Nitrous oxide emissions from an Andosol upland field amended with four different types of biochars

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Nitrous oxide emissions from an Andosol upland field amended with four different types of biochars

Authors:

Akinori Yamamoto[1, †, *], Hiroko Akiyama[2, †], Masahiro Kojima[3], Ayano Osaki[3]

Affiliations:

1 Natural Science Research Unit, Tokyo Gakugei University, 4-1-1 Nukuikitamachi, Koganei, Tokyo, 184-8501, Japan

2 Institute for Agro-Environmental Sciences, National Agriculture and Food Research Organization (NARO), 3-1-3 Kannondai, Tsukuba, Ibaraki 305-8604, Japan

3 Faculty of Education, Tokyo Gakugei University, 4-1-1 Nukuikitamachi, Koganei, Tokyo, 184-8501, Japan

†These authors contributed equally to this work.

*** Correspondence:** A. Yamamoto

Natural Science Research Unit, Tokyo Gakugei University, 4-1-1 Nukuikitamachi, Koganei, Tokyo, 184-8501, Japan

Tel.: +81-42-329-7547, Fax: +81-42-329-7504, E-mail: yakinori@u-gakugei.ac.jp

Abstract

The application of biochar can affect nitrous oxide (N_2O) emissions from the soil. Although laboratory studies reported that biochar application can reduce N_2O emissions, number of field-based study is still limited. Therefore, in this study, we investigated the effects of four different types of biochars and various other environmental parameters on N_2O emissions from an Andosol field over a 2-year period (2015–2016). The field experiment consisted of five treatments: chemical (mineral) fertilizer without biochar (CF), chemical fertilizer with rice husk biochar (RH), chemical fertilizer with chipped bamboo biochar (BA), chemical fertilizer with chipped hardwood biochar (HW), and chemical fertilizer with chipped wood briquet biochar made from a mixture of softwood and hardwood sawdust (SH). Biochar application rate was 25 t ha^{-1}. Biochar application did not affect to the cumulative N_2O emission over 2 years, despite wide range of physicochemical properties of biochar were tested. This was probably because Andosol CEC (31.3 cmol(+) kg^{-1}) was higher than those of biochar (4.52 to 19.65 cmol(+) kg^{-1}) and also high pH-buffering capacity of Andosol. The cumulative N_2O emission of biochar treatment to that of the CF treatment during N_2O peak period (17 days) after biochar and fertilizer

application increased with the increase of amount of NH_4^+-N adsorbed on the biochar. The NH_4^+-N adsorption by biochar may affect the availability of substrate for microbial N_2O production.

Keywords: Andosol, biochar, field experiment, inorganic N adsorption, nitrous oxide

62 **Introduction**

63 Nitrous oxide (N_2O) has 298 times the global warming potential of carbon
64 dioxide and degrades stratospheric ozone (Ravishankara et al. 2009; Stocker et
65 al. 2013). More than half (59%) of anthropogenic N_2O emissions are produced
66 by agriculture (Stocker et al. 2013), with nitrogen (N) fertilizers being the most
67 important source due to their effects on microbial nitrification and
68 denitrification processes in the soil (Granli and Bøckman 1994; Baggs and
69 Philippot 2010). Moreover, N_2O emissions from agriculture are expected to
70 increase as a result of the expansion of agricultural land and growing demand
71 for N fertilizers (Edenhofer et al. 2014). Therefore, the mitigation of N_2O
72 emissions from agricultural soils is crucial if we are to reduce the total
73 anthropogenic N_2O emissions. Several mitigation options have been
74 investigated to date, including nitrification inhibitors, no-tillage farming, coated
75 fertilizers, crop-residue management, and biochar application (Grandy et al.
76 2006; Akiyama et al. 2010; Basche et al. 2014; Nguyen et al. 2017).

77 Biochar is a solid, carbon-rich material that is produced by the pyrolysis of
78 biomass under no or a limited oxygen supply (Sohi et al. 2010). Biochar
79 application has been considered as a potential mitigation option for N_2O

80 emissions from agriculture ecosystems. A meta-analysis by Cayuela et al. (2014)
81 showed that application of biochar reduced N_2O emission from soil. However,
82 some studies reported that biochar has no impact on N_2O emission (Scheer et al.
83 2011; Suddick and Six 2013; Koga et al. 2017) and others reported that biochar
84 increases N_2O emissions (Clough et al. 2010; Wells and Baggs 2014; Feng and
85 Zhu 2017).

86 These contrasting effects of biochar may have been caused by its properties.
87 Previous studies have suggested that various biochar properties, such as the
88 carbon to nitrogen (CN) ratio (Cayuela et al. 2014), hydrogen to organic carbon
89 (H:Corg) ratio (Cayuela et al. 2015), volatile matter and ash contents (Butnan et
90 al. 2016), and pH (Yanai et al. 2007), affect N_2O emissions. Some studies have
91 also reported that the ammonium-nitrogen (NH_4^+-N) adsorption on biochar
92 could decrease N_2O emissions (Singh et al. 2010; Taghizadeh-Toosi et al. 2011;
93 Angst et al. 2013). Moreover, since these biochar properties vary depending on
94 the feedstock and pyrolysis conditions (Spokas et al. 2009; Enders et al. 2012;
95 Kameyama et al. 2012), the effect of biochar on N_2O emissions may also vary
96 with biochar type.

97 Many of the previous investigations into the effects of biochar on N_2O

98 emissions have been laboratory studies (e.g., Clough et al. 2010; Cayuela et al.
99 2013; Harter et al. 2014), which tend to show a larger suppression of N_2O
100 emissions after biochar application than field studies (Yanai et al. 2007; Castaldi
101 et al. 2011; Suddick and Six 2013; Case et al. 2015). This difference may be due to
102 differences in the experimental conditions, such as temperature, soil water
103 content, and substrate supply, between laboratory and field. For example, while
104 the temperature and soil water content are generally held constant in the
105 laboratory, they exhibit daily, weekly, and seasonal fluctuations in agricultural
106 ecosystems. Since these environmental factors influence microbial nitrification
107 and denitrification (Baggs and Philippot 2010), the differences in experimental
108 conditions between laboratory and field will also affect N_2O emissions.
109 Moreover, Spokas (2013) reported that field aging of biochar reduced the
110 magnitude of suppression of N_2O production. Therefore, multi-year field
111 studies are needed to elucidate the effects of different biochars on N_2O
112 emissions in agricultural ecosystems.
113 In this study, we aimed to (1) quantify the effects of four different types of
114 biochars on N_2O emissions from an Andosol field; and (2) investigate the effects
115 of biochar properties and environmental factors on N_2O emissions by

