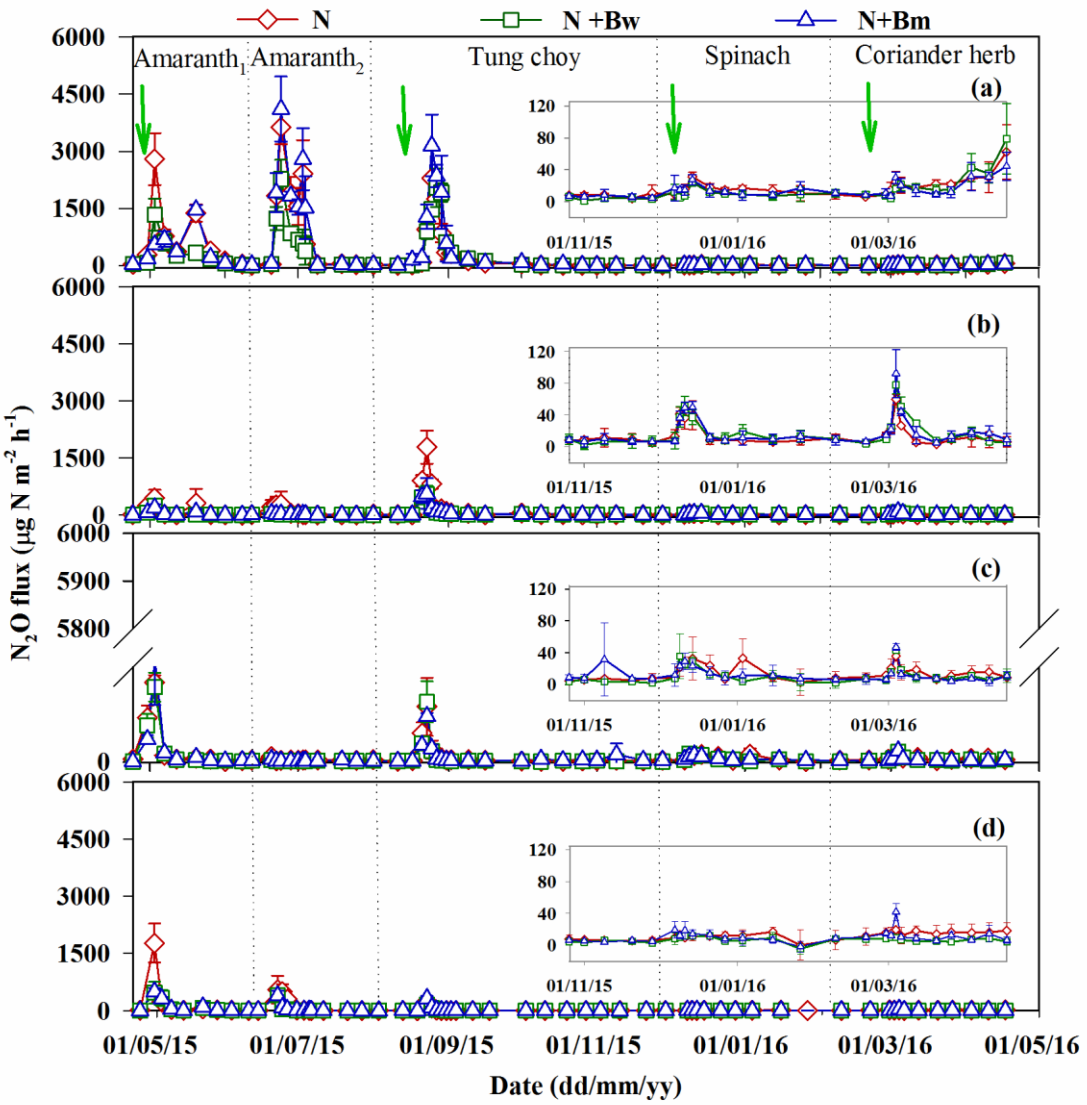
**Fig. 2** Temporal dynamics of soil $N_2O$ (μg N $m^{-2}$ $h^{-1}$ ± SD, n = 3) fluxes under different treatments in Acrisol (a), Anthrosol (b), Cambisol (c) and Phaeozem (d) with five consecutive vegetable crops. The inserted panels describe the $N_2O$ fluxes during the last two cropping seasons. The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

**Fig. 3** Temporal dynamics of soil NO (μg N $m^{-2}$ $h^{-1}$ ± SD, n = 3) fluxes under different treatments in Acrisol (a), Anthrosol (b), Cambisol (c) and Phaeozem (d) with five consecutive vegetable crops. The solid arrows indicate fertilization. See Fig. 1 for treatments codes.

