



# Effects of Modified and Nitrogen-Enriched Biochars on Ammonia Emissions and Crop Yields Under a Field Environment

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**Abstract** It has been demonstrated that biochar has a great potential to reduce volatilisations of ammonia ( $\text{NH}_3$ ) from fertilised agricultural soils. While there have been several laboratory studies to demonstrate the effects of biochar on gaseous  $\text{NH}_3$  emissions, there is hardly any data on the influence of biochar amendments on  $\text{NH}_3$  volatilisations from the soils under a field environment. Modifying biochar or enriching it with nitrogen (N) may maximise its capacity to abate gaseous  $\text{NH}_3$  emissions from the soil. Three biochars, i.e. SAB, HPB, and KHB modified through post-pyrolysis treatment with sulphuric acid, hydrogen peroxide, and potassium hydroxide, respectively as well as two biochars enriched with either molten urea (URB) or ammonium nitrate (ANB), were used alongside the pristine biochar (PRB) for comparisons. The quantity of gaseous  $\text{NH}_3$  evolved from each the biochar amendments including their effects on the growth and yield of the Chinese cabbage plus selected soil chemical properties were evaluated through a field experiment. The control experiment consisted of urea applied alone. In comparison with the control, PRB,

KHB, HPB, SAB, URB, and ANB amendments abated  $\text{NH}_3$  volatilisations from the soil by 44.18%, 45.91%, 63.23%, 65.62%, 72.66%, and 76.71%, respectively. Additionally, PRB, SAB, KHB, HPB, ANB, and URB amendments increased Chinese cabbage yields by 138.5%, 172.0%, 117.3%, 181.1%, 194.0%, and 181.1%, respectively in comparison with the control. The strong linear relationship ( $r^2=0.97$ ) between cumulative  $\text{NH}_3$  emissions and nitrogen use efficiencies indicates that biochar-induced reductions in emissions of gaseous  $\text{NH}_3$  concomitantly increased the use-efficiencies of the applied N.

**Keywords** Ammonia emissions · Crop productivity · Modified biochar · Nitrogen-enriched biochar · Nitrogen-use efficiency

## 1 Introduction

Biochar, a product of pyrolysis of biomass under conditions of no or limited oxygen supply at temperatures above 250 °C, has attracted a lot of interest as a soil amendment or a material for general environmental management (Lehmann & Joseph, 2015). While biochar has been used as a soil amendment in several parts of the world for centuries or even millennia, the current surge in its interest resulted from the discovery of the Terra Preta (the dark earths of the Amazon rich in charred biomass) (Lee et al., 2019; Wiedner & Glaser, 2015). Biochar amendment to the soil has been

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proposed as one of the measures that could sustainably support food production systems to ensure uninterrupted supply of food to the ever growing global population in the face of climate change (Wiedner & Glaser, 2015). This conviction is premised on the fact that biochar can sequester carbon for extended periods of usually 1000–10,000 years and can thus potentially aid in mitigating climate change (Cowie et al., 2015; Wiedner & Glaser, 2015). Alongside this positive effect on net greenhouse gas balance, biochar has been reported to increase crop yields especially in the tropics (Jeffery et al., 2017a, b).

Over time, more beneficial functions of biochar have been explored and discerned including remediation and or stabilisation of contaminants including heavy metals and emerging pollutants, attenuation of emissions of greenhouse gases, etc. The efficiencies of biochar in fulfilling the aforementioned functions have been elucidated through meta-analyses of the data from the piles of published literature. For example, a meta-analysis by Jeffery et al. (2016) found that only biochar produced at temperatures higher than 600 °C can reduce methane emissions when applied to acidic flooded (paddy) soils and only when nitrogen is applied at low application rates of less than 120 kg/ha. Another meta-analysis by Van Zwiiten et al. (2017) found that biochar abated emissions of nitrous oxide in both laboratory and field studies but very low application rates did not produce any noticeable effect on the reduction of gaseous emissions. Additionally, Chen et al. (2018) found that biochar reduced uptakes of cadmium, lead, copper, and zinc into the plant tissues by 38%, 39%, 25%, and 17%, respectively through a meta-analysis study.

Recently, biochar has been explored for the abatement of gaseous ammonia emissions from the soil (Mandal et al., 2016; Luyima et al., 2020, 2022) and stored or composting waste (Baitong et al., 2021; Janczak et al., 2017; Malińska et al., 2014). Ammonia is an important air pollutant because it forms particulate matter (PM) through a series of complex reactions in the atmosphere (Egyir et al., 2022; Luyima et al., 2022; Pinder & Adams, 2007) and hence, has direct impacts on both human health and environmental quality. It is important to note, however, that the previous studies have generated both negative (increment) and positive (decrement) results. For example, while studies by Mandal et al. (2016) and Luyima et al. (2020b) observed decreased volatilisations of  $\text{NH}_3$  from the biochar-amended soils, those by Subedi et al. (2015), Feng et al.

(2017), Fan et al. (2017), and Sun et al. (2017) reported increased emissions. A meta-analysis review study by Sha et al. (2019) is possibly the best summary of the effects of biochar on gaseous  $\text{NH}_3$  emissions and it discovered that only highly acidic ( $\text{pH} \leq 4$ ) woody biochar could reduce gaseous  $\text{NH}_3$  emissions and only when applied to fine textured soils rich in organic matter/carbon (Soil organic carbon > 3%).