116 conducting a 2-year field experiment in an Andosol field. In addition, we
117 measured the properties of biochars such as adsorption capacity of NH_4^+-N and
118 NO_3^--N.
119
120 **Materials and methods**
121 **Study site**
122 The study site was located at the Institute for Agro-Environmental Sciences,
123 Tsukuba, Ibaraki, Japan (36°01′N, 140°07′E), where the annual mean air
124 temperature was 13.8 °C and the total annual precipitation averaged 1282.9 mm
125 between 1981 and 2010 (Japan Meteorological Agency). The soil type was
126 Andosol (FAO/UNESCO soil classification system). The pH (H_2O) of 5.89 in the
127 topsoil (0–0.05 m), a bulk density of 0.59 Mg m^{-3}, a total carbon (C) content of
128 67.6 g kg^{-1}, a total N content of 4.7 g kg^{-1}, and a cation exchange capacity (CEC)
129 of 31.3 cmol(+) kg^{-1}.
130
131 **Experimental design**
132 The field experiment was conducted from January 1, 2015 to December 31, 2016.
133 Prior to the experiment, soybean was cultivated until October 31, 2014, and the

field was kept fallow until biochar application. We established fifteen 36-m^2 (6 m × 6 m) field plots at the study site that were laid out in a randomized block design with five treatments and three replicates per treatment:

(1) Chemical (mineral) fertilizer without biochar application (CF): A compound fertilizer containing 8% nitrogen (NH_4-N), 8% phosphorus (P_2O_5), and 8% potassium (K_2O) (w/w) was applied according to local practice.

(2) Rice husk biochar with chemical fertilizer application same as CF treatment (RH): Rice husk biochar was obtained from a local farmer and was produced through the thermal decomposition of rice husk mounds using a hood and chimney.

(3) Chipped bamboo biochar with chemical fertilizer application same as CF treatment (BA): The bamboo biochar was produced commercially using a rotary kiln (product name: *Maisetsuyo Takesumi*; Yukashitayou Takesumi Center, Miyazaki, Japan).

(4) Chipped hardwood biochar with chemical fertilizer application same as CF treatment (HW): The hardwood biochar was produced commercially using a kiln (product name: *Minori tanso*; Nara Tanka Kogyo Co., Ltd., Nara, Japan).

(5) Chipped wood briquet biochar made from a mixture of softwood and hardwood sawdust with chemical fertilizer application same as CF treatment (SH): This biochar was produced commercially using a kiln (product name: *Green tanso 2-gou*; Nara Tanka Kogyo Co., Ltd., Nara, Japan).

Each of the biochars was applied to the field at a rate of 25 t ha^{-1}. In addition, the compound fertilizer used in the five treatments was applied at the time of sowing for each crop (Table S1). The biochars and fertilizers were incorporated into the soil to a depth of 0.15 m using a rotary tiller according to the local practice of Ibaraki Prefecture. The biochars were only applied to the soil on May 13, 2015, simultaneously with the spring fertilizer application. The properties of four biochars are shown in Table 1.

In each plot, we cultivated komatsuna (*Brassica rapa* L. var. *perviridis* L.H. Bailey) for spring cropping and spinach (*Spinacia oleracea* L.) for autumn

170 cropping in 20 rows placed 0.30 m apart, according to the local practice of
171 Ibaraki Prefecture. The cultivars, N application rates, dates of fertilizer
172 application, seeding, and harvest in each of the four cropping seasons are
173 summarized in Table S1. Compound fertilizer was incorporated into the soil to
174 a depth of 0.15 m using a rotary tiller at seeding of each cropping seasons.
175 Moreover, we did not apply lime in order to investigate the effects of biochar
176 application on soil pH and N_2O emission throughout the experimental period.
177
178 **Measurements of N_2O flux and environmental factors**
179 We measured the N_2O flux in each plot using an automated chamber and gas
180 sampling system from January 1, 2015 to December 31, 2016 (Akiyama et al.
181 2009). A chamber [cross-sectional area, 0.81 m^2 (0.9 m × 0.9 m); height, 0.65 m]
182 was placed at a depth of 0.05 m in the center of each plot. Both soil and the two
183 rows of corps were included in each chamber made with transparent
184 polycarbonate. The lid of each chamber was left open at all times except during
185 gas sampling, which was conducted every 2 days during the cropping season
186 and every 4 days during the winter fallow period at 16:00 to 17:00. These times
187 were selected based on the results of a nearby field experiment, which showed

188 that the N_2O flux within a day changed with temperature, and the daily
189 average flux was observed in the morning and evening (Akiyama et al. 2000;
190 Akiyama and Tsuruta 2002, 2003). During flux measurement, the lid of each
191 chamber was automatically closed for 60 min using a pressure cylinder and gas
192 samples were automatically withdrawn from the headspace into 15-ml
193 evacuated vials at 0, 30, and 60 min after closure (Akiyama et al. 2009). [See
194 Akiyama et al. (2009) for further information regarding the N_2O flux
195 measurements using the automated chamber and gas sampling system.] The
196 chambers were then automatically opened again.
197 All gas samples were analyzed using a gas chromatograph (GC-2014;
198 Shimadzu, Kyoto, Japan) equipped with a CH_4-doped electron capture detector
199 at 340 ℃ with pure N_2 as the carrier gas. Standard gases of several N_2O mixing
200 ratios (0.3, 0.5, 1.0 and 10.0 ppmv, Saisan Co.,Ltd.) were used for gas sample
201 analysis. The rate of increase in the mixing ratio of N_2O in the chambers was
202 determined using linear regression analysis and estimates of the cumulative gas
203 emissions from periodic samples were calculated using a basic numerical
204 integration technique (i.e., the trapezoidal rule). Only those samples with a
205 regression correlation coefficient greater than 0.90 were used for calculation of

