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Ammonia and nitrous oxide emissions from a field Ultisol amended with tithonia green manure, urea, and biochar

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Abstract
Short-term mitigation of ammonia (NH_3) and nitrous oxide (N_2O) emissions by biochar soil amendments has been reported, but limited knowledge of the mechanisms, particularly those associated with long term changes, remain relatively unknown. In order to investigate potential mechanisms and residual effect of biochar on NH_3 and N_2O emission, a 3-year field trial was set up on an Ultisol in western Kenya with a three-replicate full factorial treatment structure. The factors investigated include the following: biochar (from eucalyptus wood, pyrolyzed at 550 °C, applied once before the start of the experiment at either 0 or 2.5 t ha^{-1}); tithonia green manure applied at the start of each season at either 0, 2.5, or 5.0 t ha^{-1}; mineral nitrogen (N) (as urea applied each season at either 0 or 120 kg N ha^{-1}). NH_3 as well as N_2O emission and water-filled pore space (WFPS) were monitored throughout the 3 years. In the third year, soil mineral nitrogen (exchangeable NH_4^+ and NO_3^-) contents were measured. Biochar reduced cumulative emissions of NH_3 and N_2O by 47 ± 5 and $22\% \pm 3$, respectively, over the 3 years. Over the 3 years, the effect size of biochar was reduced by 53 and 59% for NH_3 and N_2O, respectively, indicating that the residual effect of biochar on NH_3 and N_2O persists at least up to 3 years under field conditions. Tithonia and urea additions increased both gas emissions by 13–68% compared to the control. Combination of the three amendments reduced cumulative NH_3 emissions by $18 \pm 3\%$, but had no effect on cumulative N_2O. Our results show that biochar can influence emissions of NH_3 and N_2O longer than most previous studies have reported but is not explained by N dynamics. Other mechanisms such as direct interactions with oxidized biochar surfaces could be more likely to account for the residual effect of biochar on NH_3 and N_2O in agricultural soils.

Keywords Biochar · Gaseous N-loss · Soil amendments · Residual effect

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Introduction

Ammonia (NH_3) and nitrous oxide (N_2O) are major atmospheric pollutants. NH_3 contributes to water eutrophication, acidification, and changes in biodiversity, through the processes of atmospheric transportation and deposition (Ciais et al. 2013). On the other hand, N_2O is a long-lived greenhouse as well as an ozone layer-depleting gas (IPCC 2013). In the context of agriculture's contribution to climate change mitigation, management of agricultural soils should aim at either reducing the amount or form of these soil-derived gases in order to achieve low-emission agricultural production.

Growing evidence exists that addition of pyrogenic organic matter (biochar) can reduce NH_3 and N_2O emitted from agricultural soils (Cayuela et al. 2014; Sagrilo et al. 2014; Case et al. 2015). Previous studies proposed several mechanisms for both gases, which include the following: (i) retention of inorganic N through NH_4^+ adsorption and N immobilization (Kizito et al. 2014; Wang et al. 2015); (ii) biochar-induced changes in soil pH and other physico-chemical properties that affect the functions of ammonia oxidizers and nitrifiers at a microbial community level, directly changing the equilibrium between NH_4^+ and NH_3; (iii) greater N uptake by plants through enhanced plant growth (Xu et al. 2012; Abaas et al. 2012); (iv) promotion of soil aeration by reducing bulk density and increasing porosity that reduces N_2O production (Ameloot et al. 2016); and (v) greater nosZ gene expression which encodes the nitrous oxide reductase and reduces N_2O to N_2 (Harter et al. 2013).

Hitherto, denitrification has been considered as the major pathway for N_2O emissions from agricultural soils. However, there is need to draw attention to alternative pathways such as ammonia oxidation (Thomson et al. 2012) and nitrification (Kool et al. 2011; Niu et al. 2018), as may be dictated by soil moisture conditions. Ammonia (NH_3) volatilization is a major pathway of N loss in agricultural systems worldwide, and results in low fertilizer N use efficiency, environmental and health issues, and indirect N_2O emission (Pana et al. 2016). Lower emissions of N_2O in biochar-amended soils may be related to losses of NH_4^+ due to increased NH_3 volatilization. Schomberg et al. (2012) suggested that the reduced N leaching observed in their study resulted from increased NH_3 loss rather than adsorption by biochar surfaces. However, in many cases reduced NH_3 emissions were found (Taghizadeh-Toosi et al. 2012; Mandal et al. 2016). The biochar-induced reduction in NH_3 volatilization may be attributed to NH_3 adsorption on biochar surfaces, increased nitrification, and N immobilization (Mandal et al. 2016). NH_3 retention capacity depends on the properties of biochar such as its surface area, pore size, and pore structure. Very few studies have measured NH_3 emissions from biochar-amended soils and those that do (e.g., Taghizadeh-Toosi et al. 2012; Kizito et al. 2014; Song et al. 2014; Mandal et al. 2016) reported short-term results for

NH_3, N_2O or the processes that produce NH_3, leaving no clear explanation of the relationships. Clough et al. (2013) concluded that the impact of biochar on NH_3 varied with biochar characteristics. Soil and biochar pH influence soil greenhouse gas (GHG) fluxes, but to a more limited extent (He et al. 2017). Zhang et al. (2017) observed that soil pH was an important factor affecting the abundance of Ammonia-Oxidizing Bacteria (AOB), which are responsible for consumption in the soil. Therefore, under field conditions, the mechanisms and duration of effect in which biochar lowers emissions of NH3 remain relatively unknown.

Previous studies investigating effects of biochar aging on soil properties show changes in biochar surface chemistry, which could potentially affect C and N cycling and therefore the fluxes of N_2O (Fungo et al. 2014; Li et al. 2015; Zhang et al. 2015a; Mia et al. 2017). However, experimentation under carefully controlled incubation conditions (such as Singh et al. 2012) or for short periods (Nguyen et al. 2017) does not represent well the aging processes in field soils. Griffin et al. (2017) studied soil inorganic N dynamics under biochar amendment for 4 years but did not link this to N_2O emissions. Nguyen et al. (2016) linked N dynamics to N_2O emissions but this was a short-term pot trial.

Whereas some studies suggest that biochar has mainly short-term effects after application, ranging from a few days to several months, others indicate that the effects may be long-lived. For example, Spokas (2013) observed a reduced N_2O mitigation effect by biochar after 3 years of biochar aging in the field. In contrast, Lentz et al. (2014) observed a persistent effect over a 3-year period after biochar additions, suggesting that a long-term driver is involved, possibly related to biochar's enduring porosity and surface chemistry characteristics. As such, questions remain concerning the medium- to long-term implications of biochar additions given the scant literature on field-based studies. Determining the residual effect of biochar on soil N dynamics provides opportunities to identify underlying processes and mechanisms regulating N_2O fluxes in biochar-amended soil (Nguyen et al. 2017). If biochar can provide long-term mitigation potential for N-fertilized soils, it can be a low-emission innovation for soil management.