To improve or optimise the potential of biochar to attenuate gaseous  $\text{NH}_3$ , a recent incubation study by Egyir et al. (2022) proposed the usage of both modified and nitrogen-enriched biochars and they found that the biochars reduced gaseous emissions by up to 73.23% and 82.88%, respectively. The modified and nitrogen-enriched biochars, therefore, outperformed the non-modified biochar which reduced the gaseous emissions by only 57.62% in comparison with the control (urea-only amendment). Given that incubation experiments take place under controlled laboratory conditions, it is difficult to generalise the findings of such studies to real field conditions (Fisher & Wood, 2007; Brüggemann and Bizer 2016). It is against that background that we proposed the evaluation of the gaseous  $\text{NH}_3$  emissions from the modified and nitrogen-enriched biochar-amended soils under the field conditions. Along with the gaseous emissions, the effects of the biochars on the agronomic performance of Chinese cabbage were assessed. This is important because although biochar has been applauded for increasing crop yields, such high yield increases are more of an exception than the rule and a wide range of crop yield responses, including negative responses in some cases, have been reported (Jeffery et al., 2011, 2017a, b). Benign and or negative yield responses may dissuade farmers from adopting the usage of modified and nitrogen-enriched biochars if they do not provide tangible financial benefits in form of marketable yields. The objective of this study, therefore, was to assess the effects of both modified and nitrogen-enriched biochars on gaseous  $\text{NH}_3$  evolutions, agronomic performance of the Chinese cabbage, and selected soil chemical properties.

## 2 Materials and methods

### 2.1 Biochar preparations and analysis

The details of the biochar modifications and nitrogen-enrichments are outlined in Egyir et al. (2022).

Briefly, the modifications were achieved through post-pyrolysis treatment with hydrogen peroxide, potassium hydroxide, and sulphuric acid whereas both urea and ammonium nitrate were used to prepare the nitrogen-enriched biochar. Forty grams of the rice husk biochar freshly produced at 500 °C for 1 h in a muffle furnace (Lindberg/Blue M) was soaked in 1.5 L of 20% of each of the sulphuric acid, potassium hydroxide, and hydrogen peroxide solutions at room temperature for 8 h. Urea-enrichment involved impregnating non-modified biochar with molten urea whereas the ammonium nitrate-enrichment involved soaking the non-modified biochar in an ammonium nitrate solution. The nitrogen-enrichment in both cases was done in such a way that the 3% application rate of biochar supplied 150 kg of nitrogen per hectare of land (considering an incorporation depth of 20 cm). All the biochars were thoroughly dried in an oven before usage. KHB, HPB, and SAB denote biochar modified with potassium hydroxide, hydrogen peroxide, and sulphuric acid, respectively while URB and ANB denote biochar enriched with molten urea and ammonium nitrate, respectively. The non-modified biochar is denoted as PRB. The pH and EC values of the biochar were determined with a pH and EC meter (Orion Versa Star Pro; Thermo Scientific, Inc., USA) after mixing 5 g of biochar with 100 mL of distilled water and shaking for 30 min. The available phosphorus was determined following the vanadate-molybdate method after extraction with 2% formic acid. The contents of the cations in the biochar were quantified by ICP-OES (Thermo Scientific iCAP 7000 Series, Waltham, MA USA) after extraction from the biochar

ashes as instructed by Enders et al. (2017). The carbon (C), hydrogen (H), nitrogen (N), and oxygen (O) contents of biochar were determined with the automated elemental analysers (Thermo Fisher Scientific EA 1112 and FLASH 2000, Waltham, MA USA (for O and CHN, respectively)). The resultant properties of the biochars are given in Table 1 whereas the methods used for the soil analysis and resultant properties of the soil of the experimental field used are given in Egyir et al. (2022)

## 2.2 Experimental set-up

The study was conducted through a field experiment that was set up at the Chungnam national university farm located at Eoeun-dong, Daejeon, South Korea (latitude, 127° 35' E; longitude, 36° 36' N). The soil at the farm is a sandy loam and belongs to the Inceptisol and Udepts order and suborder, respectively, according to the IUSS's Working Group World Reference Base for Soil Resources (WRB). The study was set up in a completely randomized design with three replicates for each treatment. Each replicate was set up on a 2 m × 1 m furrow (plot) which equates to an area of 2 m<sup>2</sup>. There was a 1-m wide ridge between the adjacent plots to prevent the contents of one plot from contaminating the neighbouring plot. The experiment utilised Chunkwang variety of Chinese cabbage whose seeds were purchased from Nonghyup, Seoul, South Korea. The seeds were germinated on a moist filter paper inserted inside a petri dish. Two-day old seedlings were transferred to a plastic seedling tray and grown under the controlled greenhouse conditions for 3 weeks. The growing media used

**Table 1** Selected Characteristics of the biochars used

Parameter	PRB	SAB	HPB	KHB	ANB	URB
pH <sub>w</sub>	10.37 ± 0.02	6.32 ± 0.04	6.82 ± 0.02	7.58 ± 0.12	7.31 ± 0.07	7.40 ± 0.05
EC (mS/cm)	3.47 ± 0.02	3.42 ± 0.04	4.47 ± 0.04	4.48 ± 0.01	2.89 ± 0.03	3.11 ± 0.01
Av. P (mg/kg)	594.77 ± 7.29	448.68 ± 2.38	493.02 ± 4.33	519.92 ± 3.70	531.8 ± 2.75	534.3 ± 3.15
K <sup>+</sup>	10.38 ± 0.02	7.77 ± 0.09	8.11 ± 0.02	15.81 ± 0.03	9.15 ± 0.05	9.28 ± 0.03
Ca <sup>2+</sup>	4.88 ± 0.09	2.26 ± 0.07	3.20 ± 0.02	2.95 ± 0.03	4.01 ± 0.03	4.14 ± 0.06
Mg <sup>2+</sup>	2.12 ± 0.01	1.55 ± 0.05	1.82 ± 0.03	1.34 ± 0.07	1.74 ± 0.02	1.83 ± 0.02
Na <sup>+</sup>	0.15 ± 0.04	0.08 ± 0.01	0.1 ± 0.01	0.11 ± 0.02	0.09 ± 0.01	0.08 ± 0.03
CEC (cmol <sub>c</sub> /kg)	36.23 ± 0.5	54.10 ± 4.25	62.34 ± 2.37	50.69 ± 0.85	34.61 ± 1.83	33.98 ± 2.12
C	58.95 ± 2.45	47.62 ± 2.24	45.43 ± 1.27	48.67 ± 3.91	54.21 ± 3.05	56.09 ± 2.83
H	2.7 ± 0.19	2.64 ± 0.03	2.53 ± 0.03	2.81 ± 0.19	2.87 ± 0.06	2.99 ± 0.09
O	7.27 ± 0.54	20.01 ± 2.24	20.76 ± 1.14	20.41 ± 0.74	12.61 ± 0.81	9.62 ± 0.43