206 N_2O emission. We also calculated the ratio of the cumulative N_2O emission
207 with each biochar treatment (RH, BA, HW, and SH) to the cumulative N_2O
208 emission with the CF treatment ($Cum.N_2O_{biochar}/Cum.N_2O_{CF}$).
209 We measured the volumetric soil water content of each plot at a soil depth of
210 0.05 m every 60 min from May 13, 2015 to December 31, 2016 using a soil
211 moisture sensor (ECH_2O EC-5; Decagon Devices, Pullman, WA, USA). We
212 prepared a calibration curve for the soil moisture sensor by adding known
213 amounts of water to containers packed with oven-dried soil and measuring the
214 soil moisture content ($y = 0.95x + 0.086$, $r^2 = 0.99$). The volumetric soil water
215 content was then used to calculate the water-filled pore space (WFPS) based on
216 the soil porosity value. We measured the volumetric soil water content at a
217 number of points in each plot. However, there was large variation within each
218 plot (data not shown), making it difficult to detect differences among
219 treatments. Therefore, we used the average value of all plots for subsequent
220 correlation analysis between N_2O emission and environmental factors. The soil
221 depth of 0 to 0.05 m was chosen for measurements of the volumetric soil water
222 content and the soil environment factors (described below) because N_2O
223 production was highest at about 0.05 m depth in Andosol fields (Hosen et al.,

コメントの追加 [A1]: From 0 to 0.05m
引用文献の内容が上記表現 OK なら、上記のほうがよいです。

コメントの追加 [AY2]: Hosen et al: 0-8cm、Takeda et al: 4-6cm か 9-11cm で高い傾向を示しています
黒ボク土を対象にして、ちょうど 0-5cm で N2O 生成や活性が高いという論文が見つけられず、微妙な値ですので 5cm 周辺としています。

コメントの追加 [A3R2]: OK

2000; Takeda et al., 2012).

Analysis of soil and biochar properties

We analyzed the inorganic N (NH_4^+-N and NO_3^--N) content and pH of the soil. Sub-samples of surface soil (0–0.05 m) were collected randomly from five sites of each plot then mixed in a plastic bag to have a composite sample and stored at <4 °C until extraction. Within 24-hours of sampling, we extracted soil inorganic N by shaking each sample with 10% KCl (w/v) at a 1:10 ratio for 60 minutes. We then stored the KCl extracts at −25 °C until analysis. We measured the concentrations of inorganic N in the KCl extracts using a continuous flow analyzer (QuAAtro 2HR; BLTEC, Osaka, Japan). We measured the pH of a 1:2.5 slurry (soil/water, w/v) of each soil sample using an electrode-type pH meter (model FE20; Mettler Toledo AG, Schwerzenbach, Switzerland).

To analyze the properties of the different biochars, we measured the pH of a 1:10 slurry (biochar/water, w/v) of each biochar with an electrode-type pH meter, and the total C, N, and hydrogen (H) contents using an elemental analyzer (FlashEA 1112 series; Thermo Fisher Scientific, Bremen, Germany). We also determined the surface area of each biochar by degassing the samples for 3

242 h at 105 °C and measuring their nitrogen adsorption isotherms using a
243 Quantachrome A-1 Autosorb analyzer (Quantachrome Corp., Boynton Beach,
244 FL, USA), based on the Brunauer, Emmett and Teller (BET) method (Brunauer et
245 al. 1938). In addition, we determined the ash content of each biochar by
246 combusting it in a muffle furnace at 750 °C for 6 h, according to the American
247 Society for Testing and Materials D1762-84 standard analysis of charcoal (ASTM
248 2007). The cation exchange capacity (CEC) was measured by using a standard
249 procedure (Schollenberger and Simon 1945). This method involves saturation of
250 the cation exchange sites with 1M ammonium acetate (pH7), equilibration,
251 removal of the excess ammonium with 80% ethanol, replacement and leaching
252 of exchangeable ammonium with 1M NaCl. The concentrations of NH_4^+-N in
253 each extract measured by using a continuous flow analyzer (QuAAtro 2HR).
254
255 **Biochar adsorption experiment**
256 To investigate the ability of each biochar to adsorb NH_4^+-N and NO_3^-N, we
257 conducted an adsorption experiment, in which 0.2 g of the biochar was added
258 to 50 ml of either NH_4Cl or KNO_3 solution at concentrations of 10, 50, 100, and
259 300 mg L^{-1}. Each mixture was shaken in a thermostatic shaker at 25 °C and 200

260 rpm for 24 hours to achieve equilibrium (Gai et al. 2014), following which it was
261 passed through filter paper (type 5C; ADVANTEC, Tokyo, Japan). We then
262 measured the concentrations of inorganic N in each extract using a continuous
263 flow analyzer. This experiment was conducted in quintuplicate.
264 The amount of NH_4^+-N or NO_3^--N that was adsorbed on each biochar (A_N;
265 mg g^{-1}) was calculated according to the following equation (Ok et al. 2007; Gai
266 et al. 2014):
267
268 $$A_N = (C_{in} - C_{eq})V/M \quad (1)$$
269
270 where C_{in} and C_{eq} are the concentrations of NH_4^+-N or NO_3^--N in the initial and
271 equilibrium solutions, respectively (mg L^{-1}), V is the volume of the aqueous
272 solution (L), and M is the mass of biochar (g).
273 The NH_4^+-N and NO_3^--N adsorption data were fitted to the Langmuir
274 isotherm model, which is frequently used to describe adsorption isotherms (Gai
275 et al. 2014) and has previously been used to quantify and contrast the
276 performance of different bio-sorbents (Langmuir 1916; Foo and Hameed 2010).
277 The Langmuir model is as follows:

$$C_e/Q_e = C_e/Q_m + 1/(Q_m K_L) \quad (2)$$

where C_e is the concentration of NH_4^+-N or NO_3^--N in the equilibrium solution (mg L^{-1}), Q_e is the mass of NH_4^+-N or NO_3^--N adsorbed per unit mass of the biochar at equilibrium (mg g^{-1}), Q_m is the maximum adsorption capacity of the biochar (mg g^{-1}), and K_L refers to the Langmuir constants that are related to the adsorption capacity and adsorption rate. Plotting C_e/Q_e against C_e gives a straight line with a slope of $1/Q_m$ and an intercept of $1/(Q_m K_L)$.