The aim of the current study is to determine how soil mineral nitrogen (exchangeable NH_4+ and $NO_3−$) and organic matter inputs affect the long-term interaction between biochar and soil-atmosphere fluxes of NH_3 and N_2O. The specific objectives were to determine (i) the effect of continuous application of organic inputs (tithonia) and mineral N (urea) on NH_3 and N_2O fluxes; (ii) the residual effect of these amendments on soil mineral N; and (iii) the trend in effect size of the above amendments on NH_3 and N_2O over a 3-year period after basal application of 2.5 t ha^{-1} of biochar to an Ultisol under field conditions. We hypothesized that under low moisture, nitrification is an important N_2O production pathway, and that biochar partly reduces N_2O emissions via increased NH_3 volatilization. We also

hypothesized that the long-term effect of biochar on N_2O endures up to at least 3 years. This residual effect is attributed to biochar's influence on soil N dynamics that have been observed to persist for several years. The surfaces of biochar affect NH_4^+ and NO_3^- availability, the substrates for nitrification and denitrification. We also hypothesized that biochar-regulated N availability could result in reduced N_2O flux through long-term effects on air and moisture transport.

Materials and methods

Study site

The field experiment was established in September 2012 at Kapsengere on the southern Nandi hills in western Kenya (N 00° 09′ 34″ and E 34° 57′ 37″). The sites receive ~2000 mm mean annual rainfall in a bimodal distribution, with two cropping seasons per year, March–July and September–January with a mean annual temperature of 26 °C (Supplementary Online Information, S1). The soil is classified as Typic Kandiudult (Soil Survey Staff 1999) developed on biotite-gneiss parent material. This soil is highly weathered with the clay fraction dominated by kaolinite. The natural vegetation is composed of tropical rainforest of Guineo-Congolian region. The experiment was conducted for six consecutive maize cropping seasons from September 2012 to August 2015.

Preparation of the biochar and tithonia green manure

Biochar was produced from eucalyptus wood after chopping and grinding the organic matter to pass through a 2-mm sieve. The ground material was pyrolyzed to a maximum temperature of 550 °C and retained at that temperature for 1 h before cooling it to room temperature. In the laboratory, the resultant biochar was analyzed for pH, CEC, and elemental composition. Tithonia (*Tithonia diversifolia*) was prepared by cutting leaves in the field and chopping them into 50-mm lengths, air-drying, and grinding to pass through a 1-mm sieve before field application. The physical and chemical characteristics of the above materials are fully described by Fungo et al. (2017) and available as Supplementary Online Information (S2).

Experimental design

The treatments were selected to represent presence and absence of biochar as well as low and high input of tithonia green manure, with and without mineral N fertilizer. This arrangement represented a range of conventional management practices of many small-holder farmers in integrated soil fertility management systems in eastern Africa, and allowed for effects of varying organic and inorganic N to be examined. The treatments included the following: two levels of biochar (0 and 2.5 t ha^{-1}) applied once at the start of the experiment; three levels of green manure applied as tithonia (0, 2.5, and 5 t ha^{-1}) per season; and two levels of mineral N applied as urea (0 and 120 kg N ha^{-1}) per season (Table 1). Each treatment was established in 2-by-2-m plots separated by a 1-m

Table 1 Experimental treatments for determining the effect of tithonia green manure, urea, and biochar on fluxes of N_2O and NH_3 in a maize field in western Kenya

Treatment	Biochar		*T. diversifolia*			Mineral N (urea)		Total N
	(t ha^{-1})[a]	Code	(t ha^{-1})[b]	(kg N ha^{-1})	Code	Rate (kg N ha^{-1})[c]	Code	(kg N ha^{-1})
1 ($B_0T_0U_0$) (control)	0	B0	0.0	0	T0	0	U0	0
2 ($B_0T_{2.5}U_0$)	0	B0	2.5	75	T2.5	0	U0	75
3 ($B_0T_5U_0$)	0	B0	5.0	150	T5	0	U0	150
4 ($B_0T_0U_{120}$)	0	B0	0.0	0	T0	120	U120	120
5 ($B_0T_{2.5}U_{120}$)	0	B0	2.5	75	T2.5	120	U120	195
6 ($B_0T_5U_{120}$)	0	B0	5.0	150	T5	120	U120	270
7 ($B_{2.5}T_0U_0$)	2.5	B2.5	0.0	0	T0	0	U0	0
8 ($B_{2.5}T_{2.5}U_0$)	2.5	B2.5	2.5	75	T2.5	0	U0	75
9 ($B_{2.5}T_5U_0$)	2.5	B2.5	5.0	150	T5	0	U0	150
10 ($B_{2.5}T_0U_{120}$)	2.5	B2.5	0.0	0	T0	120	U120	120
11 ($B_{2.5}T_{2.5}U_{120}$)	2.5	B2.5	2.5	75	T2.5	120	U120	195
12 ($B_{2.5}T_5U_{120}$)	2.5	B2.5	5.0	150	T5	120	U120	270

Biochar C = 86.8%, *T. diversifolia* C ~48%. N input from *T. diversifolia* application is derived from the 3% N content. The biochar contained only very low N content, and was not included in the total N applied calculations

[a] One kilogram of biochar

[b] One and 2 kg of *T. diversifolia*

[c] One hundred grams, respectively, per treated 2 × 2 m plot

distance within and between rows. The experimental plots were laid out in a Randomized Complete Block Design with three replicates. Due to the inherently low fertility of the soil, 30 kg ha^{-1} of P_2O_5 as TSP and 30 kg ha^{-1} of K_2O as Muriate of Potash (MoP) were applied to each plot.

Management of experiment

Precipitation and air temperature were monitored throughout the experiment with the help of a weather station located near the experimental field. Application of biochar was done once at the start of the first season on October 3, 2012. Identical amounts of tithonia green manure, TSP, and MoP were applied to each plot once at the start of each season. Mineral N (urea) was applied in two splits: 40% at planting and 60% at 1st weeding (Table 2). The biochar, manure, and mineral fertilizer were broadcast on the soil surface by hand and incorporated into the 0.1-m topsoil. Two seeds of the maize cultivar HB 513 were planted at a spacing of 0.25 m within and 0.5 m between rows (equivalent to 40 plants per plot). The 1st and 2nd weeding were done at approximately 30 and 50 days after planting, respectively, using a hand-hoe. Thinning was done during the first weeding to retain one plant per hole.

Gas measurements

Measurements of N_2O were conducted using the static closed chamber method. The chamber consisted of a PVC tube (diameter = 0.3 m; height = 0.15 m) transversely divided into two parts to make a base (0.05 m) and a cover (0.1 m). The base was driven into the soil so that it reached ~0.02 m below the soil surface. To ensure air-tight conditions, a rubber ring was placed between the base and the cover. Inside the cuvette, air humidity and temperature were monitored by a digital thermo-hygrometer (PCE-313 A, Paper-Consult Engineering Group, Meschede, Germany) attached to the cover from the outside in a way that only the sensor reached inside the chamber through a rubber screw connector. Two chambers were set up in each plot. The chambers were relocated every month to capture within-plot variability.

