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Effects of two contrasting biochars on gaseous nitrogen emissions and intensity in intensive vegetable soils across mainland China

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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 effects of different feedstock-derived biochars on the various gaseous nitrogen emissions (GNEs, N_2O, NO and NH_3) 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 GNEs, vegetable yield and gaseous nitrogen intensity (GNI) in four typical vegetable soils from the main vegetable production regions (Hunan province (HN), Shanxi province (SX), Shandong province (SD) and Heilongjiang province (HLJ)) that are representative of the intensive vegetable ecosystems across mainland China. Results showed that remarkable GNE mitigation induced by biochar occurred in SX and HLJ soils, whereas enhancement of yield occurred in SD and HLJ soils. Additionally, both biochars decreased GNI, with Bw mitigated N_2O and NO emissions by 21.8–59.1 % and 37.0–49.5 % (except for SD), respectively, while Bm improved yield by 4.0–30.5 % (except for HN). Since the biochar's effects on the GNEs and vegetable yield strongly depended on the attributes of the soil and biochar, both soil type and biochar characteristics should be seriously considered before conducting large-scale application of biochar in order to achieve the maximum benefits under intensive greenhouse vegetable agriculture.

Keyword: Biochar, Intensive vegetable soil, Gaseous nitrogen emissions (GNEs), Gaseous nitrogen intensity (GNI)

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1 Introduction

Agriculture accounted for an estimated emission of 4.1 (1.7–4.8) Tg N yr^{-1} for N_2O and 3.7 Tg N yr^{-1} for NO, contributing 60 % and 10 %, respectively, to the total global anthropogenic emissions, largely due to increases of 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 298 times the global warming potential (GWP) of 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 nitric oxide (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). Additionally, along with the high nitrogen (N) application, ammonia 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). Consequently, the release of various reactive N species results in lower N use efficiency in agricultural systems.

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 nitrogen 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). 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, ammonia 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 becomes a central environmental challenge to meet the joint challenges of high production and acceptable environmental consequences in intensive vegetable production (Zhang et al., 2013).

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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 would increase soil carbon storage (Mukherjee and Zimmerman, 2013; Stavi and Lal, 2013), decrease GHG 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 from different soils (Saarnio et al., 2013; Wang et al., 2015a). Still, 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 in intensive vegetable cropping system in China.

Therefore, a greenhouse pot experiment was conducted in an effort to investigate the effects of different types of biochar on gaseous nitrogen emissions (GNEs), namely, N_2O, NO and NH_3, simultaneously in four typical intensified vegetable soils across main vegetable production areas of mainland China. Overall, the objectives of this research were to gain a comprehensive insight into the effects of the different types of biochar on the GNEs, vegetable yield and gaseous nitrogen intensity (GNI) 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), namely, Phaeozem, Anthrosol, Acrisol and Cambisol (FAO and ISRIC, 2012) from Jiamusi (46°48′ N, 130°12′ E), Heilongjiang province (HLJ); Yangling (34°18′ N, 108°2′ E), Shanxi province (SX); Changsha (28°32′ N, 113°23′ E), Hunan province (HN) and Shouguang (36°56′ N, 118°38′ E), Shandong province (SD), respectively were collected and 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

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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 °C dry-weight-equivalent fresh soil. For the biochar amendment pots, sieved biochar (2 mm) was mixed with the soil thoroughly before the experiment, equivalent to a 40 t ha^{-1} dose (dry weight). No more biochar was added later in the experimental period.

Two types of biochar, 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 °C. The Bm was produced through thermal decomposition at 400 °C by the State Key Laboratory of Soil Science and Sustainable Agricultural, Institute of Soil Science, Chinese Academy of Sciences. In accordance with Lu (2000), the SOC was measured by wet digestion with H_2SO_4–$K_2Cr_2O_7$, 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). The soil NO_3^-–N and NH_4^+–N were measured following the two-wavelength ultraviolet spectrometry and indophenol blue methods, 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 °C 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 completely 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

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

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

122 *2.3. Measurement of N_2O, NO and NH_3*

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

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

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

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

155 *2.4. Auxiliary measurements*

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

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

162 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}).
163 The total soil bulk density was determined with the cutting ring method according to Lu (2000).