Statistical analysis

The significance of the differences in N_2O emission, cumulative N_2O emission, environmental factors (soil NH_4^+-N and NO_3^--N contents, soil pH), and crop yield among the treatments were determined by one-way analysis of variance (ANOVA, $P = 0.05$), followed by Tukey's post hoc test to determine specific differences between the means where a significant effect was detected. Significant correlations between N_2O emission and environmental factors (soil NH_4^+-N and NO_3^--N contents, soil pH, WFPS) were identified using Pearson's

296 correlation analysis. All statistical analyses were performed with SPSS ver. 22.0
297 (IBM corp., Chicago, IL, USA).
298
299 **Results**
300 **Environmental factors**
301 The study site had a mean air temperature of 15.3 °C and 15.2 °C, a total
302 precipitation of 1256 mm and 1337 mm, and a mean WFPS of 39.7% and 36.6%
303 in 2015 and 2016, respectively (Fig. 1a, b). The WFPS ranged from 28.5% to
304 66.0% during the experimental period.
305 Soil pH showed a decreasing trend during the experimental period, changing
306 from 5.9 at the beginning of the experiment to 4.5 at the end. In addition, the
307 soil pH decreased following fertilizer application and then increased in all
308 treatments (Fig. 1c). There was generally no significant difference in soil pH
309 among the treatments throughout the experimental period. Note that we did
310 not apply lime, in order to investigate the effects of biochar application on soil
311 pH and N_2O emission throughout the experimental period.
312 The soil NH_4^+-N contents peaked just after fertilizer application, while the
313 soil NO_3^--N contents peaked approximately 1 week after fertilizer application in

314 each cropping season, suggesting that nitrification occurred after each fertilizer
315 application in all treatments (Fig. 1d, e). There was generally no significant
316 difference in soil NH_4^+-N and NO_3^--N contents among the treatments
317 throughout the experimental period.

318 There was no significant difference in crop yield among the treatments in any
319 of the cropping periods (Table S2).

320

321 **Biochar properties**

322 The pH of the four biochars ranged from 8.9 to 10.2, while the C, N, and H
323 contents of the biochars ranged from 50.39% to 72.57%, 0.21% to 0.71%, and
324 1.18% to 1.92%, respectively (Table 1). The RH biochar had a higher ash content
325 than the other biochars, while the SH biochar appeared to have a lower CEC
326 value than the other biochars. The RH biochar is presumed to have been
327 produced approximately at 300-500 °C, as judged from the ash content (Table 1)
328 and previous studies (Liu et al., 2012; Ahmad et al., 2014; Claoston et al., 2014).
329 Both the BA and SH biochars had large surface areas (204 and 261 $m^2\ g^{-1}$,
330 respectively), whereas the RH and HW biochars had small surface areas (53 and
331 25 $m^2\ g^{-1}$, respectively). Small amounts of NH_4^+-N were detected in all of the

332 biochars, whereas NO_3^--N was only detected in the RH biochar.

333

334 **Inorganic nitrogen adsorption of different biochars**

335 All four biochars exhibited some NH_4^+-N adsorption capacity, but the
336 magnitude of this differed among the biochars (Fig. 2a). In particular, the RH
337 and BA biochars tended to have higher NH_4^+-N adsorption capacities than the
338 other biochars, while the SH biochar had a lower NH_4^+-N adsorption capacity
339 than the other biochars at all initial NH_4^+-N concentrations. The RH and BA
340 biochars gave a better fit to the Langmuir isotherm for NH_4^+-N adsorption than
341 the HW and SH biochars (Table 2). Furthermore, the RH, BA, and HW biochars
342 had a higher Q_m value than the SH biochar, while the RH biochar had a higher
343 K_L value than the other biochars.

344 In contrast to NH_4^+-N, all four biochars adsorbed very little NO_3^--N at initial
345 NO_3^--N concentrations of 10, 50, and 100 mg L^{-1} (Fig. 2b). However, the RH, BA,
346 and HW biochars did adsorb NO_3^--N at an initial NO_3^--N concentration of 300
347 mg L^{-1}. Furthermore, the RH and SH biochars actually released NO_3^--N into the
348 solutions at some initial NO_3^--N concentrations (RH biochar at 100 mg L^{-1}
349 NO_3^--N; SH biochar at 100 and 300 mg L^{-1} NO_3^--N).

N_2O emissions

Temporal changes in the N_2O emissions were similar across all treatments, exhibiting a rapid increase after each fertilizer application and a subsequent decrease (Fig. 3). N_2O emissions peaked after fertilizer application and harvest during the spring cropping season in 2015 and 2016, but only peaked after fertilizer application during the autumn cropping season in both years. There was negative correlation between N_2O emissions and WFPS with all treatments in 2015 and 2015-2016 (Table 3). However, relationships between WFPS and N_2O fluxes were very scattered, while the majority of N_2O flux was very low (Fig. S1). N_2O emissions and soil NH_4^+-N content positively correlated with the RH treatment in 2015 and 2016 and the SH treatment in 2016.

The cumulative N_2O emissions were not significantly different among the treatments in any period (Table 4). $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ was closer to 1.0 in 2016 than in 2015 for all treatments, i.e., differences between cumulative N_2O emissions of biochar treatment and that of CF were larger in 2015 than those in 2016.

The physicochemical properties of biochar may change with time because

コメントの追加 [AY4]: 表 4 に $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ を入れました

コメントの追加 [A5R4]: 修正しました

コメントの追加 [A6]: 分かりにくいです。
表に比（文章どおりだと差？）をいれるとか工夫必要と思います

368 biochar oxidized in soil (Spokas 2013). Therefore, we used the cumulative N_2O
369 emission during peak period (17 days) after biochar and fertilizer application to
370 minimize the effect of change of physicochemical properties in correlation
371 analysis between cumulative N_2O emission and biochar properties.
372 $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ during peak period increased with the increase of
373 the amount of NH_4^+-N adsorbed on the biochars at all initial NH_4^+-N
374 concentration (Table 5). At an initial concentration of 300 mg L^{-1} of NH_4^+-N,
375 there was significant positive correlation between $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$
376 and the amount of NH_4^+-N adsorbed on biochar (Fig. 4). The similar
377 relationships were found $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ and the amount of NH_4^+-N
378 adsorbed on biochar at lower initial NH_4^+-N concentration (Fig. S2). By contrast,
379 there was no significant correlation between $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ and the
380 amount of NO_3^--N adsorbed on the biochars (Table 5). There were also no
381 significant relationships between $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ and the other
382 environmental factors and biochar properties (Table S3).
383
384 **Discussion**
385 Previous studies reported that biochar application has a potential to mitigate

386 N_2O emission (e.g., Cayuela et al. 2014), and the differences in properties of
387 biochar influence the magnitude of reduction of N_2O emission (Spokas et al.
388 2009; Cayuela et al. 2015). However, we found that biochars did not affect the
389 cumulative N_2O emission throughout the experimental period. These results
390 may be due to soil properties such as CEC and pH.