to raise the seedlings in the seedling tray were exactly similar to the field treatments, i.e., seedlings raised on the modified biochar-amended soil media were transplanted to the modified biochar-amended plots. Each plot was planted with two rows of Chinese cabbage with spacings of 0.4 m and 0.5 m within and between the plant rows, respectively. Along with the six biochar treatments which included KHB, HPB, SAB, URB, ANB, and PRB, a control (urea-only amendment) was included. All biochars were applied to the soil at a rate of 3% (v/v) and nitrogen in form of urea was applied at a rate 150 kg per ha. The nitrogen was split into two applications for all other treatments except URB and ANB. The field experiment lasted for 9 weeks after transplanting 3 weeks old seedlings. All proper agronomic practices including irrigation, weed management, pests and diseases control, etc. were observed throughout the experimentation period.

### 2.3 Quantification of the ammonia emissions

The gaseous  $\text{NH}_3$  emissions were quantified by strictly following the venting method as outlined by Yang et al. (2018). Briefly, the sampling device was made of polyvinyl chloride rigid plastic bucket with a diameter of 15 cm and a height of 10 cm. Two sponges uniformly impregnated with 15 mL of glycerol solution made by mixing 50 mL of phosphoric acid with 40 mL of glycerol and diluted to 1000 mL were placed in the plastic bucket. The sponges had a thickness of 2 cm and a diameter of 16 cm. The lower sponge was 5 cm from the bottom of the bucket whereas the upper sponge was flat with the top of the bucket. The role of the upper sponge was to block the atmospheric ammonia from entering the sampling device while the lower sponge absorbed the gaseous  $\text{NH}_3$  emitted from the soil. The gaseous  $\text{NH}_3$  absorbed was extracted in excess 2 M KCl solution, filtered through a 0.45- $\mu\text{m}$  filter paper using a vacuum filter and then analysed colourimetrically following the indophenol blue method. Sampling lasted for 60 days and was carried out daily in the first 7 weeks and every after 2 days from the 7<sup>th</sup> week until the end of the experiment.

### 2.4 Assessment of the Chinese cabbage yield parameters and soil chemical properties

After 8 weeks, the Chinese cabbage was harvested and its yield parameters which included fresh and dry leaf weight, fresh and dry root weight, leaf length,

leaf diameter, root length, and chlorophyll content of the leaves were assessed. The weights of leaves and roots were determined using a portable electric weighing scale (Daihan Scientific, South Korea). The weighing of the roots followed thorough washing to remove all the soil and gentle rubbing with the serviette to remove water. The dry shoot and root weights were determined after drying of the materials for 24 h at 105 °C in a forced convection oven (ON-12Gw L080125, Jeio Tech, Daejeon, South Korea). Root and leaf lengths including leaf width were measured with a metre rule. The chlorophyll content was determined using a chlorophyll meter (SPAD-502, Konica Minolta, Tokyo, Japan). Along with the yield parameters, the nitrogen use efficiencies (NUE) of the Chinese cabbage grown on the different amendments were computed using the equation adopted from Anas et al. (2020).

$$\text{NUE} = \frac{\text{N content in the cabbage}}{\text{Total quantity of N supplied}} \times \frac{\text{Chinese cabbage yield}}{\text{N content in the Cabbage}}$$

The effects of both the modified and N-enriched biochars on the selected chemical properties of the soil including pH, EC, organic carbon, available phosphorus, available N, and cations were also evaluated. The soil organic carbon content was determined colourimetrically at 645 nm using a UV-Vis spectrophotometer (Genesys 50, Thermo Scientific Inc., Waltham, Massachusetts, USA) following a method espoused by Jones (2001) but the standard curve was prepared from absorbance values of the glucose solutions of varying concentrations. Available N was computed as a sum of ammonium and nitrate contents of the soil which were extracted with 2 M KCl solution and then determined colourimetrically. The ammonium content was determined following the indophenol blue method whereas the nitrate content was determined by paying strict adherence to the Chromotropic Acid Procedure as outlined in Jones (2001). The available phosphorus was extracted with the Olsen solution and determined colourimetrically following the vanadate molybdate method. The soil cations were extracted with 1 M neutral ammonium acetate solution and quantified with the ICP-OES (iCAP 7000 series, Thermo Scientific Inc., Waltham, Massachusetts, USA). The soil pH and EC were determined with a pH and EC meter from the soil slurry prepared by dissolving 1 g of dry soil in 5 ml of water.

### 2.5 Data analysis

The analysis of the data obtained from the experiments was executed through a one-way analysis of variance (Anova) using GenStat 12<sup>th</sup> edition. The significantly different mean values at  $p < 0.05$  were subjected to a post hoc *t*-test at 5% level of significance to quantify the differences amongst the treatments. Variability of the data was expressed as the standard deviation. Additionally, linear relationships between the cumulative gaseous NH<sub>3</sub> volatilisations and the pH of the biochar, and N use efficiency were evaluated using Microsoft Excel 16 data analysis ToolPak.