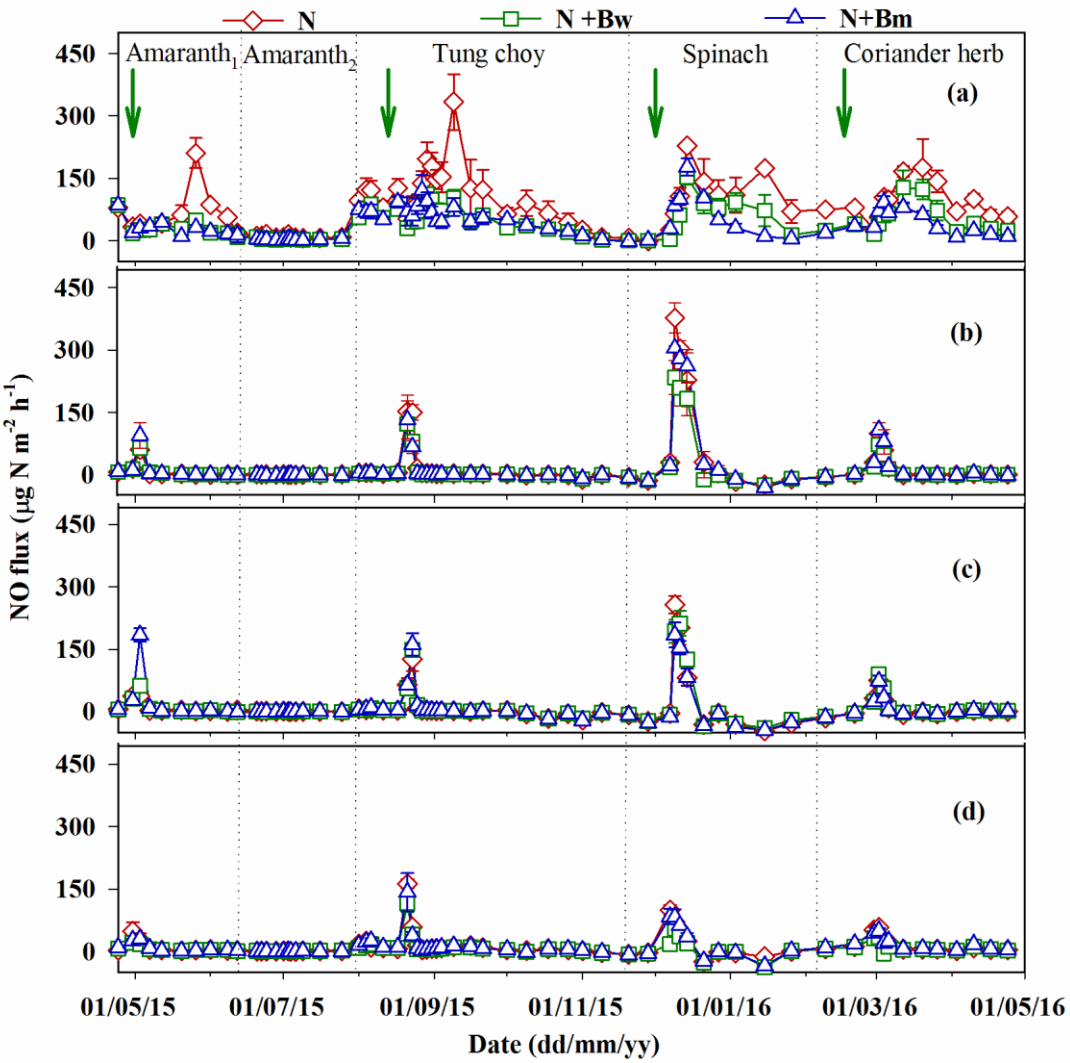
**Fig. 4** Cumulative ammonia ($NH_3$) emissions from the Acrisol (a), Anthrosol (b), Cambisol (c) and Phaeozem (d) during the four nitrogen fertilization events F: every N fertilization event. The bars indicate the standard deviation of the mean (kg N $ha^{-1}$ ± SD, n = 3) of each treatment for the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