391 Firstly, the CEC of soil affect soil mineral N contents, an important factor for
392 N_2O emission through their influence on nitrification and denitrification (Mu et
393 al. 2009). Previous study reported that reduction of N_2O emission from soil due
394 to biochar application was attributed to adsorption of NH_3 onto biochar by
395 reducing the N pool available for soil microbes (Taghizadeh-Toosi et al. 2011).
396 The present study showed different NH_4^+-N adsorption capacity among the
397 biochars. However, these biochars did not significantly reduce soil NH_4^+-N
398 content after fertilizer application at field. This result may be attributed to the
399 high CEC of Andosol compared with those of other soil types (Aran et al. 2001;
400 Guicharnaud and Paton 2006; Maejima et al. 2016). The CEC of soil (31.3 cmol(+)
401 kg^{-1}) was higher than that of four biochars in the present study (Table 1).
402 Therefore, biochar application was likely to have little influence on change in
403 soil NH_4^+-N content and resulted in non-significant difference on N_2O emission

among the treatments. Koga et al. (2017) reported that wood-residue biochar application at 0-40 Mg ha^{-1} had no effect on N_2O emission from an Andosol in a 4-year field experiment. Moreover, Shimotsuma et al. (2017) showed that rice husk biochar amendment did not reduce N_2O emission from Andosol by incubation experiment.

Secondly, soil pH is also known to have an important effect on N_2O emissions (Granli and Bøckman 1994; Baggs and Philippot 2010). Castaldi et al. (2011) reported that an increase in soil pH after biochar application might partly explain the decrease in N_2O emissions from silty-loam soil, and Liu et al. (2017) suggested that the enhanced abundance of nitrifiers and denitrifiers due to an increase in soil pH by biochar addition is an important mechanism for decreasing N_2O emissions. However, in the present study, there was no correlation between N_2O emissions and soil pH for any of the treatments (Table 3). This result could have been due to the high pH-buffering capacity of Andosol (Baba et al. 1995; Takahashi et al. 2001), as biochar application had little effect on the soil pH in the RH (from 5.95 to 5.85), BA (from 5.82 to 5.96), HW (from 5.81 to 5.71), and SH (from 5.85 to 5.78) plots (Fig. 1c). Similarly, Koga et al. (2017) reported that soil pH was unaffected by biochar addition in an

422 Andosol field.

423 Our results showed that the difference between cumulative N_2O emission
424 biochar treatments and that of CF decreased with time (Table 4). There were no
425 differences in the N application rates and crop types between 2015 and 2016,
426 and the environmental factors were also similar (Fig. 1 and Table S1). Therefore,
427 field aging of biochar might result in the decrease of the ratio of cumulative
428 N_2O emission biochar treatments to CF treatment. Biochar oxidizes in soil with
429 time, causing changes to its physical and chemical properties (Spokas 2013).
430 Spokas (2013) reported that field aging of biochar significantly reduced its N_2O
431 suppression effect due to a change in the balance of greenhouse gas production
432 and consumption following the chemical oxidation of the biochar surfaces.

433 Furthermore, we found that $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ during peak period
434 after biochar and fertilizer application increased with the amount of NH_4^+-N
435 adsorbed on the biochars (Fig. 4). Biochar can adsorb essential nutrient
436 including NH_4-N (Hale et al. 2013), and then over time, NH_4-N could slowly be
437 released and subsequently be utilized by plants (Laird et al. 2010;
438 Taghizadeh-Toosi et al. 2012a, 2012b). Taghizadeh-Toosi et al (2012a) suggested
439 that NH_3 adsorbed onto biochar can provide a source of N for plants when

440 biochar-NH_3 complex is placed in the soil. Microbial nitrification and
441 denitrification are the major pathways of N_2O production in soils, and the
442 microbes utilize mineral N in soil as substrate (Baggs and Philippot 2010).
443 Therefore, it is possible that both plants and soil microbes are utilized the
444 NH_4-N released from biochar. N_2O production via nitrification and
445 denitrification occurs simultaneously in the soil because soil is heterogeneous
446 and consist of both aerobic and anaerobic sites (Granli and Bøckman 1994; Hu
447 et al. 2015). Hence, released NH_4-N from biochar could have affected the N_2O
448 production via nitrification and denitrification by changing N availability in
449 soil.

450 Cai et al (2016) showed that approximately 10 % to 60 % of NH_4^+ adsorbed
451 onto biochar was released and the factors such as feedstock and pyrolysis
452 condition affect the release ratio of NH_4^+. Taghizadeh-Toosi et al. (2012a)
453 suggested that NH_3 adsorbed onto biochar when the biochar was incorporated
454 into soil. Moreover, Wang et al. (2011) reported that an increase in N_2O
455 emissions due to biochar addition could be partly explained by the release of
456 NH_4^+-N following the initial adsorption of NH_3 on the biochar.

457 In contrast to the NH_4^+-N adsorption capacity, there was no clear correlation

コメントの追加 [A7]: 文献もみたのですが、意図した意味がよくわかりませんでした。
また、この論文は実験的に吸着を証明しているというわけではないようなので、修正しました。

458 between the NO_3^--N adsorption capacity and Cum.$N_2O_{biochar}$/Cum.N_2O_{CF} during
459 peak period after biochar and fertilizer application (Table 5). Our results
460 showed that biochars had little or no NO_3^--N adsorption capacity and the
461 narrow range of NO_3^--N adsorption capacities of biochars may explains the
462 insignificant relationship.
463
464 **Conclusion**
465 The effect of biochar application on N_2O emission was investigated by 2-year
466 field experiment using with wide range of physicochemical properties of
467 biochars. All of the biochars had NH_4^+-N adsorption capacity, but adsorbed
468 very little NO_3^--N. Although previous studies reported that biochar application
469 reduced N_2O emission, biochar application did not have clear effect on N_2O
470 emission from an Andosol in our field experiment. We also found that biochars
471 did not affect soil pH and soil NH_4^+-N contents during the experimental period.
472 High CEC and high pH-buffering capacity of Andosol may be the reasons that
473 no clear effect of biochar on N_2O emission was observed. Our results suggest
474 that biochar application may affect substrate availability for microbial N_2O
475 production.