## 3 Results

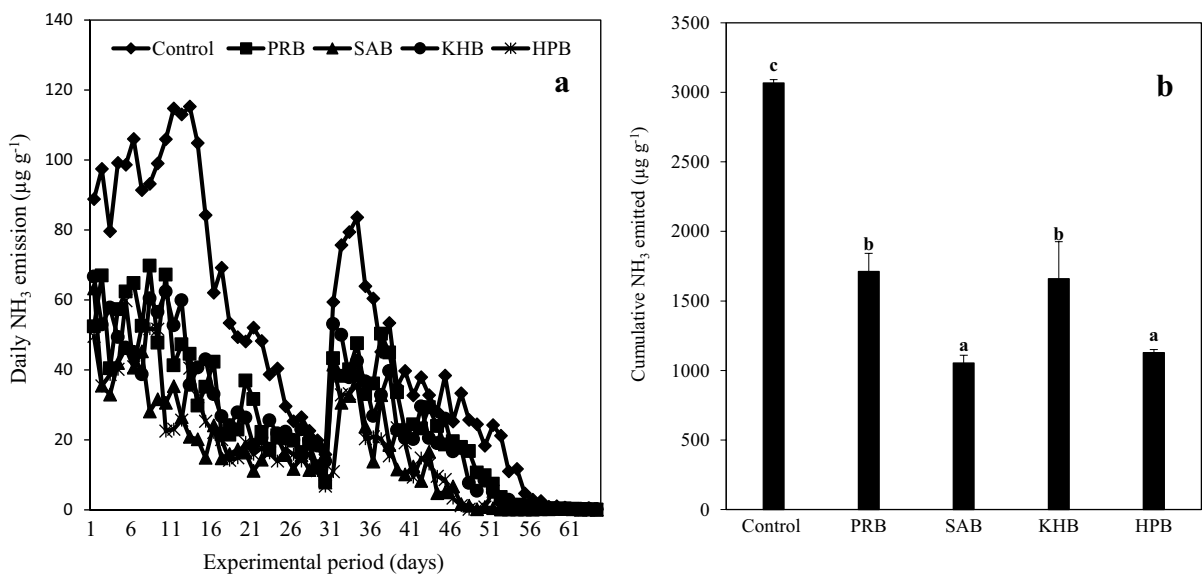
### 3.1 Ammonia emissions

As seen in Figs. 1 and 2, the daily emissions of gaseous NH<sub>3</sub> from the urea-only amendment by far exceeded those of the biochar amendments. Usually, the emissions are expected to either cease or greatly diminish after the first week of applying the N fertilisers to the soil but our observation contravenes that assumption since the emissions remained relatively high through the third week. Additionally, the

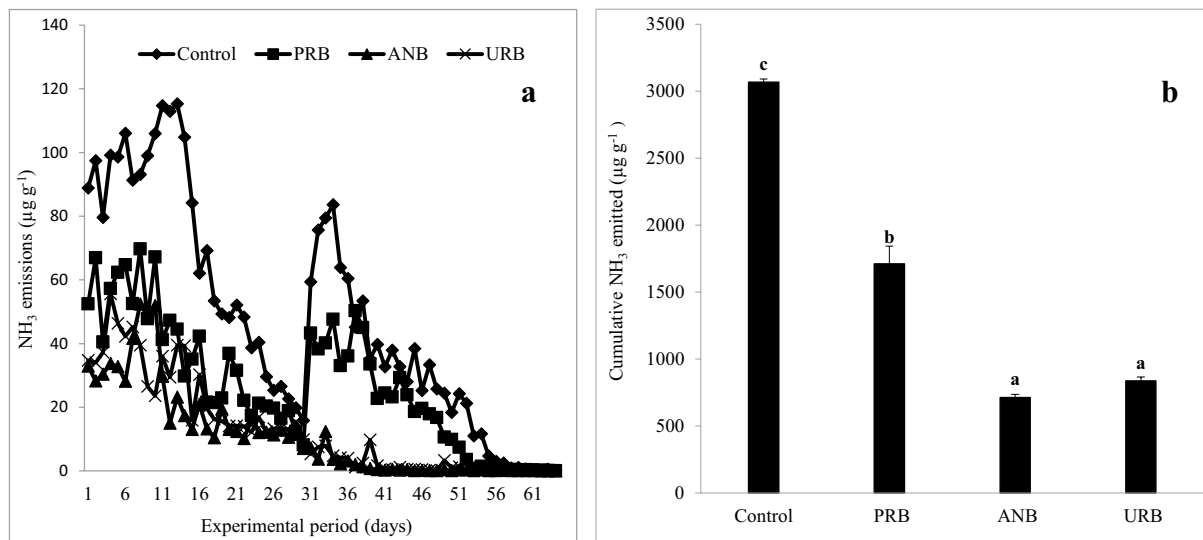
emissions from the first instalment of urea peaked on the 13<sup>th</sup> day of the experiment which was late since the emissions from the second urea instalment peaked only after 4 days. While urea was equally split into two applications, the emissions ensuing from the first instalment were far higher than those that resulted from the second application. Cumulatively, the control (urea-only amendment) volatilised 3066.7 µg of gaseous NH<sub>3</sub> for every gram of N fertiliser applied to the soil. The emissions from the control dwarfed those of the biochar amendments which cumulatively volatilised 1711.90 µg, 1054.28 µg, 1658.64 µg, and 1127.61 µg of NH<sub>3</sub> per gram of N fertiliser applied in the PRB-, SAB-, KHB-, and HPB-amended soils, respectively. The cumulative emissions from the soils amended with N-enriched biochar were even lower, standing at just 714.17 µg and 838.42 µg of NH<sub>3</sub> per gram of N applied.