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

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

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

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

174 *2.5. Data processing and statistics*

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One-way ANOVA was performed to test the effects of the treatments on cumulative N_2O, NO and NH_3 emissions; GNE; vegetable yield and GNI. Two-way ANOVA was used to analyze the effects of the biochar type; soil type; and their interactions on N_2O, NO and NH_3 emissions, vegetable yield, GNE and GNI throughout the experimental period. Multiple comparisons among the treatments were further explained 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

Obvious differences in all observed soil properties existed among soil types (Table 1, $p < 0.001$), suggesting the wide variations of soil characters across mainland China. Additionally, biochar amendments had significant influences on all the soil properties ($p < 0.05$). 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 resulted in higher contents of SOC and TN by 5.8–20.5 % and 9.5–14.2 %, respectively, whereas EC values were higher by 3.3–21.5 % induced by Bw than Bm amendment over all soils. Additionally, biochar amendments significantly enhanced soil pH by 0.27–0.64 and 0.08–0.10 units compared with N treatment in HN and SX soils ($p < 0.05$), respectively, and higher values were detected with Bm than Bw amendment in all soils. Furthermore, biochar amendments tended to increase MBC in SD and HLJ soils, and Bm performed better in MBC enhancements than 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 HLJ while exerted no influences on SD soil (Fig. 1a). Compared with Bw, Bm amendment significantly increased PNR in HN and SX soils. Moreover, compared with N, biochar amendments significantly reduced DEA by an average of 40.1 and 37.8 % in SX and HLJ ($p < 0.05$), respectively, while producing no influence in SD soils (Fig. 1b). In comparison with Bw, remarkable enhancements were observed by 42.5 and 74.4 % with Bm amendment in HN and SX soils, 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

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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 HN, SX, SD and HLJ 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 SX and HLJ vegetable soils (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 HN soil (Fig. 3a).

3.3. Cumulative N_2O, NO and NH_3 emissions

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 all the soils during the vegetable cultivation period (Table 3a). Biochar amendments had significant influences on the cumulative N_2O emissions, reducing N_2O emissions by 13.7–41.6 % (Table 2). In comparison with the N treatment, biochar amendment decreased N_2O emissions by an average of 56.4 % and 47.5 % in SX and HLJ (Table 3a, $p < 0.05$), respectively, with no remarkable influence in SD soil, indicating significant interactions between biochar and soil types (Table 2, $p < 0.001$). Compared with Bm, Bw amendment performed better mitigation effects which decreased N_2O emissions by 11.8–38.4 % across all the soils, significantly in HN soil (Table 3a, $p < 0.05$). In comparison with N_2O emission, the cumulative NO emission was much smaller, with a remarkable variation of 0.20–8.99 kg N ha^{-1} across all soils (Table 3b). Though pronounced effects on NO emissions with a reduction by average of 45.8 % (Table 2, $p < 0.05$), biochar amendments had no consensus effects across soils, reducing NO emissions in HN soil (Table 3b, $p < 0.05$) and producing no remarkable influence on SD soil, which suggested significant interactions between biochar and soil types (Table 2, $p < 0.001$). Compared with Bm, Bw amendment significantly reduced NO emissions in SX and HLJ soils (Table 3b, $p < 0.05$). As shown in Table 4, N_2O emissions had positive relationships with DEA both in SX and HLJ soils, and were affected positively by PNR in HN soil. Additionally, NO emissions had positive correlations with both PNR and DEA in SX soil. However, neither N_2O nor NO emissions were influenced significantly by PNR and DEA in SD soils.

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. Though significantly enhancing NH_3 emissions (Table 2), 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

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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 N emissions 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 2, $p < 0.001$). 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 SD and HLJ soils against HN and SX soils (Tables 3e), denoting pronounced interactions between soil and biochar (Table 2, $p < 0.05$). Compared with Bm, Bw amendment lowed total yield over all the soils (Table 3e), significantly in HN and SD soils ($p < 0.05$).

Table 3f presents the GNI during the whole experiment period, with a pronounced variation among soils (Table 2, $p < 0.001$). The GNI was greatly affected by biochar amendment during the whole experiment period (Table 2, $p < 0.01$). Compared to N treatment, biochar amendments reduced the GNI by 4.3–27.8 % across all soils, significantly in SX and HLJ soils (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 GNEs 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 SX and 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 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 SD soil. In

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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 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 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.