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665

Table 1

Physiochemical properties of the biochars

Biochar	Feedstock	Pyrolysis temperature (°C)	pH (H_2O)	Ash (%)	C (%)	N (%)	H (%)	CEC (cmol(+) kg^{-1})	BET surface area (m^2 g^{-1})	NH_4-N (μg N g DW^{-1})	NO_3-N (μg N g DW^{-1})
RH	Rice husk	No data	8.9±0.1	41.87±0.1	50.39±14.5	0.67±0.2	1.73±0.6	19.65	53	4.12±2.4	0.25±0.0
BA	Bamboo	850	10.2±0.1	6.50 ±0.0	71.26±11.5	0.21±0.1	1.18±0.4	10.61	204	5.89±3.7	nd
HW	Hardwood	600	9.2±0.0	6.67±1.1	72.57±7.0	0.71±0.2	1.92±0.7	17.97	25	1.67±1.8	nd
SH	Softwood and hardwood [a]	>800	9.6±0.0	2.05±0.0	68.56±22.1	0.45±0.1	1.18±0.4	4.52	261	4.21±1.7	nd

nd: not detected

[a]Wood briquet made from a mixture of softwood and hardwood sawdust

Values of pH, C content, N content, H content, NH_4-N content, and NO_3-N content are the means ± standard deviations of

three replicates. Values of ash content are the means ± standard deviations of two replicates. There is no replication in analysis of CEC and BET surface area.

Table 2

Regression parameters of Langmuir isotherms describing the adsorption of NH_4^+-N to each biochar

Biochar	Q_m [a]	K_L [b]	r^2
RH	6.057	0.014	0.84
BA	7.639	0.008	0.93
HW	5.397	0.006	0.55
SH	3.108	0.004	0.18

[a] Maximum adsorption capacity of biochar (mg g^{-1})

[b] Langmuir constants related to the adsorption capacity and adsorption rate

Table 3

Pearson's correlation coefficients between N_2O emission and water-filled pore space (WFPS), soil NH_4^+-N content, soil NO_3^--N content, and soil pH

Treatment[a]	Pearson's correlation coefficient											
	2015				2016				2015-2016			
	WFPS	NH_4^+-N	NO_3^--N	soil pH	WFPS	NH_4^+-N	NO_3^--N	soil pH	WFPS	NH_4^+-N	NO_3^--N	soil pH
CF	−0.241**	0.374	0.158	−0.366	−0.106	0.479	0.099	0.020	−0.196**	0.141	0.142	−0.121
RH	−0.250**	0.614*	0.311	−0.384	−0.082	0.548*	0.192	0.143	−0.171**	0.332	0.204	0.029
BA	−0.206*	0.574	0.194	−0.411	−0.05	0.357	0.182	−0.038	−0.142*	0.322	0.159	−0.060
HW	−0.266**	0.419	0.142	−0.543	−0.035	0.465	0.239	−0.112	−0.162**	0.188	0.234	−0.194
SH	−0.276**	0.546	0.155	−0.470	−0.036	0.518*	0.096	0.003	−0.169**	0.256	0.118	0.105

[a] RH: rice husk biochar; BA: bamboo biochar; HW: hard wood biochar; SH: wood briquet biochar made from a mixture of softwood and hardwood sawdust

*$P < 0.05$, **$P < 0.01$

Table 4

Cumulative N_2O emissions and Cum.$N_2O_{biochar}$/Cum.N_2O_{CF} ratios for the five treatments. Emissions values are the means ± standard deviations of three replicates

Treatment[a]	2015		2016		2015–2016	
	N_2O flux (kg N_2O-N ha^{-1})	Cum.$N_2O_{biochar}$/Cum.N_2O_{CF}[b]	N_2O flux (kg N_2O-N ha^{-1})	Cum.$N_2O_{biochar}$/Cum.N_2O_{CF}	N_2O flux (kg N_2O-N ha^{-1})	Cum.$N_2O_{biochar}$/Cum.N_2O_{CF}
CF	0.46 ± 0.11 a	—	0.68 ± 0.12 a	—	1.14 ± 0.21 a	—
RH	0.57 ± 0.16 a	1.25	0.73 ± 0.17 a	1.07	1.30 ± 0.29 a	1.15
BA	0.58 ± 0.19 a	1.28	0.73 ± 0.35 a	1.08	1.32 ± 0.54 a	1.16
HW	0.52 ± 0.22 a	1.13	0.69 ± 0.21[c] a	1.01	1.08 ± 0.26[c] a	0.95
SH	0.34 ± 0.19 a	0.74	0.56 ± 0.16 a	0.82	0.89 ± 0.28 a	0.79

[a] RH: rice husk biochar; BA: bamboo biochar; HW: hard wood biochar; SH: wood briquet biochar made from a mixture of softwood and hardwood sawdust

[b] Ratio of the cumulative N_2O emission of biochar treatment to that of the chemical fertilizer (CF) treatment

[c] Mean of two replicates were used due to the trouble of sampling system

Values followed by the same letter are not significantly different at $P < 0.05$.

Table 5

Pearson's correlation coefficients for the relationships between $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ and the amounts of NH_4^+-N or NO_3^--N adsorbed onto the biochars (A_N) at different initial NH_4^+-N or NO_3^--N concentrations

Pearson's correlation coefficient							
A_N of NH^{4+}-N				A_N of NO_3^--N			
10 mg L^{-1}	50 mg L^{-1}	100 mg L^{-1}	300 mg L^{-1}	10 mg L^{-1}	50 mg L^{-1}	100 mg L^{-1}	300 mg L^{-1}
0.868	0.936	0.931	0.958*	−0.168	−0.857	nd	nd

$Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ indicates the ratio of the cumulative N_2O emission of biochar treatment to CF treatment during peak period (17 days) after biochar and fertilizer application

nd indicates that the correlation coefficient could not be calculated because the biochar did not adsorb NO_3^--N

*$P < 0.05$

Figure legends

Fig. 1

Temporal variations in (a) daily air temperature (line) and precipitation (bars), (b) water-filled pore space (WFPS), (c) soil pH, (d) soil NH_4^+-N content, and (e) soil NO_3^--N content in the study plots. The vertical arrows indicate the timing of fertilization (F), biochar application (B), and harvest (H). Error bars represent standard deviations (n = 3). RH: rice husk biochar; BA: bamboo biochar; HW: hard wood biochar; SH: wood briquet biochar made from a mixture of softwood and hardwood