Sampling was done every 7 days. Fertilizer application was done 2 days before the next sampling event. The sampling events were the same for both NH_3 and N_2O. For each N_2O sampling event, four samples were taken at 0, 10, 20, and 30 min after closing the chamber, by taking 20 ml of gas from the chamber. The gas samples were collected using a 20-ml syringe and injected into pre-evacuated 10-ml gas vials. Analysis of gas samples was done on a gas chromatograph fitted with an electron capture detector (ECD) for N_2O quantification (SRI GC Model 8610V). Operating conditions for the GC were as follows: injector temperature 60 °C, column temperature 400 °C, and detector temperature 320 °C. Samples were introduced using a Gilson 40-vial autosampler

Table 2 Activity calendar for the management of the field trial in maize crop western Kenya amended with biochar, tithonia, and biochar

Activity	Season 1	Season 2	Season 3	Season 4	Season 5	Season 6
Biochar application	3rd October 2012	–	–	–	–	–
Application of manure and 40% urea; planting	3rd October 2012	5th March 2013	10th August 2013	3rd April 2014	7th September 2014	10th Aril 2015
1st weeding and top-dressing with 60% urea	7th November 2012	10th April 2013	10th September 2013	5th May 2014	7th October 2014	20th May 2015
2nd weeding	4th December 2012	12th May 2013	15th October 2013	9th June 2014	11th November 2014	17th June 2015
Harvesting	30th January 2012	24th July 2013	17th December 2013	7th August 2014	14th January 2015	13th August 2015

(Gilson Inc., Middleton, Italy). One standard N_2O gas sample (CGDI, USA) was used for every four samples. Data processing was performed using the PeakSimple Chromatography software (SRI Inc., Silicon Valley, CA, USA). Coefficient of variation in mean measurements was 1.6%. Fluxes of NH_3 were measured using a photo-acoustic infrared field gas monitor (INNOVA 1402, Lumasense Technologies A/S, Ballerup, Denmark). Weekly NH_3 gas flux measurements were conducted using chambers identical to those used for N_2O and the sampling was done at the same time for both gases. A photo-acoustic infrared multi-gas monitor (INNOVA 1312–5, LumaSense Technologies A/S, Ballerup, Denmark) was used for gas analysis. To ensure accuracy of the measurements, INNOVA was calibrated every 3 months.

Soil sampling and analysis

Soil samples for analysis of mineral N (NH_4^+ and NO_3^-) were taken from a depth of 0–0.15 m with a soil core (0.05 l; 0.05 m d) during the third year (from October 7, 2014 to August 12, 2015). Soil from four locations within each plot were taken, composited, and approximately 200 g was packed under ice blocks in a cooler box before transfer to the laboratory for extraction and the remaining portion (~ 200 g) was used to determine water-filled pore space (WFPS). These soil samples were collected on the same days as were the N_2O and NH_3 gas measurements. For soil mineral N analysis, a total of 18 data points were collected during the two seasons in the third year of the experiment between October 2014 and August 2015. For bulk density, soil was taken at the beginning and end of the third experimental year. NH_4^+-N and NO_3-N were extracted with 2 M KCl in 100 ml of solution for 20 g of soil and the content analyzed using spectrophotometry according to International Standards Organization (ISO standard EN 14256-1). WFPS was calculated based on water content, soil bulk density, and a particle size density of 2.65 g cm^{-3} according to Eq. 1;

$$\%WFPS = \frac{soil\ water\ content \times bulk\ density \times 100}{1-(bulk\ sensity/2.65)} \quad (1)$$

Data management and statistical analysis

The NH_3 and N_2O cumulative flux for each treatment during the entire experimental period was derived using linear interpolation with sampling dates as the time intervals (Trapezoidal rule). Treatment-induced differences (effect size) in NH_3 and N_2O emission for each treatment were calculated as the difference between the treatment value and that of the control. The relationship between effect size and experimental time was examined using linear regression functions. Treatment effects and their interaction on cumulative emissions were examined using three-way full factorial analysis of variance (ANOVA). Post

hoc separation of means was done using least significant difference (LSD) at 5% allowable error. A power function was fitted to test dependence of NH_3 and N_2O emission on WFPS and mineral soil N content. For correlation between soil N and gas fluxes, only data collected on the same day was used in the analysis. Effect size of the treatments was computed as the difference between treatments with amendments and the unamended control. Positive values indicate greater emissions from the amended plots compared to the unamended control. Delta emission of N was calculated using Eq. 2;

$$Prop.of\ biochar\ induced\ N\ loss\ (\%) = \frac{(Cum\ N_{B0}-Cum\ N_{B2.5})}{Applied\ N} \times 100 \quad (2)$$

Where Cum. N_{B0}, and Cum. $N_{B2.5}$ is the cumulative N emissions for non-biochar and biochar plots, respectively, and N applied is the total amounts of applied N in the respective season (tihonia N + urea N). The resultant value was expressed as a percentage. We compare the correlation coefficients of each trendline to determine whether the differences are statistically significant. Where $p > 0.05$, it implies that the trend is not significantly different.

Results

Daily dynamics of NH_3 and N_2O emissions

The mean emission rates of NH_3 were 1.0 µg NH_3-N m^{-2} h^{-1}, with a range of 0.1 to 2.9 µg NH_3-N m^{-2} h^{-1} (Table 3). The mean daily emission of N_2O was 1.2 ± 0.6 µg N_2O-N m^{-2} h^{-1}, with a range of 0.07 to 8.2 µg N_2O-N m^{-2} h^{-1}. Peaks in N_2O emissions occurred 1–2 days after fertilization but those for NH_3 were inconsistent. Variability in daily emissions, as expressed by the coefficient of variation (cv), was higher (40%) for NH_3 compared to that of N_2O (20%). A biochar effect was observed for both NH_3 and N_2O, where lower emissions ($p < 0.05$) were observed in biochar-amended plots. Mean emissions of NH_3 were 1.2 ± 0.3 and 1.4 ± 0.3 µg NH_3-N m^{-2} h^{-1} in biochar and non-biochar plots, respectively, while those for N_2O were 1.4 ± 0.4 and 1.6 ± 0.3 µg N_2O-N m^{-2} h^{-1} for biochar and non-biochar plots, respectively.

Effects of amendments on emissions dynamics

NH_3 emissions

Figures 1 and 2 show comparison in the trend in effect of the treatments on emissions, Fig. 3 shows the direct comparisons of cumulative values for each treatment at the end of the study period. All N sources (tithonia and urea) increased emission of NH_3. The increase ranged from 21 to 58% for tithonia and urea, respectively, compared to the control (S3). No significant difference in NH_3 emissions were observed between the

Table 3 Mean hourly flux and effect size of NH_3 and N_2O after soil amendment with tithonia, urea, and biochar to an Ultisol under maize in western Kenya. Effect size of the treatments was computed as the difference between treatments with amendments and the unamended control

