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Original article

Influence of individual and co-application of organic and inorganic fertilizer on NH_3 volatilization and soil quality

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ABSTRACT

The use of nitrogen fertilizers to enhance crop growth tends to increase every year. In addition, as eco-friendly agriculture is emphasized, organic fertilizers are preferred over inorganic fertilizers. However, since most of organic fertilizers in South Korea use imported ingredients, an alternative ingredients is needed. Biochar is an eco-friendly way to recycle various biomass and has a high pH and carbon contents. The objective of this study was to evaluate the effect of individual and co-application of organic and inorganic fertilizers on ammonia (NH_3) volatilization and soil quality. Organic fertilizers used in this study were divided into conventional organic fertilizers (CF_1 and CF_2) and biochar-based organic fertilizers (BF). As a result of the experiment, NH_3 volatilization and soil quality were significantly affected by the inorganic fertilizers. Also, NH_3 volatilization effected by inorganic fertilizer was rapidly increased between 4 and 7 days. When different organic fertilizers were treated, NH_3 emissions by BF was highest at 17.49 and 28.97 kg ha^{-1} compared to CF_1 and CF_2, but no statistically significant different was observed. A similar trend was appeared when organic and inorganic fertilizers was co-applied. Therefore, biochar-based organic fertilizers are similar to conventional organic fertilizers in terms of soil quality and NH_3 volatilization, but it is expected to contribute to the formation of a stable fertilizer market by reducing the percentage of imported ingredients.

1. Introduction

Nitrogen (N) is an important nutrient of plant growth and one of the main factors contributing crop productivity. Application of N fertilizers is an essential agricultural practice for crop quality and quantity, and is vital for sustaining crop yields (Liao et al., 2020). Thereafter, the use of nitrogen fertilizers worldwide increased from 11.6 Tg in 1961 to 100.5 Tg in 2008 (Turner et al., 2012). N fertilizers applied to the soil surface are the major pathway for losses of N such as ammonia (NH_3), and approximately 11.0 Tg yr^{-1} estimates to arise the form of NH_3 (Beusen et al., 2008; Kang et al., 2022). The lost NH_3 acts as a main source of the nitrous oxide (N_2O) and generates secondary particulate matter called PM2.5 (Park et al., 2020; Kang et al., 2021a). In addition, emitted NH_3 indirectly effects to biodiversity deterioration, water eutrophication, and air pollution (Fungo et al., 2019). The NH_3 emission process is affected by various environmental and factitious factors such as air temperature, moisture, soil pH, type of fertilizers, precipitation, etc (Bouwmeester et al., 1985).

Fertilizers are extensively embezzled worldwide to improve soil fertility. In South Korea, co-application inorganic and organic fertilizers is customary, but recently, individual treatment of organic

Abbreviations: CF, conventional organic fertilizers; BF, biochar-based organic fertilizers; NPK, Inorganic fertilizers; EC, electrical conductivity; T-C, total carbon contents; T-N, total nitrogen content; Av. P_2O_5, available phosphate contents; T-P_2O_5, total phosphate contents.

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fertilizer is recommended. The application of inorganic fertilizers was essential to improve crop productivity (Parris, 2011). However, excessive inorganic fertilizers treatment can decrease soil pH and increase soil EC (Kang et al., 2022). So, it aggravates soil quality and plant growth, reduces soil fertility, and accelerates soil acidification (Wu et al., 2020; Wang et al., 2020). The use of organic fertilizers was not preferred because it needs more labor, and lacks direct response to plant production (Yang et al., 2020). However, organic fertilizers can continuously offer various nutrients needed for plant growth and improvement, and amend soil physico-chemical properties such as soil structure, pH, electrical conductivity, etc (Chauhan and Bhatnagar, 2014). In addition, it can also make beneficial conditions for soil microbial, improve water retention and soil fertility (Bell et al., 2015; Liu et al., 2016). Organic fertilizers used as an alternative for inorganic fertilizer were mainly manufactured by blending plant and animal ingredients, and in South Korea, organic fertilizers using two or more kinds of ingredients were mostly used (Yoon et al., 2012; Zhu et al., 2018). So, the influences of organic fertilizers produced from different materials on crop growth are divergent (Fallah et al., 2018).