### 3.2 Chinese cabbage yields and soil chemical properties

As shown in Table 2, biochar application resulted in higher Chinese cabbage marketable yields. In comparison with the urea-only amendment, PRB, SAB, KHB, HPB, ANB, and URB amendments increased Chinese cabbage yields by 138.5%, 172.0%, 117.3%, 181.1%, 194.0%, and 181.1%, respectively.



**Fig. 1** a Daily and (b) cumulative ammonia emitted from the modified biochars amendments



**Fig. 2** a Daily and (b) cumulative gaseous ammonia emitted from the nitrogen-enriched biochars amendments

Consequently, the weights of the dry shoots of the cabbage produced with the biochar amendments were heavier than the dry shoot weight of the control with both ANB and URB producing the heaviest dry shoots with no significant statistical differences between them. There were no significant statistical differences between SAB and HPB, and KHB and PRB amendments regarding the dry shoot weights. Additionally, the marketable yields of the Chinese cabbage grown with HPB and URB amendments were statistically similar and did not significantly differ from the marketable yields of both ANB and SAB statistically. In the same vein, there were no statistically significant differences between the yields obtained from the PRB and KHB amendments.

ANB and URB amendments produced the Chinese cabbage with the longest leaves of all the treatments

with no significant statistical differences between them. These were followed by HPB and SAB amendments with no significant statistical differences between them. It is worthy a note that the lengths of the leaves produced with HPB, and SAB did not differ significantly from those of ANB and URB statistically. The shortest leaves came from the Chinese cabbage produced with the urea only amendment followed by those of the PRB and KHB amendments which did not exhibit any significant statistical differences between them. The widths of the leaves followed a similar trend as the lengths of the leaves but there were no significant statistical differences between the control and PRB, and between KHB and SAB amendments. Additionally, the average widths of the leaves of the cabbage produced with HPB amendment were not statistically different from those of the cabbage produced with ANB, URB, SAB, and KHB amendments.

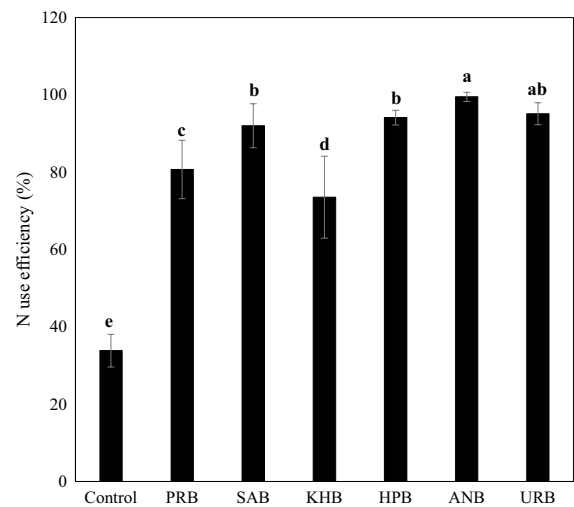
**Table 2** Selected yield parameters of the Chinese cabbage grown with the various soil amendments

Treatment	Fresh shoot weight (g)	Dry shoot weight (g)	Leaf length (cm)	Leaf width (cm)	Fresh root weight (g)	Dry root weight (g)	Root length (cm)	Chlorophyll content (SPAD)
Control	1015 ± 126.9 <sup>d</sup>	74.5 ± 12.26 <sup>c</sup>	31.00 ± 2.47 <sup>d</sup>	15.23 ± 0.35 <sup>c</sup>	15.30 ± 0.88 <sup>d</sup>	9.07 ± 0.66 <sup>d</sup>	20.43 ± 3.62 <sup>a</sup>	36.97 ± 0.60 <sup>c</sup>
PRB	2421 ± 227.3 <sup>c</sup>	157.5 ± 2.61 <sup>b</sup>	35.83 ± 0.31 <sup>c</sup>	15.90 ± 0.36 <sup>c</sup>	34.67 ± 1.83 <sup>c</sup>	14.50 ± 1.57 <sup>c</sup>	21.10 ± 0.70 <sup>a</sup>	42.73 ± 0.66 <sup>a</sup>
SAB	2761 ± 170.5 <sup>b</sup>	170.8 ± 5.22 <sup>ab</sup>	41.00 ± 1.75 <sup>ab</sup>	18.57 ± 0.70 <sup>b</sup>	43.63 ± 2.35 <sup>a</sup>	16.27 ± 2.35 <sup>bc</sup>	21.87 ± 0.48 <sup>a</sup>	43.17 ± 0.49 <sup>a</sup>
KHB	2206 ± 317.24 <sup>c</sup>	158.1 ± 4.86 <sup>b</sup>	38.70 ± 1.01 <sup>b</sup>	18.33 ± 0.45 <sup>b</sup>	38.67 ± 1.80 <sup>b</sup>	14.90 ± 1.80 <sup>c</sup>	20.30 ± 0.72 <sup>a</sup>	39.87 ± 0.90 <sup>b</sup>
HPB	2853 ± 105.22 <sup>ab</sup>	174.9 ± 0.85 <sup>ab</sup>	41.40 ± 0.66 <sup>ab</sup>	19.90 ± 0.72 <sup>ab</sup>	42.90 ± 0.61 <sup>a</sup>	17.20 ± 0.65 <sup>b</sup>	20.60 ± 0.69 <sup>a</sup>	42.87 ± 0.50 <sup>a</sup>
ANB	2984 ± 96.64 <sup>a</sup>	180.4 ± 2.09 <sup>a</sup>	43.70 ± 1.05 <sup>a</sup>	21.70 ± 0.87 <sup>a</sup>	45.17 ± 0.60 <sup>a</sup>	20.10 ± 1.05 <sup>a</sup>	20.80 ± 0.20 <sup>a</sup>	43.93 ± 0.75 <sup>a</sup>
URB	2853 ± 84.9 <sup>ab</sup>	176.0 ± 3.17 <sup>a</sup>	42.63 ± 1.09 <sup>a</sup>	21.50 ± 0.89 <sup>a</sup>	44.07 ± 1.17 <sup>a</sup>	20.43 ± 1.09 <sup>a</sup>	20.83 ± 0.25 <sup>a</sup>	43.77 ± 0.70 <sup>a</sup>