Treatment	Mean hourly flux (μg N m^{-2} h^{-1})				*Mean effect size (μg N m^{-2} h^{-1})			
	NH_3	SE	N_2O	SE	NH_3	SE	N_2O	SE
1 ($B_0T_0U_0$)	0.90	0.03	0.66	0.05	0.00	–	0.00	–
2 ($B_0T_{2.5}U_0$)	1.09	0.03	0.73	0.06	0.64	0.04	0.52	0.03
3 ($B_0T_5U_0$)	1.13	0.02	0.62	0.03	0.59	0.03	0.34	0.02
4 ($B_0T_0U_{120}$)	1.23	0.02	0.49	0.03	0.85	0.05	0.59	0.03
5 ($B_0T_{2.5}U_{120}$)	1.20	0.02	0.56	0.05	0.73	0.04	0.47	0.03
6 ($B_0T_5U_{120}$)	1.24	0.02	0.53	0.05	0.83	0.05	0.58	0.03
7 ($B_{2.5}T_0U_0$)	0.48	0.02	0.37	0.04	− 0.39	0.02	− 0.64	0.04
8 ($B_{2.5}T_{2.5}U_0$)	0.37	0.02	0.44	0.04	− 0.34	0.02	− 0.59	0.03
9 ($B_{2.5}T_5U_0$)	0.80	0.03	0.50	0.05	0.09	0.01	− 0.17	0.01
10 ($B_{2.5}T_0U_{120}$)	1.05	0.02	0.49	0.05	0.38	0.02	0.13	0.01
11 ($B_{2.5}T_{2.5}U_{120}$)	1.02	0.04	0.58	0.07	0.47	0.03	0.22	0.01
12 ($B_{2.5}T_5U_{120}$)	0.72	0.02	0.53	0.04	0.08	0.00	− 0.19	0.01

tithonia application rates. Biochar amendments decreased NH_3 emissions with a range of 11–37% compared to the control (mean = 22 ± 2% in the first year and 10 ± 2% by the end of the third year). Biochar lowered cumulative NH_3 emissions when no or low doses of N were applied but had no effect when high doses (U120 and T5 + U120) were applied. The effect size due to tithonia or urea additions did not change significantly over the 3-year period (Fig. 1). However, the effect size for adding biochar with or without tithonia at low application rates ($B_{2.5}T_0U_0$ and $B_{2.5}T_{2.5}U_0$) decreased from 0.49 ± 0.1 μg NH_3-N m^{-2} h^{-1} in the first year to 0.16 ± 0.1 μg NH_3-N m^{-2} h^{-1} in the third year (Fig. 1).

Compared to the control, the effect size of adding biochar with a high application rate of tithonia ($B_{2.5}T_{5.0}U_0$) decreased only until the 12th month after which it increased (Fig. 1). Adding biochar to urea ($B_{2.5}T_0U_{120}$) suppressed NH_3 emissions compared to urea without biochar to the same level as the completely unamended control in the first year but the effect size increased progressively to 0.41 ± 0.1 μg NH_3-N m^{-2} h^{-1} by the end of the third year. High amounts of tithonia (5 t ha^{-1}) in combination with biochar and urea lowered the initial effect size from 0.33 ± 0.1 μg NH_3-N m^{-2} h^{-1} to zero by the 18th month, compared to the control. However, by the 6th season, the effect size had increased to 0.49 ± 0.1 μg NH_3-N m^{-2} h^{-1} compared to the control and not different from urea and tithonia without biochar (Fig. 1).

N_2O emissions

Overall, the patterns in N_2O emissions were similar to those of NH_3 (S3). Tithonia or urea increased N_2O emissions by 13 to 47% (mean ± SE of 16 ± 3%), with the highest increase observed where urea was applied alone or in combination with high amounts of tithonia (S3). For these treatments, changes in N_2O across seasons did not vary significantly. With biochar

added on its own (S3), N_2O emissions significantly lowered by 42 ± 3% in the first year but lowered by an additional 17 ± 2% by the end of the third year, representing a 59% decrease in effect size over 3 years. Biochar added with either low amounts of tithonia or urea, alone or in combination, resulted in the N_2O mitigation effect lasting only until the second year compared to the control, after which the effect gradually lowered relative to the control. However, a longer N_2O mitigation effect was observed when higher amounts of tithonia were applied in the combination with biochar and urea (Fig. 2). As was the case with NH_3, biochar lowered cumulative N_2O emissions where no or low doses of N were applied but had no effect when high doses (U120 and T5 + U120) were applied.

Cumulative emissions of NH_3 and N_2O

NH_3 emissions

Biochar applied alone significantly reduced cumulative emissions of NH_3 by up to 47 ± 5% without tithonia (Fig. 3a). The reduction was 39 and 18% when biochar was combined with 2.5 and 5 t ha^{-1} of tithonia, respectively, compared to the control. For plots with only tithonia or urea, emission of NH_3 increased significantly (13 to 68%; average of 20%) compared to the control (Fig. 3a). Urea, alone or in combination with tithonia, increased NH_3 emissions by 50–68% compared to the control. Biochar reduced NH_3 emission in most treatments except where all three amendments were added (Fig. 3a).

N_2O emissions

Biochar applied alone significantly decreased cumulative N_2O emissions compared to the control but no difference was found where a biochar-urea combination was applied (Fig. 3b). Without urea additions, N_2O emissions were between 12 and
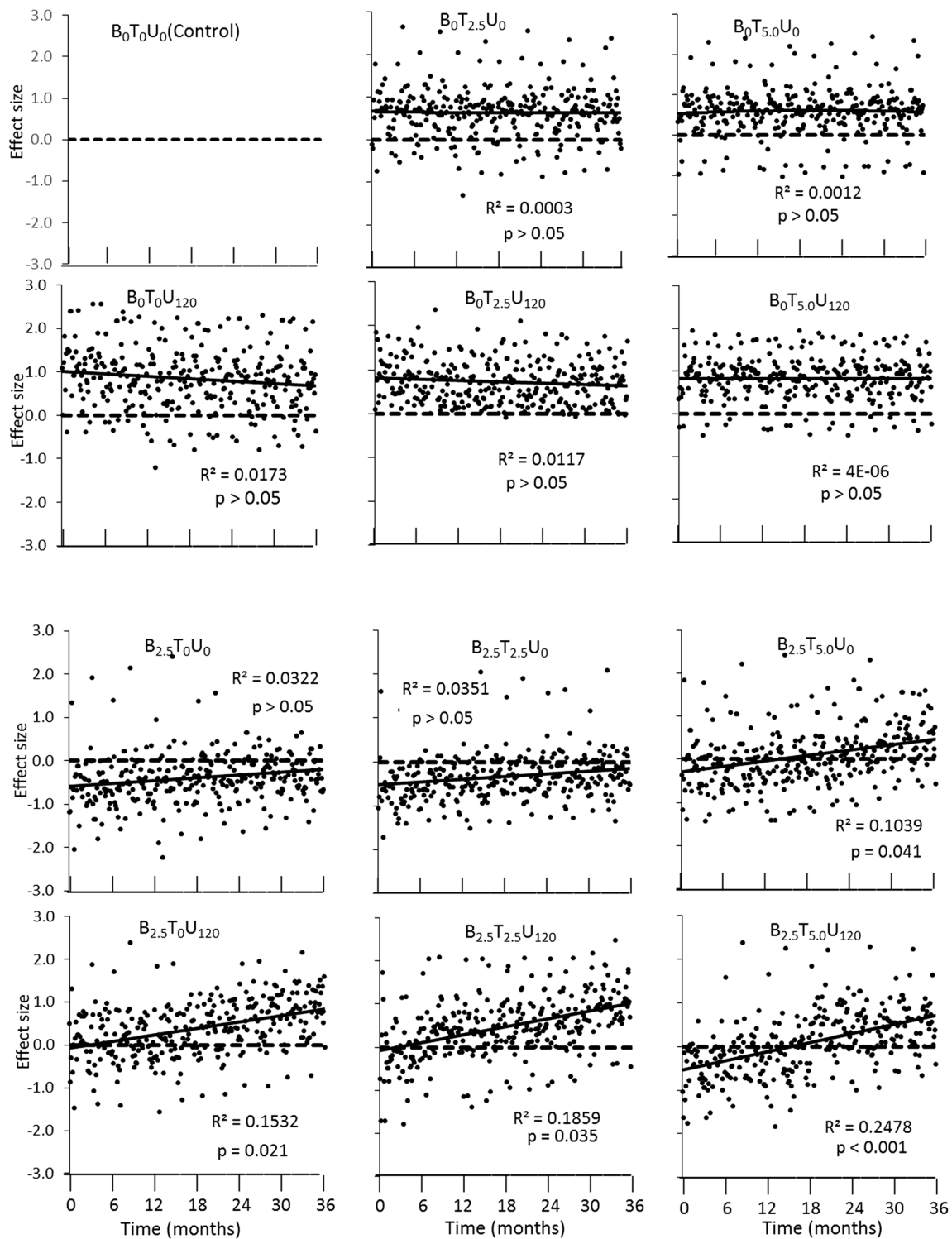
Fig. 1 Effect size of treatments on NH_3 emissions after additions of tithonia green manure, urea, and biochar in an Ultisol cropped to maize in western Kenya over three consecutive years. The dotted line is the control and the solid one is the trend of the treatment. Time after a single biochar addition. Positive values indicate greater emissions from the amended plots compared to the unamended control