As a new way of recycling various biomass and organic wastes in agriculture sector to the soil, biochar has a direct and indirect effect on NH_3 emission on the soil (Shi et al., 2019). Biochar is a carbon-rich substance manufactured by pyrolysis of biomass and organic materials (e.g., rice husk, maize stalk, and cattle manure) under the oxygen-limited conditions (Martin et al., 2015; Oh et al., 2017; Lee et al., 2019; Kang et al., 2021b). Biochar has led multiple note because of abundant surface functional groups, intensive adsorption capacity, abundant porosity, and high levels of carbon sequestration (Lehmann and Joseph, 2015; Kang et al., 2021c). Several researches have shown that the utilization of biochar to the soil may improve soil aeration and structure, raise soil pH, enhance water and nutrient availability of crop, and alter the soil microbial community, thus promoting growth and yield of plant (Woo, 2013; Lee et al., 2018; Wu et al., 2020). However, the biochar was produced from low pyrolysis temperature had a high level of volatile content, which could have a negative effect on environment ecosystem (Deenik et al., 2011). Combination of organic fertilizers and biochar could reduce negative effects of biochar pyrolyzed low temperature (Schmidt et al., 2014). Many studies reported the positive influences of biochar, but effect of organic fertilizers combined biochar was still insufficient (Sasmita et al., 2017).

In this study, we hypothesize that fertilizer conditions (type, dose, ingredient, etc) will affect NH_3 volatilization from agricultural soil, and that ingredients of organic fertilizers can be replaced to the biochar. Therefore, we conducted a static chamber experiment to investigate the effects of fertilizer conditions and substitutability of biochar on NH_3 volatilization and soil quality.

2. Materials and methods

2.1. Experimental site

The field experiment was conducted in test field belonging to the College of Agriculture and Life Science of the Chungnam National University in Daejeon, Republic of Korea (36°22′02.1″ N 127°21′12.1″ E). The research was carried out for 77 days in the period the 5th of September 2020 to the 21th of November 2020. The soil of test field was classified as Inceptisols with 12.8% clay, 41.4% silt, and 45.8% sand. The physico-chemical properties of the soil are represented in Table 1. This region has both humid continental climate and humid subtropical climate affected by the East Asian monsoon, with high precipitation in summer, which begins between June and July. The average annual temperature and total precipitation of the experimental site were 13.0 °C and 1458.7 mm. Detailed meteorological conditions during this experiments are shown in Fig. 1.

2.2. Experimental design

The area of each treatments was approximately 3.0 m × 3.5 m (10.5 m^2), which was separated by 1 m to avoid interference among different fertilizers. Treatments divided into 36 units and organic and inorganic fertilizers were treated to the soil surface. In addition, total of 36 experimental plots were randomly arranged. Organic fertilizers were treated only as basal fertilizer and applied with 120 kg N ha^{-1}. Inorganic fertilizer was treated with 320 kg N ha^{-1} in the experimental group and sprayed four times (i.e., 110–70–70–70 kg N ha^{-1}). Experimental plots co-applied organic and inorganic fertilizers were treated with 440 kg N ha^{-1} (i.e., organic fertilizer 120 kg N ha^{-1} + inorganic fertilizer 320 kg N ha^{-1}). Treated dose of inorganic fertilizers was conducted based on Soil Management and Fertilizer Recommendations of the Rural Development Administration, South Korea. Also, inorganic fertilizers used in this experiment were the same type. The basal fertilizer was applied on September 25, 2020 (Day 1), and the topdressing was treated on October 9, 2020 (Day 15), October 24, 2020 (Day 30), and November 8, 2020 (Day 45). Water management was followed the local conventional practice, and irrigation was performed twice a week.

The experiment to investigate NH_3 volatilization on by organic and inorganic fertilizers individual application or co-application were separated as eight treatments. Control is an untreated treatment without organic and inorganic fertilizers, NPK is the treatment where only inorganic fertilizers were applied. CF_1 (conventional organic fertilizer), CF_2, and BF (biochar-based organic fertilizer) were treated with organic fertilizers and CF_1 + NPK, CF_2 + NPK, and BF + NPK were applied with organic and inorganic fertilizers.