The heaviest fresh roots came from the cabbage grown on SAB, HPB, ANB, and URB amendments with no significant statistical differences amongst them. The lightest fresh roots were obtained from the cabbage grown on the control (urea-only) amendment followed in an ascending order by the roots of the cabbage grown on the KHB and PRB amendments. The ANB and URB produced the Chinese cabbage with the heaviest dry roots with no significant statistical differences between them followed by the HPB amendment. The weight of the dry roots of the cabbage grown on the SAB amendment was statistically similar to the weights of PRB, KHB and HPB amendments. The control produced Chinese cabbage with the lightest dry roots followed by PRB and KHB with no significant statistical differences observed between them. The lengths of the roots of the Chinese cabbage produced from all the amendments did not statistically differ significantly from one another.

The chlorophyll content was highest in all biochar amended soils with no significant statistical differences amongst them except the KHB amendment whose Chinese cabbage contained lower chlorophyll content than the rest of biochars. The control produced the Chinese cabbage with the lowest content of chlorophyll. As shown in Fig. 3, the N-use efficiencies were generally higher in the biochar amendments than the control with the ANB amendment registering the highest N-use efficiency. The urea-only amendment resulted into an N-use efficiency of 33.83%. The lowest N-use efficiency amongst the biochar amendments came from the KHB amendment which registered an N-use efficiency of 73.53%. This was followed by the PRB amendment with an N-use efficiency of 80.69%. Even though the HPB amendment registered higher N-use efficiency of 94.12% than the SAB amendment whose efficiency stood at 92.03%, there were no significant statistical differences between the amendments. N-enriched biochar amendments of URB and ANB resulted in the highest N-use efficiencies of all the biochar amendments registering efficiencies amounting to 95.09% and 99.48%, respectively.

As can be seen from Table 3 and soil data outlined in Egyir et al. (2022), SAB, HPB, and ANB amendments decreased soil pH whereas KHB, URB, and the control amendments increased it. The reduction from the pH value of 7.20 before experiment to the value of 6.60 after experiment registered in the SAB



**Fig. 3** Nitrogen use efficiencies obtained from the various amendments

amendment was the largest reduction of all. There were no significant statistical differences amongst the pH values of the soil amended with KHB, URB, and the control after the experiment. The pH values of the soil amended with HPB and ANB did not significantly differ statistically from those of SAB and KHB, URB, and the control. All amendments increased soil EC with the highest increment recorded in the KHB amended soil whereas the control amendment led to the lowest increment. Generally, the modified biochar amendments increased soil EC higher than any other amendment. All biochar amendments increased the soil organic carbon (SOC) content of the soil whereas there were no noticeable differences in the SOC content of the soil in the control amendment.

Generally, the modified biochars resulted into the lowest increments in SOC contents of all the biochars. The PRB amendment produced the highest increment in the SOC content which increased from 0.71% before the experiment to 4.46% after the experiment. All the biochar amendments increased the available phosphorus content with no significant statistical differences amongst them whereas the control amendment led to the reduction in the content of available phosphorus. All amendments increased the concentration of available N. The available N content was highest in the N-enriched biochar amendments of ANB and URB with no significant statistical differences between them. The lowest concentration

**Table 3** Effects of the different amendments on the selected chemical properties of the soil

Treatment	pH	EC (dS/m)	SOC (%)	Avail. P (mg/ kg)	Avail. N (mg/ kg)	Ca <sup>2+</sup>	Mg <sup>2+</sup> (cmol <sub>e</sub> /kg)	K <sup>+</sup>	Na <sup>+</sup>
Control	7.36±0.25 <sup>b</sup>	0.41±0.04 <sup>d</sup>	0.78±0.18 <sup>d</sup>	142.5±4.10 <sup>b</sup>	212.4±13.05 <sup>c</sup>	2.85±0.11 <sup>c</sup>	1.44±0.50 <sup>d</sup>	0.85±0.09 <sup>d</sup>	0.06±0.01 <sup>a</sup>
PRB	8.43±0.32 <sup>a</sup>	1.12±0.03 <sup>c</sup>	4.46±0.51 <sup>a</sup>	277.9±8.51 <sup>a</sup>	253.4±9.40 <sup>bc</sup>	3.81±0.12 <sup>a</sup>	2.64±0.09 <sup>a</sup>	2.85±0.12 <sup>a</sup>	0.07±0.02 <sup>a</sup>
SAB	6.60±0.20 <sup>c</sup>	1.40±0.08 <sup>b</sup>	1.59±0.49 <sup>c</sup>	263.3±3.38 <sup>a</sup>	302.5±8.81 <sup>ab</sup>	3.6±0.06 <sup>b</sup>	2.21±0.07 <sup>bc</sup>	2.18±0.11 <sup>c</sup>	0.07±0.01 <sup>a</sup>
KHB	7.63±0.21 <sup>b</sup>	1.58±0.07 <sup>a</sup>	1.78±0.61 <sup>c</sup>	264.2±5.35 <sup>a</sup>	236.2±7.44 <sup>c</sup>	3.5±0.04 <sup>bc</sup>	2.27±0.10 <sup>b</sup>	2.95±0.12 <sup>a</sup>	0.07±0.01 <sup>a</sup>
HPB	6.97±0.38 <sup>bc</sup>	1.44±0.06 <sup>ab</sup>	1.63±0.58 <sup>c</sup>	267.4±3.70 <sup>a</sup>	315.0±15.77 <sup>ab</sup>	3.31±0.11 <sup>cd</sup>	2.11±0.06 <sup>bc</sup>	2.17±0.08 <sup>c</sup>	0.07±0.02 <sup>a</sup>
ANB	6.96±0.18 <sup>bc</sup>	1.23±0.05 <sup>c</sup>	3.77±0.43 <sup>ab</sup>	263.8±4.26 <sup>a</sup>	350.8±10.71 <sup>a</sup>	3.12±0.04 <sup>d</sup>	2.06±0.07 <sup>c</sup>	2.54±0.05 <sup>b</sup>	0.07±0.01 <sup>a</sup>
URB	7.66±0.11 <sup>b</sup>	1.29±0.07 <sup>bc</sup>	3.23±0.22 <sup>b</sup>	266.1±7.19 <sup>a</sup>	328.3±56.07 <sup>a</sup>	3.16±0.05 <sup>d</sup>	2.16±0.06 <sup>bc</sup>	2.51±0.08 <sup>b</sup>	0.08±0.01 <sup>a</sup>