Fig. 2

Adsorption isotherms of (a) NH_4^+-N and (b) NO_3^--N for each biochar. A_N and Ce indicate the amount of nitrogen adsorbed on each biochar and the equilibrium concentration of NH_4^+-N or NO_3^--N in solution, respectively. Error bars represent standard deviations (n = 5). RH: rice husk biochar; BA: bamboo biochar; HW: hard wood biochar; SH: wood briquet biochar made from softwood and hardwood sawdust

Fig. 3

Temporal variation in N_2O emissions. The vertical arrows indicate the timing of fertilization (F), biochar application (B), and harvest (H). Values are the means of three replicate plots. RH: rice husk biochar; BA: bamboo biochar; HW: hard wood biochar; SH: wood briquet biochar made from softwood and hardwood sawdust

Fig. 4

Relationship between the amount of NH_4^+-N adsorbed on each biochar (A_N) at an initial NH_4^+-N concentration of 300 mg L^{-1} and $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$. $Cum.N_2O_{biochar}/Cum.N_2O_{CF}$ is the ratio of the cumulative N_2O emission of biochar treatment to that of chemical fertilizer (CF) treatment during peak period (17 days) after biochar and fertilizer application. RH: rice husk biochar; BA: bamboo biochar; HW: hard wood biochar; SH: wood briquet biochar made from softwood and hardwood sawdust

Figure 1

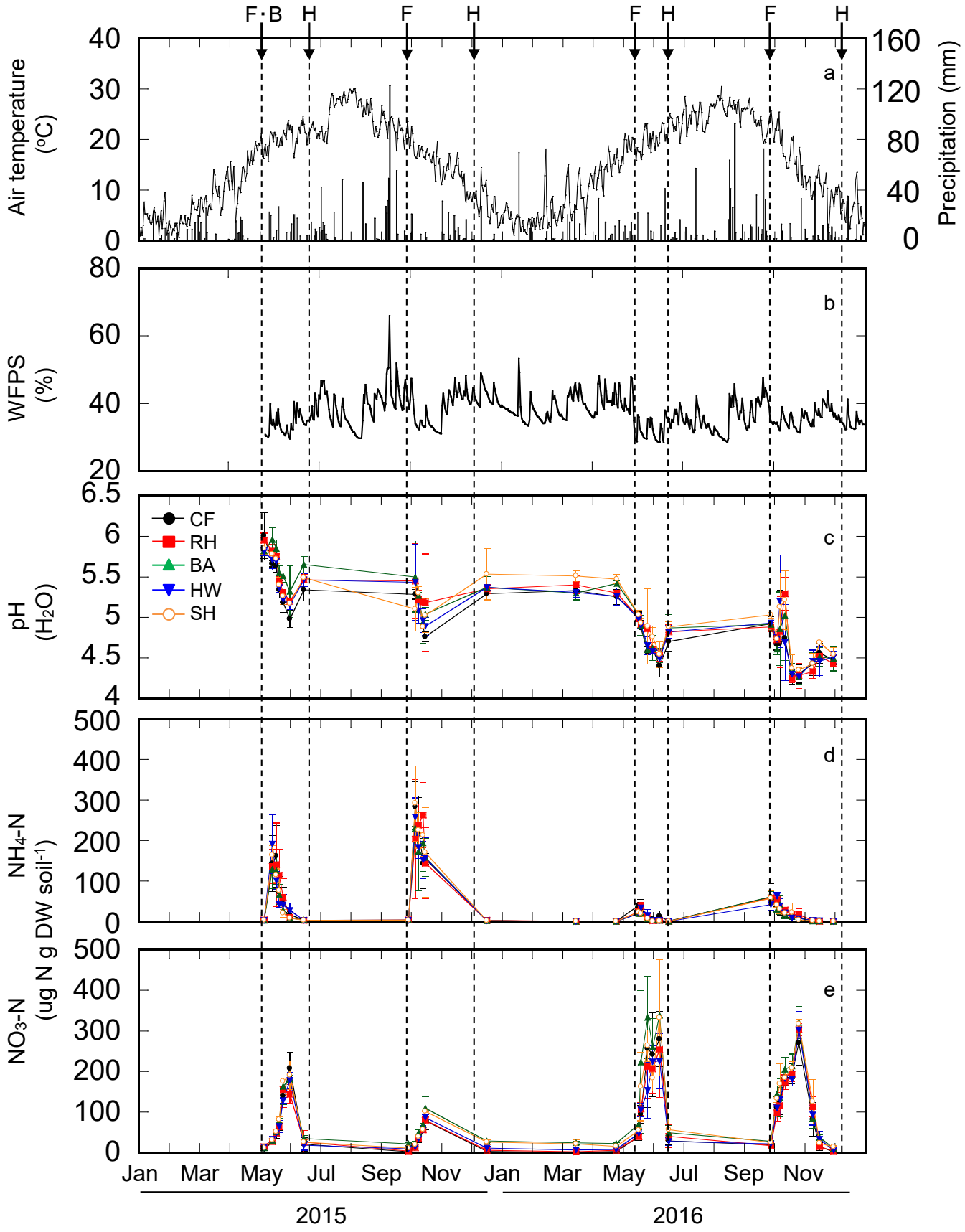

F·B
H
F
H
F
H
F
H
a
b
c
d
e
Air temperature (°C)
Precipitation (mm)
WFPS (%)
pH (H2O)
NH4-N (ug N g DW soil-1)
NO3-N (ug N g DW soil-1)
CF
RH
BA
HW
SH
Jan
Mar
May
Jul
Sep
Nov
2015
2016