2.3. NH_3 volatilization measurement

Measurement of NH_3 volatilization from each experimental plots was conducted using a static chamber (h: 30.0 × Ø: 12.0 cm) made of acrylic. Two pieces of sponge (h: 2.0 × Ø: 12.5 cm) as NH_3 absorbers in the chamber were moistened in Glycerol-phosphoric acid solution, which consisted of 40 ml L^{-1} glycerol (C_3H_8O) and 68.6 ml L^{-1} phosphoric acid (H_3PO_4). The upper sponge prevented the ingress of external gasses, and the lower sponge had the function of capturing NH_3 occurred in the soil. The sponge absorbed NH_3 was extracted by 2 M KCl solution. The NH_4^+ concentration in KCl extracts was determined by Indophenol blue method using a UV/Vis-spectrophotometer (GENESYS 50, Thermo Scientific Inc., Waltham, Massachusetts, USA). Daily NH_3 emissions were calculated based on soil surface area covered by the chambers (0.011 m^2), temperature in chamber, and the amount of fertilizers. Total NH_3 volatilization was calculated by summing daily NH_3 emissions.

2.4. Analysis of soil and organic fertilizers

Soil samples were collected from total 10 points in the experimental plot, and blended fully. After mixing samples, soils were dried for 1 week in grass greenhouse and passed through a 2 mm sieve. An analysis of soil physico-chemical properties was conducted as follows. Soil texture was determined by hydrometer method. pH and EC (electrical conductivity) of soil were measured using a Benchtop Meter with pH and EC (ORION™ Versa Star Pro™, Thermo Scientific Inc., Waltham, Massachusetts, USA) after blending soil samples and distilled water at a ratio 1:5 (w v^{-1}) and

Table 1
Physico-chemical properties of the soil in experimental field.

Sample	Texture	pH (1:5)	EC ($dS\ m^{-1}$)	T-C (%)	T-N	Av. P_2O_5 ($mg\ kg^{-1}$)	Ca^{2+} ($cmol_c\ kg^{-1}$)	K^+	Mg^{2+}	Na^+
Soil	Inceptisols	6.13 ± 0.05	0.74 ± 0.06	0.51 ± 0.01	0.06 ± 0.00	25.90 ± 3.94	5.49 ± 0.17	0.16 ± 0.01	1.84 ± 0.04	0.09 ± 0.01

Abbreviation: EC, electrical conductivity; T-C, total carbon contents; T-N, total nitrogen contents; Av. P_2O_5, available phosphate contents.

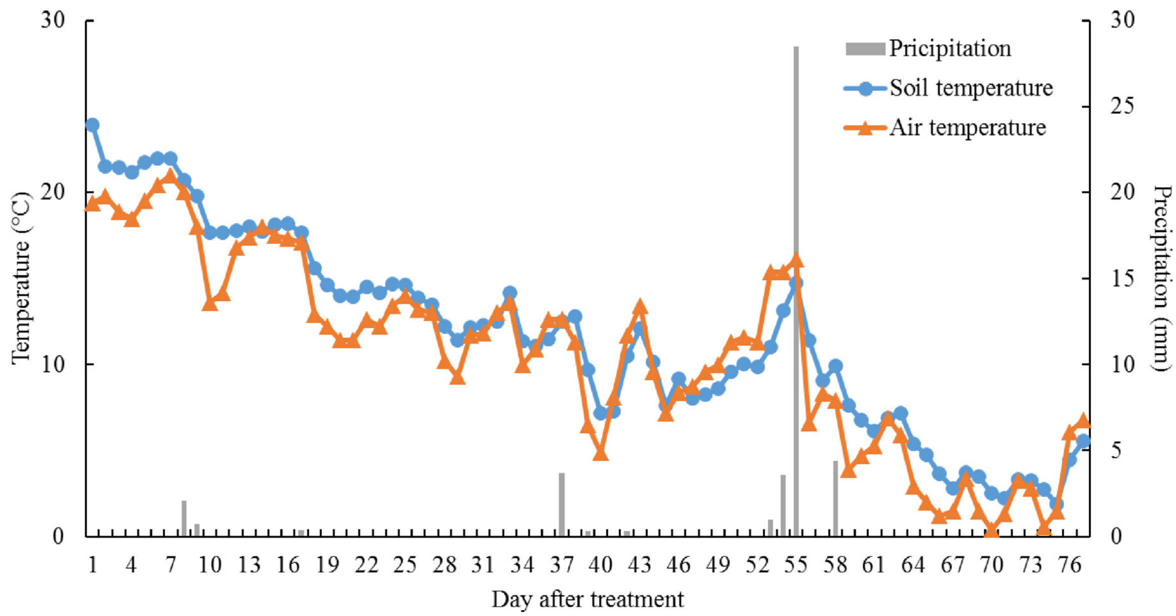

Fig. 1. Meteorological conditions during the experiments.

stirring for 30 min. T-C (total carbon contents) and T-N (total nitrogen contents) were measured by CHN analyzer (TruSpec Micro, Leco, Michigan, USA). Av.P_2O_5 (available phosphate contents) was analyzed using a Lancaster method by UV/Vis-spectrophotometer. ICP-OES (ICAP 7000series ICP spectrometer, Thermo Scientific Inc., Waltham, Massachusetts, USA) were used to measured Exchangeable cations (Ca^{2+}, K^+, Mg^{2+}, Na^+).