Intensive 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 and duration time. Soil texture is an important factor impacting NH_3 transfer and release. More clay contents were present in the SX soil (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. Overall, compared with previous studies (Ro et al., 2015; Mandal et al., 2016), no significant reductions were found in cumulative NH_3 volatilizations over the whole

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observation period when biochar was added to current vegetable soils. In general, freshly produced biochar typically has very low ability to absorb ammonium (Yao et al., 2012). Over time, biochar surfaces are oxidized and increase adsorption (Wang et al., 2016). Moreover, the recorded increase in CEC by Cheng et al. (2006) indicated that biochars that are sufficiently weathered over a period would increase their ability to retain cations such as NH_4^+–N. Further, relatively long-term experiments are required to elucidate the mechanism and duration of effect.

4.2. Biochar effects on vegetable yield and GNI 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 bicohar amendment occurred in SD and HLJ soils (Table 3e). However, no promotion of yield was observed with biochar amendments in HN and SX. 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 causing soil salinity (Hussain et al., 2016). After the addition of the two salt-rich biochars, the EC values of HN and SX vegetable soils increased and reached the limits to tolerance for the leafy vegetables (Shannon and Grieve, 1998).

Additionally, the mixed performance of biochars as an amendment is related to the wide diversity of physicochemical characteristics that translates into variable reactions in soil (Novak et al., 2014). First, compared to Bw, more DOC content was in the Bm (Table S1), through which more nutrients may be directly introduced to the soil (Rajkovich et al., 2012). In addition, besides their large amount of plant-available nutrients (Hass et al., 2012), manure biochars 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 (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.

Here, we assessed two feedstock-derived biochar effects on GNI in typical cultivated vegetable soils across mainland China. Overall, biochar amendments reduced GNI over all the soils, with the magnitude largely depending on soil type. Remarkable reduction in GNI had been detected due to the efficient mitigation induced by biochar in SX and HLJ (Table 3f). However, despite enhanced vegetable yield, no significant decreases in GNI were observed in SD, mainly because of the absence of mitigation effects on N_2O, NO and NH_3 emissions of biochars (Table 3a, b and c) Additionally, mitigation efficacy on GNI were not notably different between Bw and Bm amendments across the four

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

5. Conclusion

The study demonstrated that biochar amendments generally reduced N_2O and NO emissions without influencing 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 GNI in intensive vegetable soils across mainland China. Furthermore, Bw was superior to Bm in mitigating the GNE 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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523 **Table legends**

524 **Table 1**

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

526 (MBC) as affected by different treatments across the four vegetable soils.

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

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

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

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

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Table 2

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

Factors	DF	N_2O emission			NO emission			NH_3 emission			GNE			Vegetable yield			GNI		
		SS	F	P	SS	F	P	SS	F	P	SS	F	P	SS	F	P	SS	F	P
Bc	2	271.9	65.1	***	46.4	174.7	***	0.5	0.8	n.s.	380.5	86.4	***	76.2	3.2	n.s.	0.1	7.9	**
S	3	1429.9	228.1	***	152.2	382.1	***	4.1	3.8	*	2322.6	351.5	***	4316.9	123.3	***	2.3	110.3	***
Bc×S	6	179.3	14.3	***	33.4	41.9	***	1.4	0.7	n.s.	234.5	17.7	***	230.4	3.3	*	0.1	1.6	n.s.
Model	11	4009.7	174.5	***	225.3	154.3	***	29.1	7.5	***	5290	218.3	***	15962.0	124.4	***	5.8	77.0	***
Error	24	50.1			3.2			8.5			52.9			280.0			0.2		
biochar effect (n = 9)																			
N mean		12.01±1.44a			2.86±0.24a			5.92±0.24b			43.81±1.25b			20.50±1.60a			0.57±0.05a		
N+Bw mean		7.01±0.58b			1.55±0.14b			6.65±0.27a			43.53±1.67b			14.94±0.84b			0.45±0.04b		
N+Bm mean		10.37±0.56a			1.55±0.10b			7.01±0.25a			49.53±1.11a			18.60±0.65a			0.49±0.03ab		
Soil effect (n = 9)																			
HN mean		27.20±1.85a			5.80±0.50a			5.31±0.16c			33.06±1.65c			38.04±1.90a			1.15±0.11a		
SX mean		4.89±0.45b			1.08±0.13b			12.69±0.46a			25.05±1.11d			12.69±0.46b			0.51±0.01b		
SD mean		2.25±0.26c			0.25±0.09c			9.51±0.55b			44.88±0.49b			9.51±0.55c			0.21±0.01c		
HLJ mean		4.48±0.68b			0.81±0.04b			11.79±0.71a			79.50±2.41a			11.79±0.71b			0.15±0.01c		

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.