of available N was detected in the control and KHB amendments with no significant statistical differences between them followed by the PRB amendment. The PRB and the control amendments elicited the highest and lowest increases, respectively, in the concentrations of Ca, K and Mg. However, there were no noticeable differences in the concentrations of Na both before and after experiments.

## 4 Discussions

### 4.1 Ammonia emissions

In agreement with several formerly published studies, biochar amendments reduced gaseous NH<sub>3</sub> emissions from the soil. PRB, KHB, HPB, SAB, URB, and ANB amendments abated NH<sub>3</sub> volatilisations from the soil by 44.18%, 45.91%, 63.23%, 65.62%, 72.66%, and 76.71% respectively in comparison with the control amendment. These reductions were lower than those reported in the incubation experiments by Egyir et al. (2022) where the modified biochars abated NH<sub>3</sub> volatilisations by 63.06–74.85% while URB and ANB amendments attenuated gaseous emissions by 79.93% and 82.88%, respectively. These observations underpin the limitations of the incubation studies in providing accurate real-field trends which calls for our caution to avoid making general conclusions with data from laboratory experiments (Fisher & Wood, 2007; Brüggemann and Bizer 2016). Additionally, the daily NH<sub>3</sub> emissions contravened the observations made by several previous studies including Mandal et al. (2016), Luyima et al. (2020), etc., since the emissions did not greatly reduce after the first week of applying the N fertilisers to the soil as expected.

An earlier study by Egyir et al. (2022) indicated that modifying biochar with hydrogen peroxide and sulphuric acid increased the content of oxygen-containing surface groups especially the carboxylic and sulphoxide groups in HPB and SAB, respectively. The increase in the oxygen-containing surface groups enhanced the protonation of gaseous NH<sub>3</sub> to ammonium and oxidation of ammonium to nitrates hence optimising the abatement of NH<sub>3</sub> volatilisation. In the incubation study, KHB reduced gaseous NH<sub>3</sub> emissions from the soil better than the PRB amendment but in this field study, there were no significant statistical differences between the two amendments. Egyir et al. (2022) opined that modification of the biochar with potassium hydroxide increased the sorption of nitrates into the biochar through the potassium exchange sites which resulted into higher reduction of NH<sub>3</sub> volatilisation than the non-modified biochar. However, that mechanism seemed ineffective under the field conditions but it's hard for us to come up with the reasons to explain this observation.

Similar to what was observed in the incubation studies, the N-enriched biochar amendments caused the largest reductions in the emissions of gaseous NH<sub>3</sub>. This observation concurred with that of Luyima et al. (2020) who observed that nutrient-enriched biochar abated gaseous NH<sub>3</sub> emissions by as high as 85.93% and was more effective than the urea-only amendment in reducing the emissions. The instrumental analysis conducted by Egyir et al. (2022) indicated that N in the N-enriched biochars reacted with the oxygen-containing surface groups which slowed its release, concomitantly abating gaseous NH<sub>3</sub> emissions. In a study reported by Nutt (2019), a group of scientists discovered the formation of covalent bonds between nitrogen and biochar carbon with an accompanying reduction in the amount of gaseous NH<sub>3</sub> volatilised.



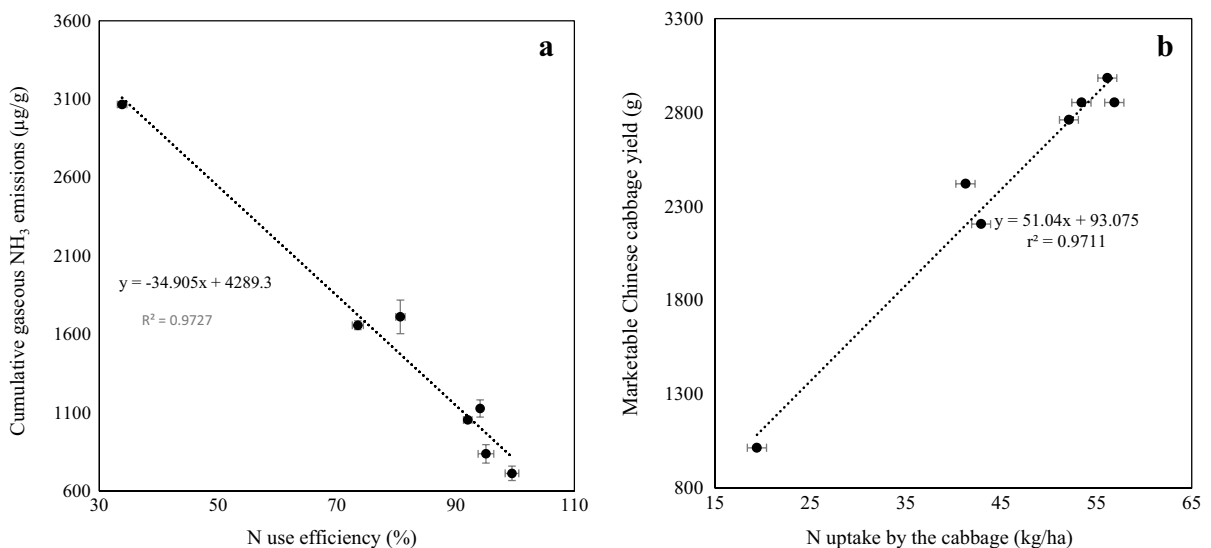
## 4.2 Chinese cabbage yields and soil chemical properties