The pH and EC of organic fertilizers were determined using a Benchtop Meter with pH and EC after mixing samples and distilled water at a ratio 1:10 ($w\ v^{-1}$) and stirring for 30 min. T-C and T-N were analyzed using CHN analyzer. UV/Vis-spectrophotometer was used for the determination of T-P_2O_5 (total phosphate contents) using a vanadate method. Inorganic contents (CaO, K_2O, MgO, Na_2O) were measured by ICP-OES.

2.5. Statistical analysis

The results of NH_3 volatilization and soil physico-chemical properties during cultivation were expressed as average value. Statistical significant difference between each treatments was compared using Duncan multiple range test after ANOVA using a statistical analysis program (IBM SPSS Statistics version 26, New York, USA). Statistical significance could have been set on the basis of the 95% confidence interval.

3. Results and discussions

3.1. Chemical properties of organic fertilizers

The constituent ingredients and blend ratios of organic fertilizers were represented in Tables 2, and 3 recorded the chemical properties of biochar used material of organic fertilizers. Table 4 showed the chemical properties of organic fertilizers. The pH of organic fertilizers was lower in BF (pH 6.30) compared to other organic fertilizer. CF_1 and CF_2's pH were pH 6.70 and pH 7.57, respectively and it has a higher pH than normal soil, which may negatively affect the soil and crop. On the contrary, the pH of BF was fit in the appropriate pH range (pH 5.5–6.5), so it will be no negative effect on growth of crop during cultivation. EC was relatively lower at 20.41 $dS\ m^{-1}$ for CF_1 and higher at 66.56 $dS\ m^{-1}$ for CF_2 compared to BF in 25.17 $dS\ m^{-1}$. In the case of T-C, CF_1 and CF_2 were measured to be 37.10% and 37.50%, respectively and BF was determined to be 47.70%, which is 10% higher than CF_1 and CF_2. It is thought to be due to the high carbon contents of biochar in BF. T-N tended to be higher in CF_1 and CF_2 compared to the BF and was highest in CF_2 at 5.99%. T-P_2O_5 showed a similar tendency to those of the T-N and was highest in CF_1 at 2.20%. CaO contents and K_2O contents were 2.03% and 1.99% for BF, which was higher than CF_1 and CF_2. Especially, K_2O contents were 5.6 times higher in BF compared to CF_1 and CF_2. MgO contents were highest in CF_1 at 1.78% and Na_2O contents were highest in CF_2 at 0.32%. Organic fertilizers used in South Korea are stipulated that the sum of two of N, P_2O_5, and K_2O is 7% or more. In the case of BF produced using biochar, the total amount of N and K_2O is more than 7%, so it can used as an organic fertilizers. Also, the high carbon content of BF compared to CF_1 and CF_2 can increase the organic matter contents in the soil and improve soil fertility.

3.2. Change in the soil chemical properties

Chemical properties of the soil affected organic and inorganic fertilizers were shown in Table 5. Compared with the soil before the experiment, the pH of control, CF_1, CF_2, and BF was lower, but increased when applied with inorganic fertilizers. Also, the soil

Table 2
The constituent ingredients and blend ratios of organic fertilizers used in this experiment.

Treatments	Biochar	Castor oil-cake	Soybean-cake	Coffee meal	Rice bran	Rape seed oil-cake
	(%, v v^{-1})					
CF_1	–	47	23	-	20	10
CF_2	–	78	–	–	14	8
BF	10	30	45	5	10	–

Abbreviation: OF, conventional organic fertilizers; BF, biochar-based organic fertilizers.

Table 3
Chemical properties of biochar used as ingredient of organic fertilizers.