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 among treatments at $p < 0.05$ level.

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539 **Table 3**

540 Cumulative gaseous nitrogen (N_2O, NO and NH_3) emissions, gaseous nitrogen emission (GNE), vegetable yield and

541 gaseous nitrogen intensity (GNI) under the different treatments across the four soils.

Treatments	HN	SX	SD	HLJ
(a) Cumulative N_2O 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) GNE (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) GNI (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

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

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

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Table 4

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

Item	HN		SX		SD		HLJ	
	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.

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Figure legends

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

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

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

Fig. 4 Cumulative ammonia (NH_3) emissions from the HN (a), SX (b), SD (c) and HLJ (d) soils during the four nitrogen fertilization events F: every N fertilization event. The bars indicate the standard deviation of the mean (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 $p < 0.05$.

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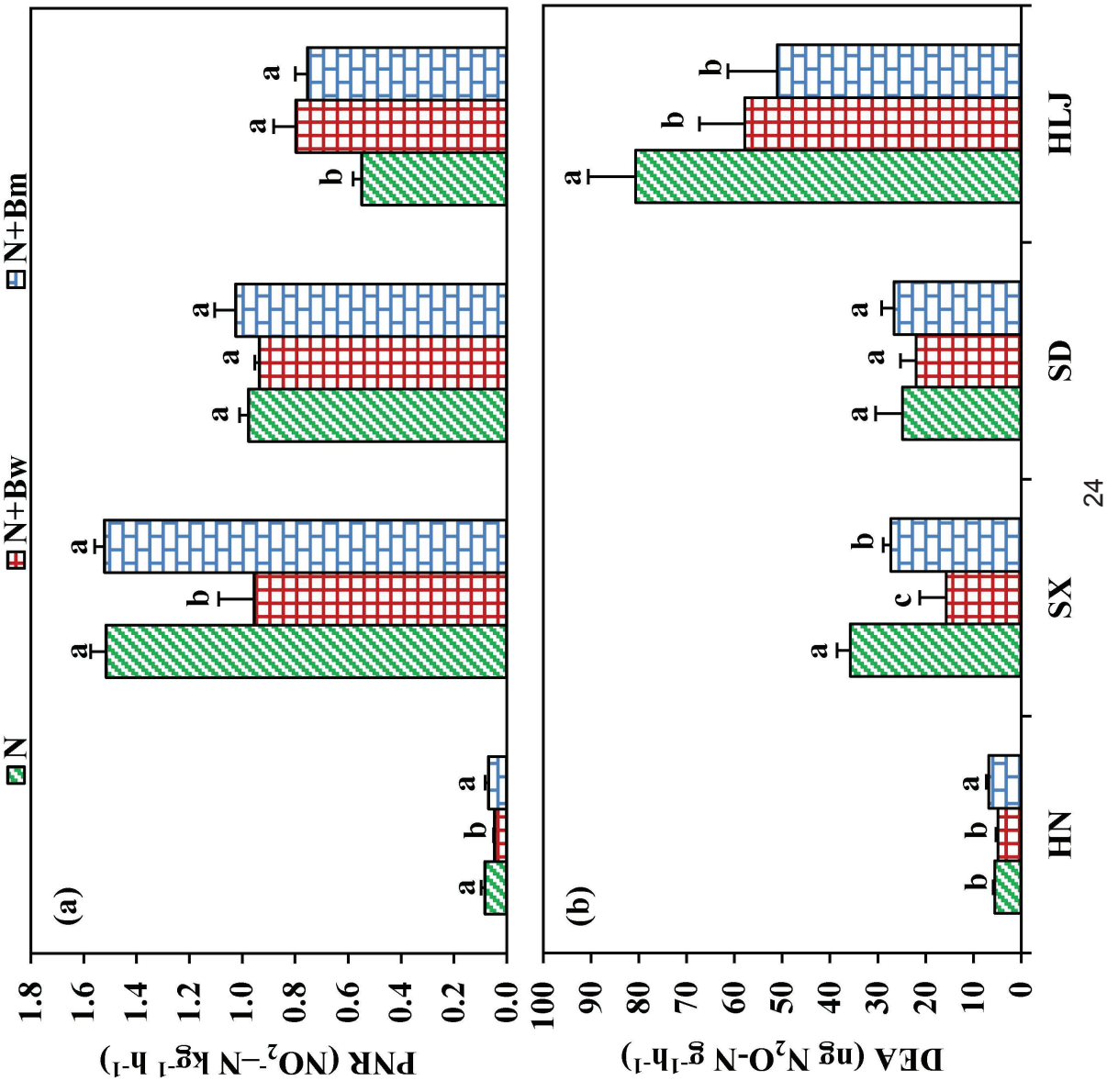