22% lower compared to the control after biochar additions, irrespective of tithonia additions. Both tithonia and urea additions significantly increased cumulative N_2O emission (20 ± 4 and $43 \pm 5\%$, respectively) but the amount of tithonia did not significantly affect N_2O emission with or without urea, compared to the control. The biochar-urea combination increased cumulative N_2O by $25 \pm 3\%$ compared to the unamended control but the biochar-tithonia-urea combination (independent of
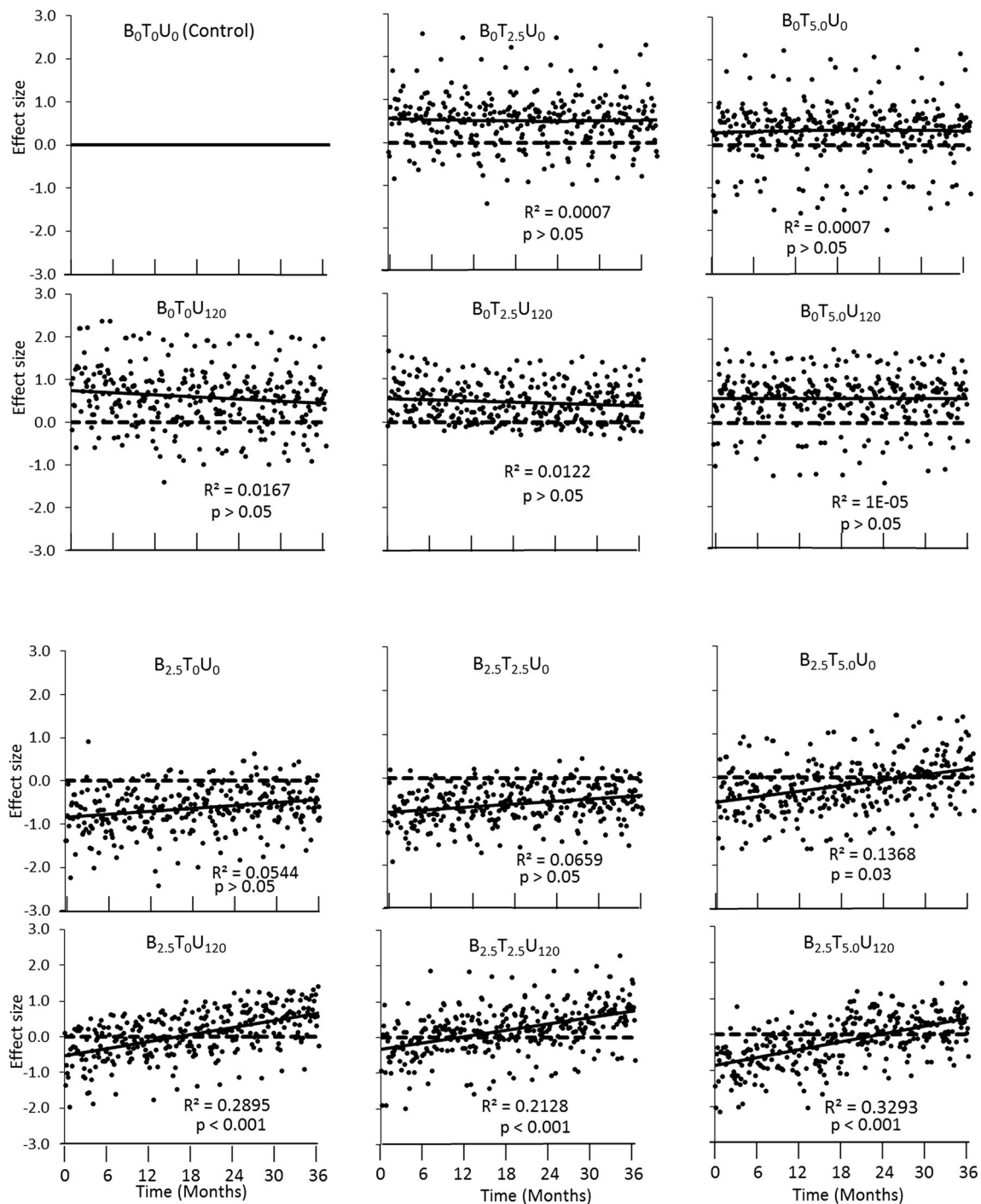
Fig. 2 Effect size of treatments on N_2O emissions after additions of tithonia green manure, urea, and biochar to an Ultisol cropped to maize in western Kenya over three consecutive years. The dotted line is the control and the solid one is the trend of the treatment. Time after a single biochar addition. Positive values indicate greater emissions from amended plots compared to the unamended control

the level of tithonia) increased N_2O emission by $41 \pm 5\%$ compared to the unamended control.

Proportion of gaseous N emissions

The amount of NH_3-N lost, as a proportion of total N applied, ranged from 0.2 to 0.8% (Fig. 4). For all levels of applied N, the proportion of biochar-dependent NH_3 lowering decreased significantly over the 3 years and the decrease was highest where urea was applied without tithonia (120 kg N ha^{-1}) or where total N applied was highest (270 kg N ha^{-1}). For N_2O-N, the trend in proportion of N emitted was similar to that of NH_3 but the slope (0.4 to 1.2% N_2O-N) was higher compared to that of NH_3 (75, 195, and 270 kg N ha^{-1}). The continuous decline in effect size