Treatment	pH	EC	T-N	T-P_2O_5	K_2O	OM	CEC
	(1:10)	(dS m^{-1})	(%)				($cmol_c$ kg^{-1})
Biochar	9.80 ± 0.01	8.80 ± 0.02	0.44 ± 0.03	0.33 ± 0.05	1.56 ± 0.00	62.90 ± 0.07	38.60 ± 0.00

Abbreviation: EC, electrical conductivity; T-N, total nitrogen contents; T-P_2O_5, total phosphate contents; K_2O, potassium oxide contents; OM, organic matter contents; CEC, cation exchange capacity.

Table 4
Chemical properties of organic fertilizers used in this experiment.

Treatments	pH	EC	T-C	T-N	T-P_2O_5	CaO	K_2O	MgO	Na_2O
	(1:10)	(dS m^{-1})				(%)			
CF_1	6.70 ± 0.01	20.41 ± 0.20	37.1 ± 0.00	5.35 ± 0.00	2.20 ± 0.53	1.21 ± 0.07	0.19 ± 0.01	1.78 ± 0.25	0.19 ± 0.01
CF_2	7.57 ± 0.01	66.56 ± 1.02	37.5 ± 0.00	5.99 ± 0.00	2.14 ± 0.56	1.57 ± 0.14	0.32 ± 0.01	0.72 ± 0.13	0.32 ± 0.01
BF	6.30 ± 0.01	25.17 ± 1.56	47.70 ± 0.00	5.17 ± 0.00	0.94 ± 0.00	2.03 ± 0.01	1.99 ± 0.00	0.16 ± 0.02	0.18 ± 0.04

Abbreviation: OF, conventional organic fertilizers; BF, biochar-based organic fertilizers; EC, electrical conductivity; T-C, total carbon contents; T-N, total nitrogen contents; T-P_2O_5, total phosphate contents.

Table 5
Chemical properties of the soil affected by organic and inorganic fertilizers.

Treatment	pH	EC	T-C	T-N	Av. P_2O_5	Ca^{2+}	K^+	Mg^{2+}	Na^+
	(1:5)	(dS m^{-1})	(%)		(mg kg^{-1})	($cmol_c$ kg^{-1})			
Control	5.96 ± 0.44 cd	0.28 ± 0.02c	0.54 ± 0.02b	0.07 ± 0.00b	26.32 ± 7.69b	6.53 ± 0.39a	0.21 ± 0.03c	2.54 ± 0.25a	0.12 ± 0.01c
NPK	8.35 ± 0.18a	3.98 ± 0.86a	0.77 ± 0.02a	0.14 ± 0.01a	37.97 ± 9.35ab	6.49 ± 0.48a	4.13 ± 1.02a	1.91 ± 0.22b	0.19 ± 0.04a
CF_1	5.87 ± 0.67d	0.43 ± 0.10c	0.59 ± 0.05b	0.07 ± 0.00b	35.22 ± 7.81ab	5.85 ± 0.92a	0.20 ± 0.03c	2.26 ± 0.30ab	0.12 ± 0.02c
CF_1 + NPK	7.60 ± 0.66b	3.74 ± 0.61ab	0.82 ± 0.02a	0.14 ± 0.01a	38.28 ± 6.67ab	6.05 ± 1.38a	2.86 ± 1.64b	1.93 ± 0.44b	0.17 ± 0.04ab
CF_2	6.07 ± 0.37c	0.45 ± 0.06c	0.55 ± 0.06b	0.07 ± 0.00b	19.92 ± 5.57c	6.33 ± 0.99a	0.18 ± 0.03c	2.45 ± 0.29a	0.13 ± 0.02c
CF_2 + NPK	8.28 ± 0.31ab	4.29 ± 0.51a	0.79 ± 0.04a	0.14 ± 0.01a	43.90 ± 10.24a	6.32 ± 0.27a	3.48 ± 1.18ab	1.92 ± 0.26b	0.20 ± 0.03a
BF	6.12 ± 0.36c	0.36 ± 0.03c	0.57 ± 0.05b	0.07 ± 0.01b	25.87 ± 12.55bc	6.07 ± 0.66a	0.19 ± 0.01c	2.34 ± 0.21a	0.12 ± 0.02c
BF + NPK	7.99 ± 0.40ab	3.86 ± 0.65ab	0.72 ± 0.02a	0.15 ± 0.01a	42.52 ± 14.97a	5.93 ± 1.46a	3.05 ± 1.03ab	1.82 ± 0.32b	0.17 ± 0.04ab