N
N+Bw
N+Bm
PNR ($NO_2^-$–N $kg^{-1}$ $h^{-1}$)
DEA (ng $N_2O$-N $g^{-1}h^{-1}$)
Acrisol
Anthrosol
Cambisol
Phaeozem

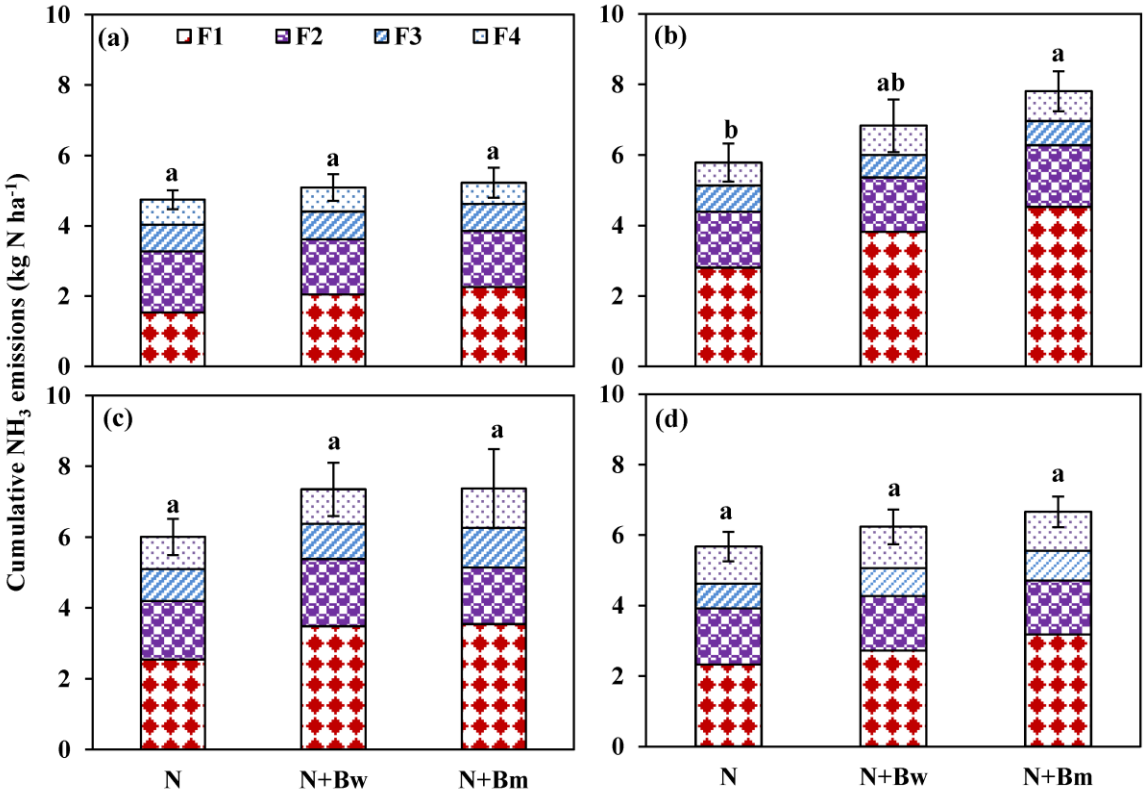
1


N
N +Bw
N+Bm
Amaranth1
Amaranth2
Tung choy
Spinach
Coriander herb
(a)
(b)
(c)
(d)
N2O flux (μg N m-2 h-1)
Date (dd/mm/yy)
01/05/15
01/07/15
01/09/15
01/11/15
01/01/16
01/03/16
01/05/16

1


N
N +Bw
N+Bm
Amaranth1
Amaranth2
Tung choy
Spinach
Coriander herb
(a)
(b)
(c)
(d)
NO flux (μg N m-2 h-1)
450
300
150
0
01/05/15
01/07/15
01/09/15
01/11/15
01/01/16
01/03/16
01/05/16
Date (dd/mm/yy)

1




1