Figure 2

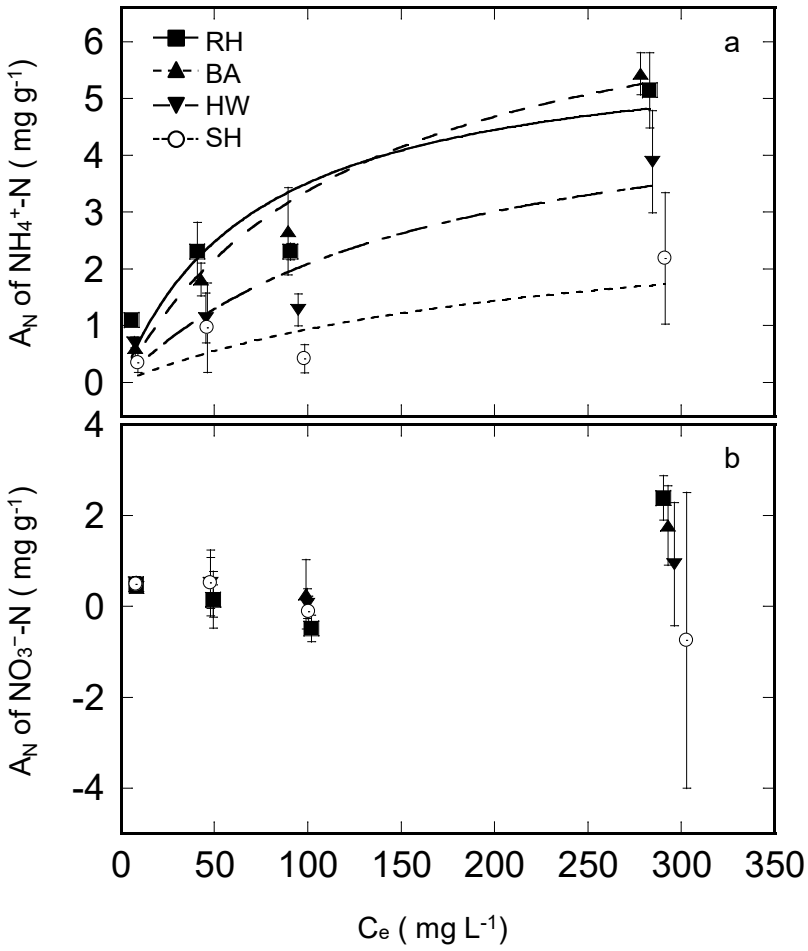
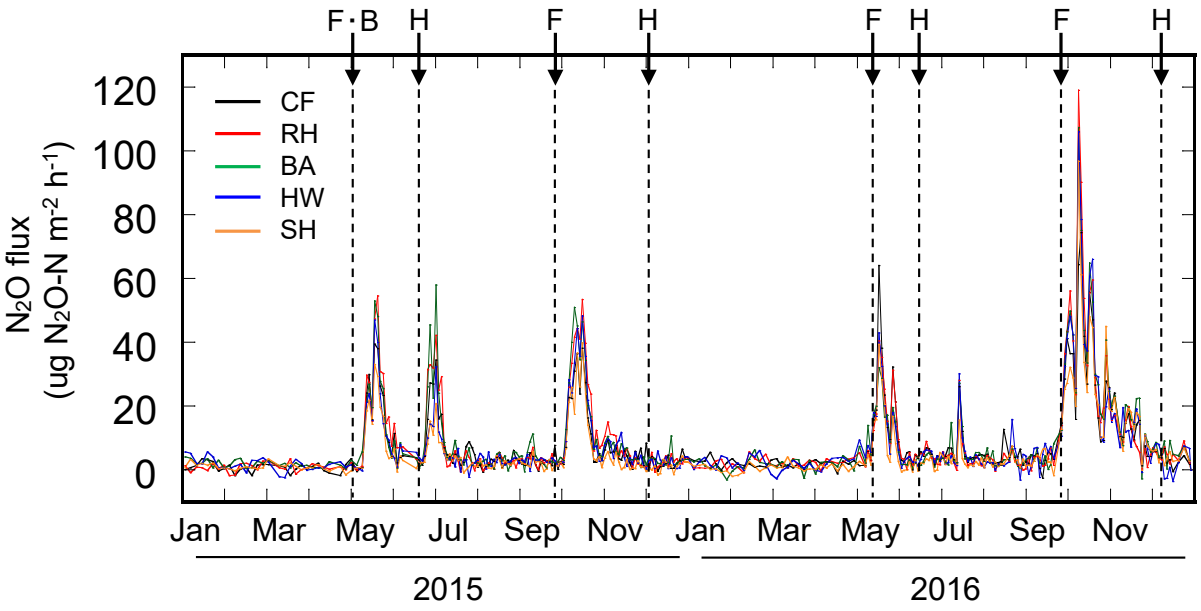

RH
BA
HW
SH
a
b
A_N of NH_4^+-N (mg g^{-1})
A_N of NO_3^--N (mg g^{-1})
C_e (mg L^{-1})
6
5
4
3
2
1
0
4
2
0
-2
-4
0
50
100
150
200
250
300
350

Figure 3


F
B
H
F
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F
H
F
H
120
100
80
60
40
20
0
CF
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SH
N2O flux
(ug N2O-N m-2 h-1)
Jan
Mar
May
Jul
Sep
Nov
Jan
Mar
May
Jul
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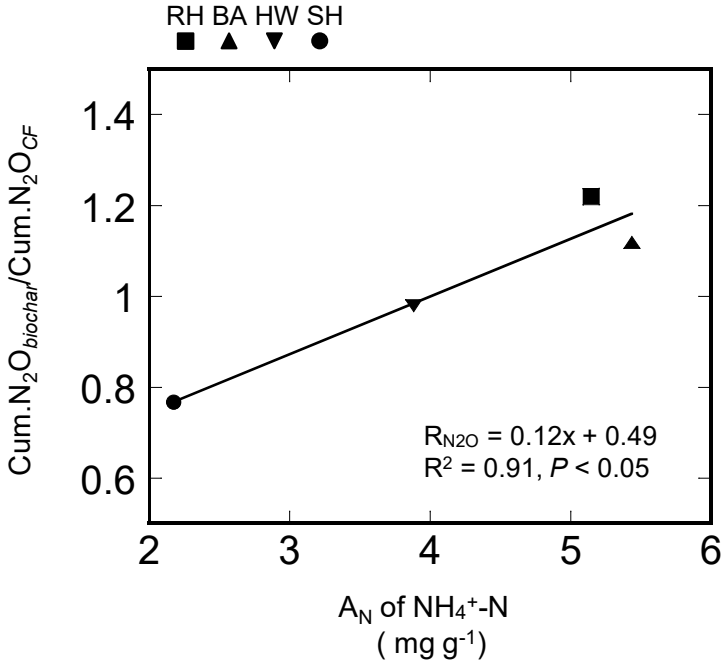
2015
2016

Figure 4


RH BA HW SH
1.4
1.2
1
0.8
0.6
2
3
4
5
6
Cum.N2Obiochar/Cum.N2OCF
RN2O = 0.12x + 0.49
R2 = 0.91, P < 0.05
AN of NH4+-N
(mg g-1)