Abbreviation: NPK, treatments applied with inorganic fertilizer; OF, conventional organic fertilizers; BF, biochar-based organic fertilizers; EC, electrical conductivity; T-C, total carbon contents; T-N, total nitrogen contents; Av. P_2O_5, available phosphate contents.
a – d: Each value with different letters within a column are statistically significant difference from each other as determined by Duncan's multiple range test ($p < 0.05$).

pH was increased in all units except for CF_1 in comparison with control treatment. NPK was revealed the highest pH at pH 8.35, and control was shown the lowest pH at pH 5.96. This phenomenon is considered to be caused by the K_2O fertilizers (pH 11.0) used in this study. EC showed a similar tendency to soil pH, and it was highly increased when co-applied with organic and inorganic fertilizers. Especially, the EC was highest in CF_2 + NPK (4.29 dS m^{-1}) compared to other treatments, and it is thought because the EC value of CF_2 (66.56 dS m^{-1}) was higher than other organic fertilizers (CF_1, BF). The T-C and T-N of the soil after the experiment were increased beside the soil before the experiment. Also, T-C and T-N in units co-applied with organic and inorganic fertilizers were higher than those treated with organic fertilizers alone. In the case of T-C, all treatments was increased compared to the control, but T-N was enhanced in the units co-applied with organic and inorganic fertilizers. Av. P_2O_5 was increased in all treatments except for CF_2, and was the highest at 44.52 mg kg^{-1} in BF + NPK. Exchangeable cations contents showed an overall tendency to increase after fertilization. In particular, Ca^{2+} contents were highest at 6.53 $cmol_c$ kg^{-1} in control, and K^+ contents were highest at 4.13 $cmol_c$ kg^{-1} in NPK.

3.3. NH_3 volatilization

The NH_3 volatilization from individual organic fertilizer application were shown in Figs. 2 and 3. All of the treatments applied with organic fertilizer mainly occurred within the 10 days after fertilization, and the peaks of NH_3 emissions was highest at Day 6 – Day 8, respectively. After NH_3 volatilization was reached the maximum, emitted NH_3 rate decreased gradually until there was similar to control (Fig. 2). Especially, the peak of NH_3 emissions treated by BF reached the highest value on Day 8 at 857.22 g ha^{-1} h^{-1}. The NH_3 peak of CF_1 and CF_2 appeared on Day 6 and Day 7, respectively. The trend of NH_3 emissions from individual application of BF was sharply proceed in the initial period than CF_1 and CF_2 from Day 1 to Day 24, but CF_1, CF_2, and BF showed a similar trend of NH_3 emissions after Day 25. The total amount of NH_3 volatilization from Day 1 to Day 77 was highest in BF with 17.49 kg ha^{-1}, and lowest in CF_1

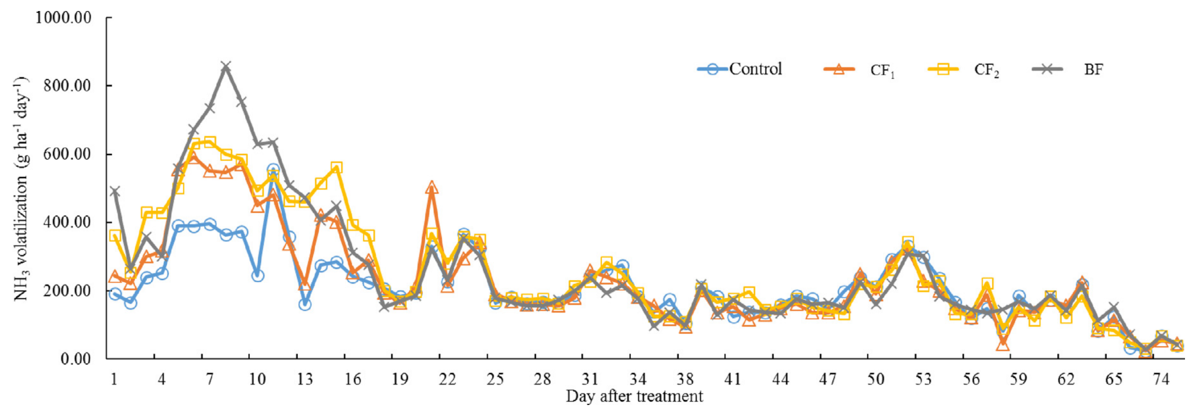

Fig. 2. Daily NH_3 volatilization applied with only organic fertilizers.