Fig. 3 Cumulative emissions of NH$_3$ (**a**) and N$_2$O (**b**) during 3 years of maize cultivation on an Ultisol in western Kenya after amendment with tithonia green manure, urea, and biochar ($N = 3$)
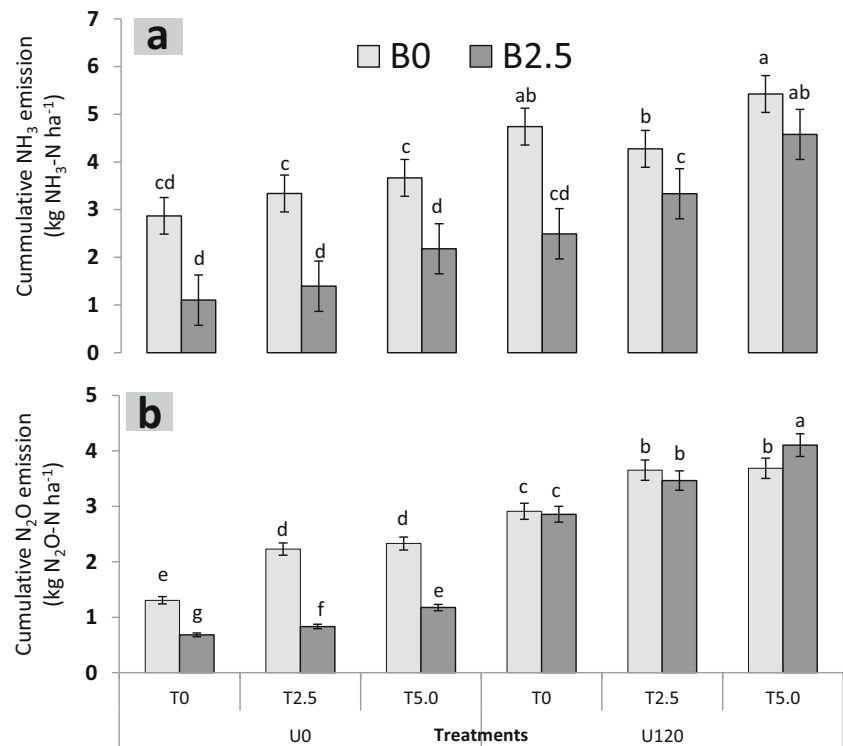
was predominantly observed where 270 kg N ha^{-1} was applied without tithonia (Fig. 4).

Relationships between gas fluxes and WFPS and extractable mineral N

Mean values for NH$_3$, N$_2$O, WFPS, and extractable mineral N are presented in Supplementary Online Information (S3). Emissions of NH$_3$ were neither related to soil moisture nor to NO$_3$-N contents (Fig. 5a, c), but were positively related to NH$_4^+$-N (Fig. 5b). However, WFPS significantly and positively correlated with N$_2$O emission (Fig. 5d). A significant positive relationship was observed between N$_2$O emission and NH$_4^+$-N and a positive one between N$_2$O and NO$_3^-$-N content (Fig. 5f). Data were not sufficient to determine the trend in N$_2$O emission beyond a moisture content of 60%.
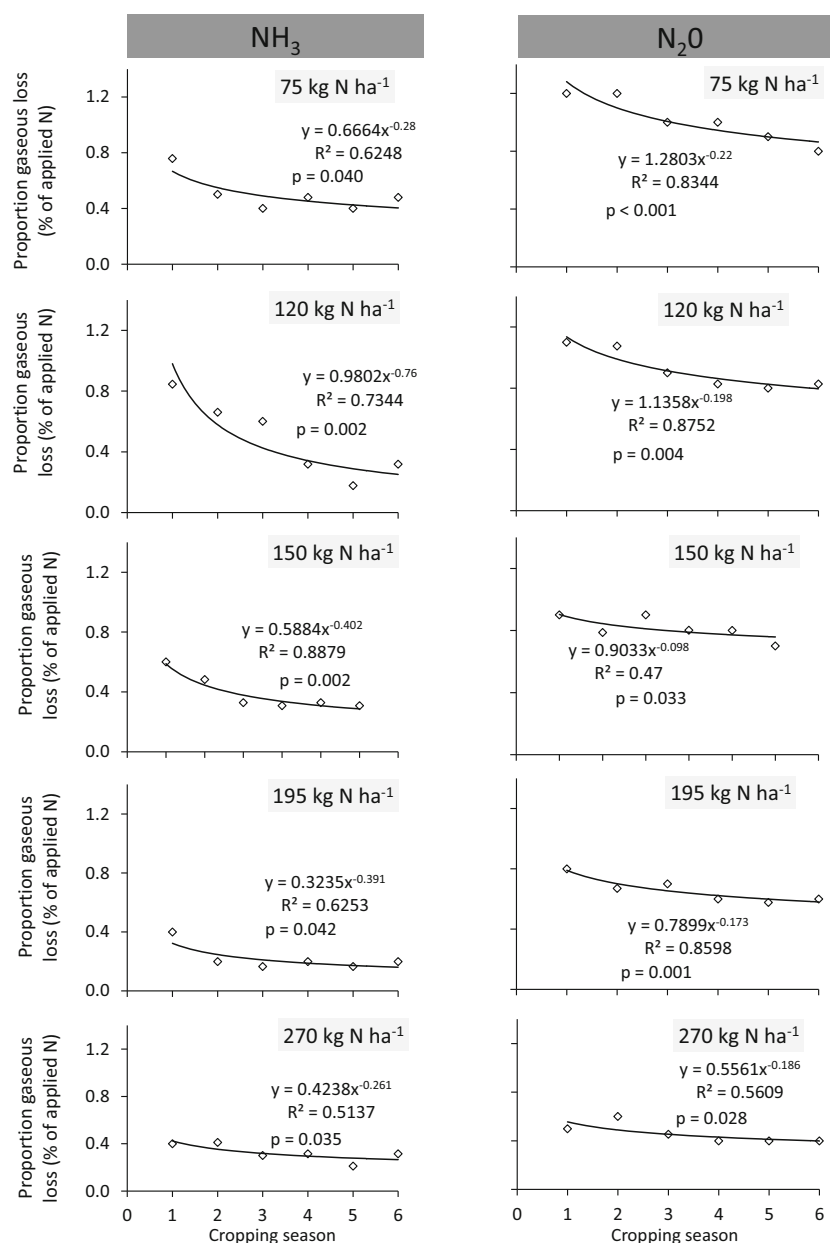
Discussion

Emissions of NH$_3$

Several studies have reported an effect of biochar on NH$_3$ emissions (e.g., Spokas et al. 2011; Taghizadeh-Toosi et al. 2012; Mandal et al. 2016). In all of these cases, reduction in NH$_3$ emissions due to biochar was reported, as was the case in our study (Fig. 2; Table 2). In principle, reductions in NH$_3$ emissions by biochar may be a result of (i) lower pH that would drive the equilibrium NH$_4^+$ ⇆

NH$_3$ towards NH$_4^+$; (ii) reduced biological production of NH$_4^+$ (ammonification and urease activity); (iii) increased biological consumption of NH$_4^+$ (nitrification, immobilization, and plant uptake); (iv) increased adsorption of NH$_4^+$; or (v) increased adsorption of NH$_3$. From this study, we have provided detail of the residual effect of biochar on some of the above processes and their influence on emission of NH$_3$ and N$_2$O under tropical field conditions. In the following, each of these mechanisms is discussed.

pH of biochar

The pH of biochar may differ from that of the soil and may increase or decrease and thereby also either increase of decrease NH$_3$ emissions. In our study, the pH of the biochar was slightly higher than that of the soil at the beginning of the experiment and a pH effect is therefore assumed to play no major role. López-Cano et al. (2016) observed that biochar addition could slow down the ammonification process. This is also in line with negative C priming effects as a result of biochar additions to soil (Wang et al. 2016). A positive relationship between NH$_3$ and N$_2$O observed in our study is consistent with a similarity in the mechanisms regulating both gases such as lower NH$_4^+$ production thus reducing losses of both NH$_3$ and N$_2$O (Steiner et al. 2010; Prendergast-Miller et al. 2011; Spokas et al. 2011; Jassal et al. 2015).