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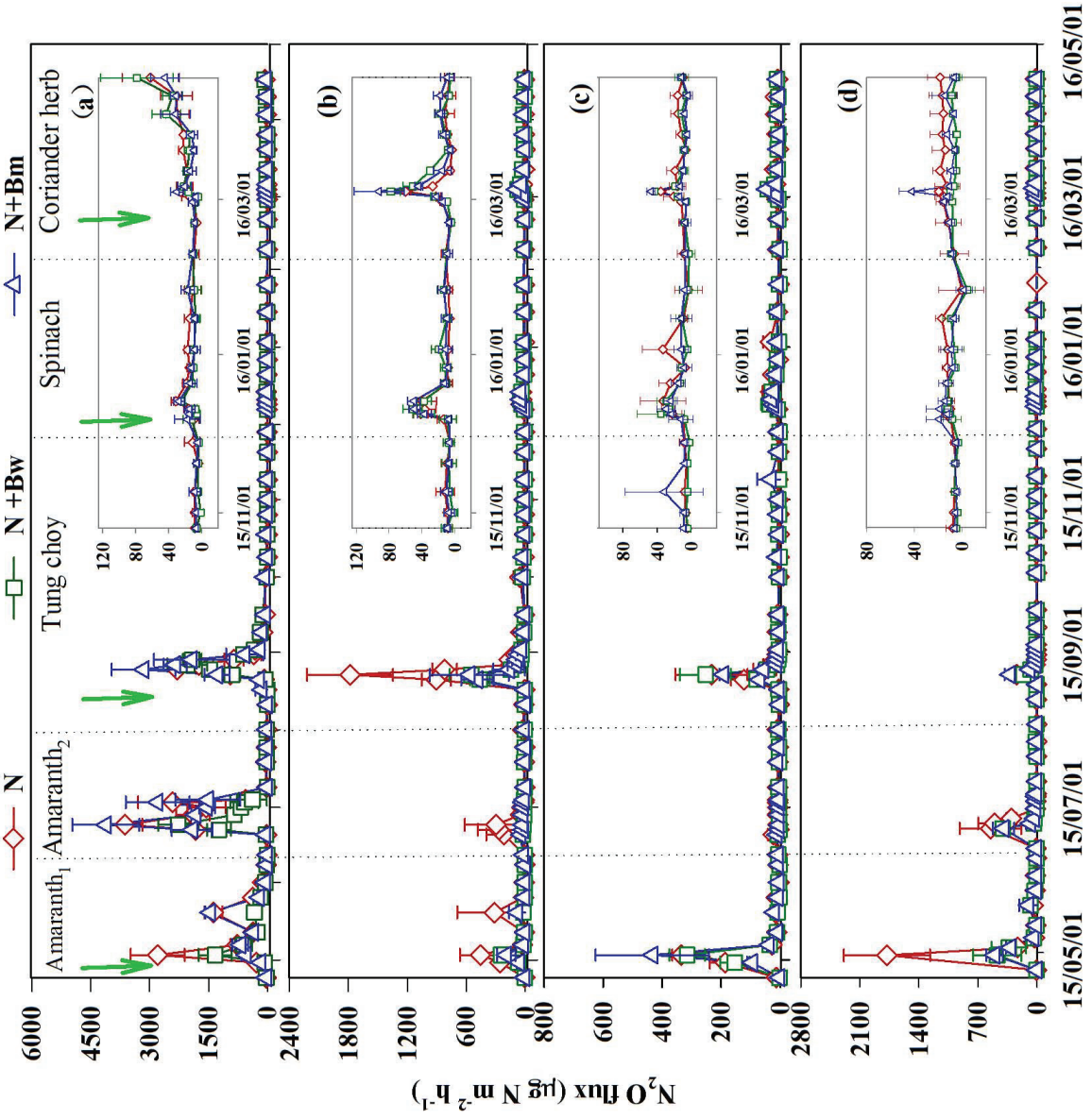