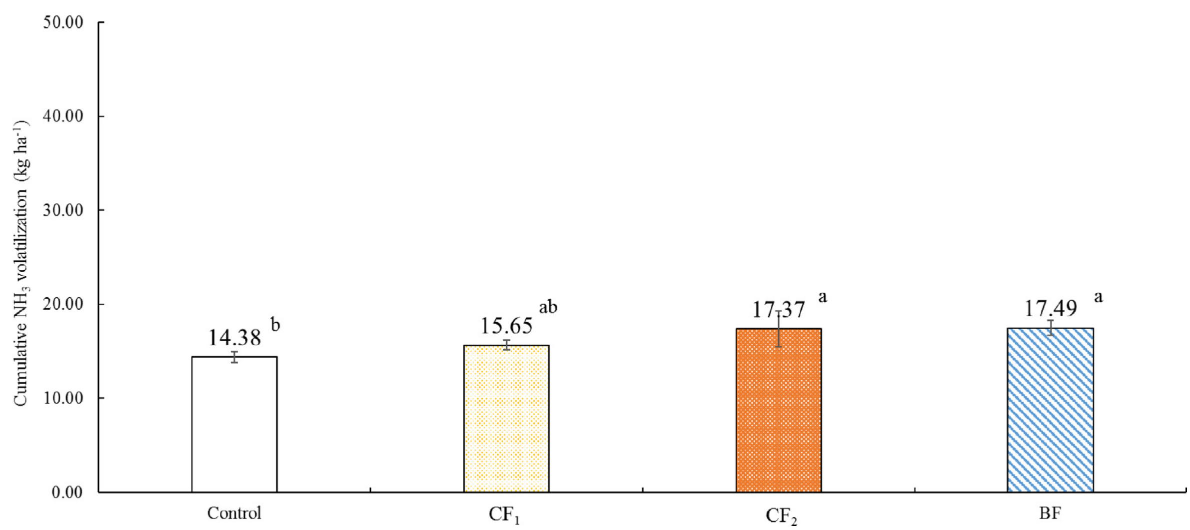

Fig. 3. Total NH_3 volatilization applied with only organic fertilizers. Error bars indicate standard deviations of the means (n = 3). a – b: Each value with different letters within a column are statistically significant difference from each other as determined by Duncan's multiple range test ($p < 0.05$).

with 15.65 kg ha^{-1} (Fig. 3). However, there was no statistically significant difference between CF_1, CF_2, and BF. The results recorded on NH_3 volatilization by co-application of organic and inorganic fertilizers were represented in Figs. 4 and 5. The trend of NH_3 volatilization occurred within the initial period after co-application of organic and inorganic fertilizers, and appeared the highest peak on Day 3 or Day 4. The highest rate of NH_3 emission was detected in the Day 4 at 2780.49 g ha^{-1} h^{-1} on CF_1 + NPK (Fig. 4). After basal and top dressings, the NH_3 volatilization in the all treatments except for control was sharply proceed, and decreased rapidly. The highest value was 28.97 kg ha^{-1} in the BF + NPK treatment, and the lowest value was 19.13 kg ha^{-1} in the NPK treatment. Other treatments (CF_1 + NPK and CF_2 + NPK) were 28.13, 28.87 kg ha^{-1}, respectively. Also, no statistically significant difference was observed when treatments co-applied with organic and inorganic fertilizers.