Fig. 4 Gaseous N losses as a proportion of the applied N for NH_3 (left) and N_2O (right) during 3 years of maize cultivation on an Ultisol in western Kenya after amendment with tithonia green manure, urea, and biochar. Each data point represents the net proportion of loss at the completion of the crop cycle. Data was divided into 6-month periods for each season to account for the cropping period and fallow

NH_3

75 kg N ha^{-1}
$y = 0.6664x^{-0.28}$
$R^2 = 0.6248$
$p = 0.040$

120 kg N ha^{-1}
$y = 0.9802x^{-0.76}$
$R^2 = 0.7344$
$p = 0.002$

150 kg N ha^{-1}
$y = 0.5884x^{-0.402}$
$R^2 = 0.8879$
$p = 0.002$

195 kg N ha^{-1}
$y = 0.3235x^{-0.391}$
$R^2 = 0.6253$
$p = 0.042$

270 kg N ha^{-1}
$y = 0.4238x^{-0.261}$
$R^2 = 0.5137$
$p = 0.035$

N_2O

75 kg N ha^{-1}
$y = 1.2803x^{-0.22}$
$R^2 = 0.8344$
$p < 0.001$

120 kg N ha^{-1}
$y = 1.1358x^{-0.198}$
$R^2 = 0.8752$
$p = 0.004$

150 kg N ha^{-1}
$y = 0.9033x^{-0.098}$
$R^2 = 0.47$
$p = 0.033$

195 kg N ha^{-1}
$y = 0.7899x^{-0.173}$
$R^2 = 0.8598$
$p = 0.001$

270 kg N ha^{-1}
$y = 0.5561x^{-0.186}$
$R^2 = 0.5609$
$p = 0.028$

Proportion gaseous loss (% of applied N)

Cropping season

Liming effects of biochar

Increased biological consumption of NH_4^+ by biochar through increased nitrification may be a result of liming effects of biochar in acid soils or the removal of inhibiting substances such as polyphenols or tannins (DeLuca et al. 2006; Ball et al. 2010). Neither of these explanations are valid in our study. The above-mentioned positive relationship between NH_3 and N_2O may also suggest that a biological consumption of NH_4^+ is unlikely to explain NH_3 emission reductions as it would increase N_2O emissions. Increased NH_4^+ removal could also be the result of the improvement in soil structure that allows NH_4^+ to percolate from the surface to greater depths where volatilization is less likely. However, this is an

unlikely explanation, because most studies report reduced NH_4^+ leaching for reasons including reduced water percolation, increased adsorption (Lehmann et al. 2003), increased plant uptake (Major et al. 2010), or increased microbial immobilization (Güereña et al. 2013).

Sorption reactions

Sorption of either NH_4^+, NH_3, or of both chemical species on biochar surfaces was proposed as a responsible mechanism (Yao et al. 2012; Taghizadeh-Toosi et al. 2012; Zhang et al. 2013). An adsorption of NH_3 gas is more likely to be less readily reversible as it may generate amine functional groups (Kastner et al. 2009). Oxidation of biochar surfaces,
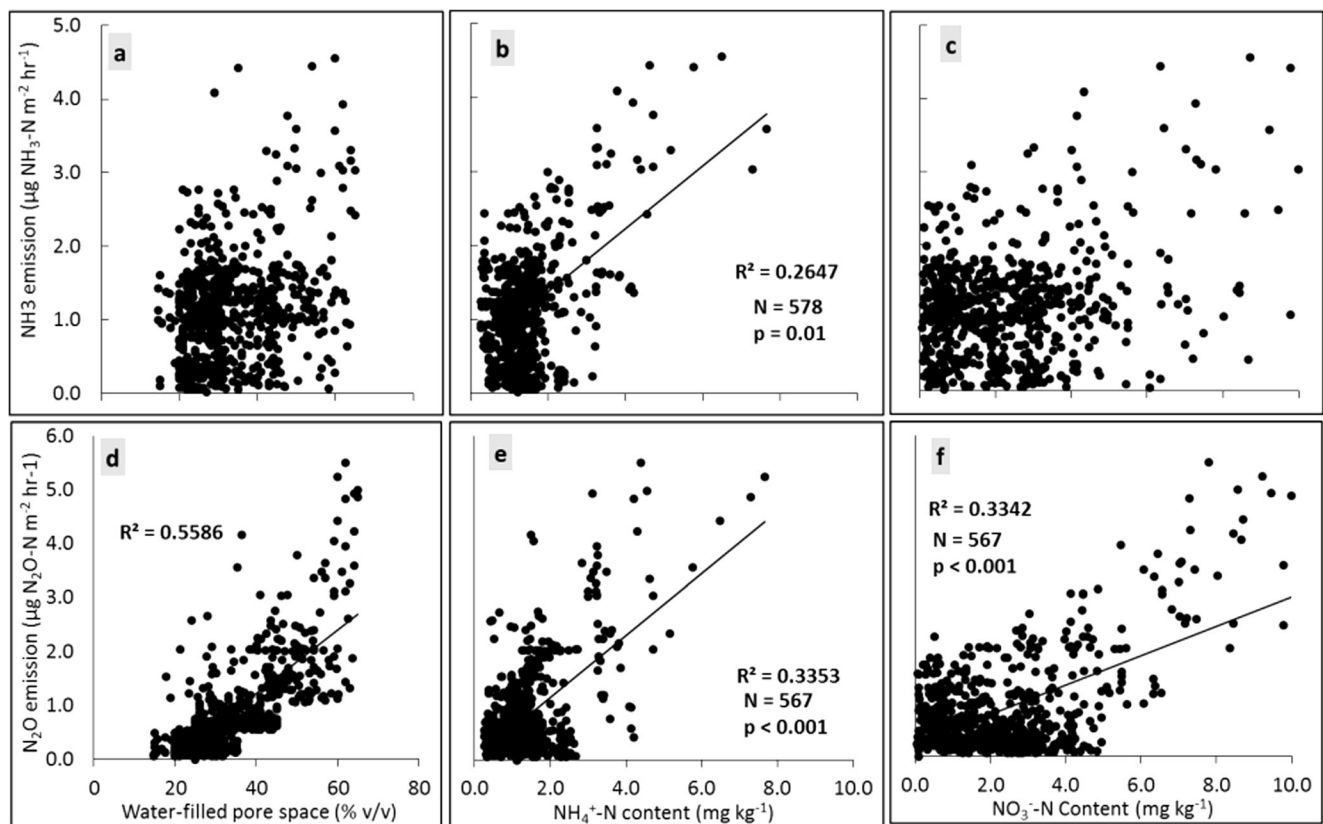
Fig. 5 Relationship between gas fluxes and water-filled pore space and mineral N during the third year of an Ultisol cropped to maize in western Kenya amended with tithonia, urea, and biochar

particularly in low-pH soils, over time (Li et al. 2015; Zhang et al. 2015b; Shen et al. 2016) may increase the reactivity with either NH_4^+ species. Thus, the observed effect size of biochar with respect to NH_3 emission reductions (Fig. 1) showed a decreasing trend over the 3 years possibly because of the oxidized surfaces on biochar.