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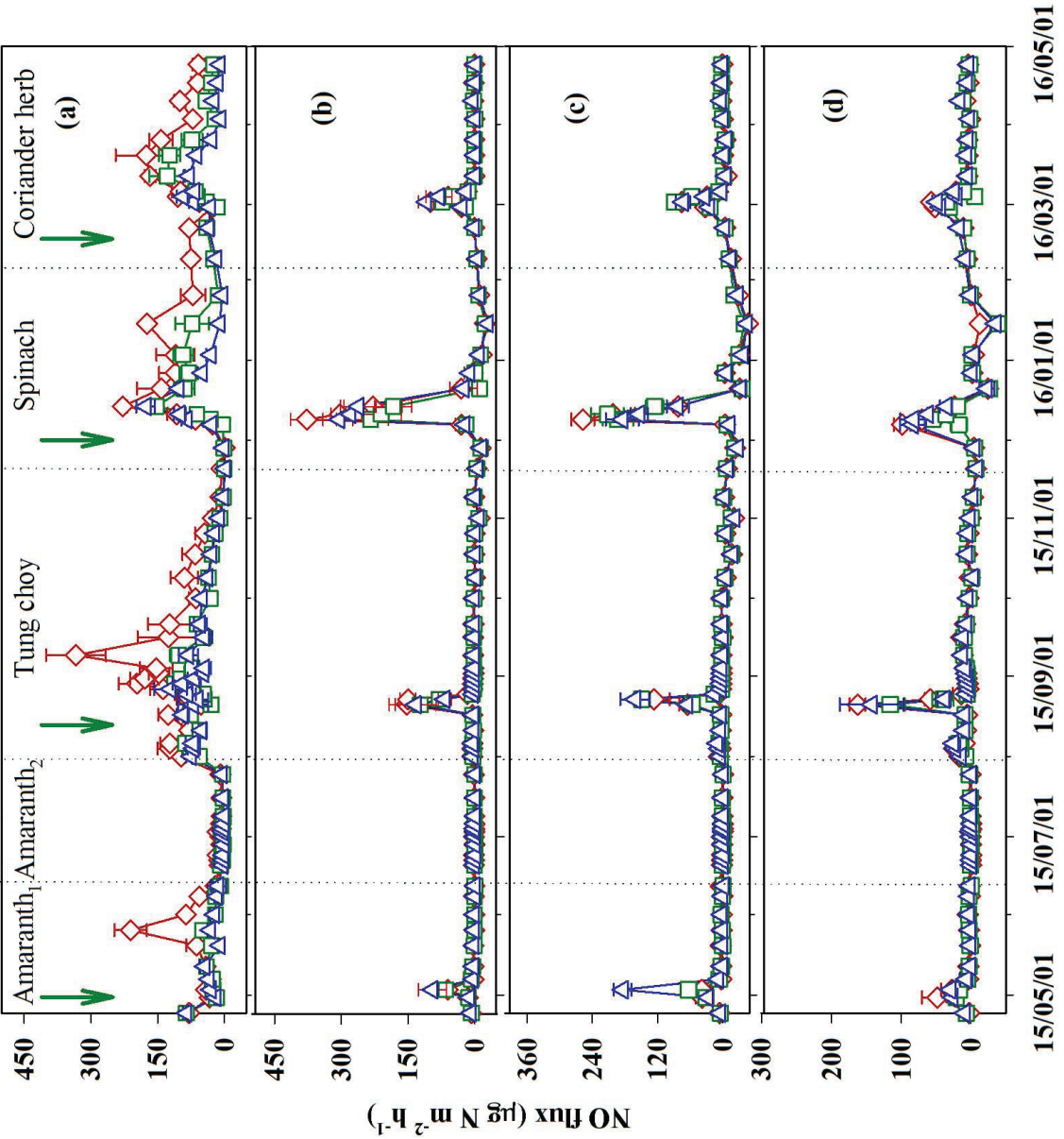

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