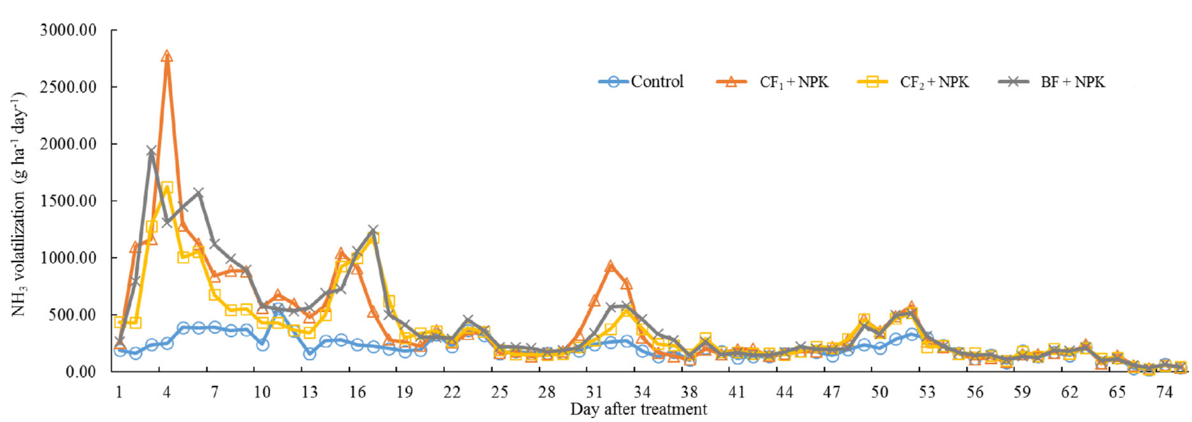

Fig. 4. Daily NH_3 volatilization applied with organic and inorganic fertilizers.

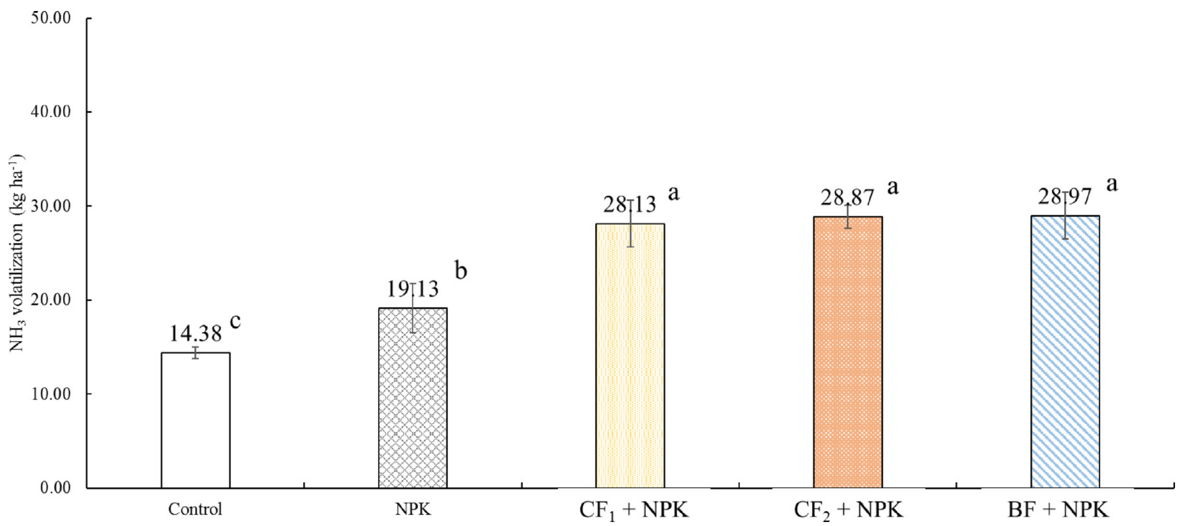

Fig. 5. Total NH_3 volatilization applied with organic and inorganic fertilizers. Error bars indicate standard deviations of the means (n = 3). a – c: Each value with different letters within a column are statistically significant difference from each other as determined by Duncan's multiple range test ($p < 0.05$).

4. Conclusions

This study was conducted to investigate the effects of individual and co-application of organic and inorganic fertilizers on NH_3 volatilization and soil quality. Biochar-based organic fertilizers had lower pH, T-N, and T-P_2O_5 but higher T-C and K_2O contents compared to the conventional organic fertilizers (CF_1 and CF_2). After fertilization to the soil, most of the soil chemical properties were decreased in the treatments treated with only organic fertilizers, whereas all of parameters were increased in treatments co-applied with organic and inorganic fertilizers·NH_3 volatilization by treating with organic fertilizers was higher in BF in comparison with the CF_1 and CF_2. However, there was no statistically significant difference between CF_1, CF_2, and BF. In addition, a similar trend was observed when organic and inorganic fertilizers were co-applied. In this study, it was observed that biochar-based organic fertilizers had a similar effect on the NH_3 volatilization and soil quality as with conventional organic fertilizers. Also, the NH_3 volatilization and soil quality was mostly affected by inorganic fertilizers than organic fertilizers. Therefore, biochar-based organic fertilizers are considered to be able to sequestrate carbon for a long time and reduce the price of organic fertilizers by using biochar as part of the ingredients.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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