NH_3 emission lowering after additions of biochar was less in the presence of tithonia and urea, may be a result of the concomitant C additions. According to Anand et al. (2015), high SOC can increase soil urease activity. It follows that tithonia may have contributed to increased NH_3 through its additions of metabolizable C far more that its N addition. In terms of NH_3 emission reductions, biochar may therefore be more effective in its effects on N than in its effects on C. Sommer et al. (1991) demonstrated that a doubling of the infiltration rate of total available N away from the soil surface could half cumulative ammonia emissions. Thus, biochar could have reduced emissions by adsorbing NH_3 and reducing its emission in the atmosphere.

Emissions of N_2O

Between the start of the first year and the end of the third year, cumulative emission of N_2O had decreased by 22% due to biochar application, a value lower compared to the ∼50%

decrease observed from previous short-term (≤ 2 years) studies (cf. Zhang et al. 2015b; Fungo et al. 2017). These comparisons show a progressive decrease of the effect of biochar on N_2O emission reduction over time. This trend is similar to the observation made by Zhang et al. (2015b) in a 2-year field trial where the mitigating effect of biochar on N_2O decreased by 59–70% in the first year and with 54–67% slightly less in the second year. In our study, biochar additions decreased N_2O emission by 32 ± 4% during the first year and by 15 ± 2% during the third year. The small mitigation of N_2O emission over time reported in our study compared to Zhang et al. (2015b) could be due to the larger amount of biochar (20 to 40 t ha^{-1}) applied by Zhang et al. (2015b). Cayuela et al. (2015) found that on average, field studies showed lower reductions in N_2O emissions (28 ± 16%) compared to laboratory studies (54 ± 5%). Thus, our results fall within the range for most field studies.

The decreasing effect size of biochar on N_2O emission over time (Fig. 2) has been reported in previous studies (e.g., Singh et al. 2012). Some studies have proposed that biochar regulates denitrification and N_2O emission via reducing necessary substrates such as easily mineralizable C (Joseph et al. 2010), direct retention of N_2O on biochar surfaces (Cornelissen et al. 2013), and mineral N (Cayuela et al. 2013). An additional mechanism is the reaction of biochar surfaces with N_2O

(resulting in greater N compounds on biochar surfaces) mediated through redox processes (Armor and Taube 1971). Fungo et al. (2014) proposed the possible formation of complexes between N_2O and transitional metals similar to that observed with Ru, favoring the observed lowering in N_2O emission. Quin et al. (2015) used X-ray photoelectron spectroscopy and identified changes in surface functional groups suggesting interactions between N_2O and the biochar surfaces. Quin et al. (2015) have also shown increases in -O-C=N pyridine pyrrole/NH_3, suggesting reactions between N_2O and the C matrix upon exposure to N_2O. However, our data (Fig. 3b) suggest that in the presence of key resources (mineralizable C and N) necessary for microbial activity, improved efficiency of complete denitrification to N_2 is a more likely outcome. Hence, the cumulative emission of N_2O was lower when both tithonia and urea were present. However, under high N availability, the lack of difference in N_2O emissions with or without biochar may be due to the excess mineral N that facilitates N_2O formation.

Singh et al. (2012) found that biochar C mineralization increased between 2.5 and 4 years for 10 out of 11 biochar types and then decreased or stabilized between the 4th and 5th year. During such mineralization, biochar surfaces may be oxidized, thereby generating quinone functional groups (Cheng et al. 2008). These surface functional groups (Chen et al. 2014; Sun et al. 2016) could be responsible for direct electron transfer, promoting N_2 production. Avdeev et al. (2005) hypothesized that an O atom is transferred through the 1,3-dipolar cyclo-addition of N_2O to the C=C bond with the resulting intermediate decomposing to yield a ketone and N_2.

Available evidence (Nguyen et al. 2008; Cheng et al. 2008) suggests that surface functional groups on biochar surfaces typically increase with longer exposure in soil. Furthermore, greater biochar oxidation has been shown to decrease electron transfer through the biochar-C matrix (Sun et al. 2016). It should be noted though that there is a limit to this increase. Electron transfer, according to Cayuela et al. (2014), may enhance the last step of denitrification (i.e., the reduction of N_2O to N_2). However, we observed a reducing effect size of biochar on N_2O emission (Fig. 2). In addition to surface functional groups, the C matrix itself can transfer electrons and do so even more rapidly (Sun et al. 2016).

As found in our study, a positive correlation between N_2O emission and soil moisture (Fig. 5d) has been reported in previous studies (Saarnio et al. 2013; Yanga et al. 2014). The denitrification that usually occurring in the micro-pores of these relatively fine-textured soils may have contributed significantly to denitrification despite the relatively low soil moisture content.

The lack of a biochar effect on N_2O when urea was added but not when tithonia was added or without additions (Fig. 4b) may indicate that the lowering of N_2O emissions by biochar may be influenced by the form of nitrogen in the soil as well as the availability of other substrates such as SOM, which support other microbial processes. The added organic matter from tithonia provides energy to the denitrification process in addition to N, and consumes O_2, favoring denitrification to reduce N_2O to N_2. Furthermore, the manure could have affected the size of the soil aggregates and the microorganisms that perform denitrification. However, the response with tithonia remained unexplained because also the tithonia-N was nitrified and when only biochar was added, the nitrate continued to be produced.

The continuous decline in effect size observed where urea was applied without tithonia (Fig. 4) can be attributed to the more rapid decline in SOC. Mori and Hojito (2012) observed that combining tithonia manure with reduced application of mineral N fertilizer may be a possible option to mitigate N_2O emissions. Therefore, application of biochar in combination with 2.5 t ha^{-1} of T. diversifolia and a lower than recommended rate of mineral N (< 120 kg N ha^{-1}) may be a low-emission as well as a cost-reduction strategy for resource-constrained farmers in sub-Saharan Africa. However, this optimum N application rate needs to be determined experimentally for various soil types. More importantly, the timing and method of application to optimize N use efficiently should be assessed.

Conclusion

Our results have demonstrated that biochar can have residual effect of lowering emissions of NH_3 and N_2O under field conditions on low fertility tropical soils. This reduction and ancillary information was consistent with reduced ammonification and possible adsorption of NH_3 to biochar surfaces either or both of which could be the reason for lower NH_3 emissions. We also found that soil inorganic N dynamics were not affected by biochar amendment 3 years after application to the soil. However, soil nitrate content was positively correlated with N_2O fluxes at relatively low soil moisture contents but it remains unclear if nitrification may have played a significant role in N_2O emissions in addition to alternative mechanisms such as direct N_2O adsorption on biochar surfaces, and N_2O reduction to N_2. Tithonia and urea additions did not alter the mitigating effect of biochar on both NH_3 and N_2O emissions. Furthermore, unlike previous studies suggesting that biochar has mainly short-term effects on N_2O fluxes, we found residual effects of biochar up to the third year under field conditions although the magnitude of the effect is reduced by over 50%. Further studies are needed to demonstrate the mechanism of N_2O emission reduction by biochar and the fate of NH_3 captured by biochar under low moisture conditions. As the emission factors of N_2O and NH_3 decline over time, it is worth noting that large-scale application of biochar might require reassessing N_2O inventories in the context of reporting GHG emissions from agricultural soils. Further studies using

different soil properties such as SOC content are needed to improve our understanding of the regulatory mechanisms for NH_3 and N_2O.

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