Biochar has been reported to increase crop yields in tropical but not temperate soils (Jeffery et al., 2017a, b). Contrary to this observation, however, all biochar amendments increased the yields of the Chinese cabbage with the worst performing amendment producing more than twice the yield obtained from the urea-only amendment. The increase in crop yields observed upon biochar applications may be ascribed to a variety of reasons including; biochar's role in the dynamics of plant nutrients (Jeffrey et al., 2017b; Luyima et al., 2021), its liming effect (Jeffrey et al., 2011), and its effect on both soil hydrology and biotic interactions (Jeffrey et al., 2017b). Biochars supply important macro and micro plants nutrients (Jeffrey et al., 2017b; Luyima et al., 2021) while its liming effect reduces the concentrations of Fe and Al in the soil solution with a resultant increase in the availability of the previously bound P to plants (Cui et al., 2011). Biochar supports the growth of arbuscular mycorrhizal fungi (AMF) important for the increased acquisition of P by plants as Shen et al. (2016) observed.

Biochar plays a huge role in the sustainable utilisation of the applied N through reducing gaseous emissions and leaching (Taghizadeh-Toosi et al., 2012). It also increases N inputs through increased N fixation

(Rondon et al., 2007), the net outcome of which is a higher N availability to the growing crop and higher N-use efficiency. Indeed, there was a strong negative linear relationship ( $r^2=0.97$ ) between the cumulative gaseous ammonia evolved from the different amendments and the N-use efficiency (see Fig. 4a) in the present study. This implies that biochar amendment increased use efficiencies of the applied N by abating gaseous  $\text{NH}_3$  emissions. The higher use-efficiencies of the applied N obtained from the biochar amended soils resulted from higher N uptake by the Chinese cabbage. The higher N uptake in turn resulted into higher Chinese cabbage yields as confirmed by the high positive linear relationship ( $r^2=0.97$ ) between the Chinese cabbage yields and the quantity of N taken up by the Chinese cabbage (see Fig. 4b).

The KHB amendment produced lower yields than even the non-modified biochar possibly because it contained higher amounts of chloride which competed with nitrate ions for uptake into the growing Chinese cabbage, thus affecting its yielding potential (Geilfus, 2018). Additionally, both KHB and the non-modified biochars were ineffective at abating N losses which limited the amount of nutrients available to the growing crops and hence lower yields than the rest of the biochar amendments. The non-modified biochar might have contained high amounts of labile carbon (C) at its surface which immobilised some of



**Fig. 4** Linear relationships between (a) the gaseous ammonia cumulatively emitted from the different amendments and nitrogen use efficiencies, and (b) the marketable cabbage yields and nitrogen uptake

the applied N as Jeffrey et al. (2017b) opined, leading to lower yields than those of the modified biochars. The chlorophyll contents were higher in the Chinese cabbage grown on the modified and N-enriched biochars than on the control probably because they supplied adequate nutrients required in the formation of chlorophyll. N, magnesium (Mg), and iron (Fe) have huge direct impacts on the formation of chlorophyll as Ciompi et al. (1996) and Laing et al. (2000) demonstrated.

Therefore, since biochar amendments greatly reduced loss of N from the soil in form of  $\text{NH}_3$  and possibly through leaching, they supplied it to the growing Chinese cabbage in quantities sufficient for the normal chlorophyll formation process. Additionally, the biochar amendments contained substantial quantities of Mg which they supplied to the growing Chinese cabbage resultantly boosting the formation of chlorophyll. Given the sheer importance of chlorophyll in influencing customer choice and their recognised roles in health such as prevention of several diseases associated with oxidative stress, including cancer, cardiovascular diseases, and other chronic diseases (Sangeetha et al., 2010; Yang et al., 2021), it is commendable to conclude that the biochar amendments produced Chinese cabbage with the highest health value and marketability. The dry matter accumulation (dry shoot and root weights) was higher in the N-enriched biochars than the rest of the biochars which indicates that the N-enriched biochars supplied more N to the growing Chinese cabbage than the rest of the amendments. This is because studies by Mehrotra and Singh (1982), and Kumar and Sharma (1999) demonstrated that the dry matter accumulation in rice and wheat increased with increasing application rates of N which underpins the irreplaceable role of N in dry matter accumulation in crops.

The increases in soil pH and EC upon biochar application have been demonstrated by several studies including Chintala et al. (2013), Shen et al. (2016), Trupiano et al. (2017), Luyima et al. (2019), Lee et al. (2019), and others. The biochar-induced increases in soil pH have been ascribed to the liming power of biochar by Trupiano et al. (2017) whereas the increases in EC are attributed to the exchange of electrons between the soil solution and the added biochar (Joseph et al., 2010). In the present study, only PRB, KHB, and URB amendments caused considerable increases in soil pH, SAB caused considerable

decreases in soil pH while the rest of the amendments generally had a benign effect on soil pH. The modification processes de-ashed the biochar which negated the liming potentials of the biochar but the alkalinity of potassium hydroxide might have compensated for the lost liming potential of the KHB biochar. The strong acidity of ammonium nitrate in solution might have masked the liming potential of biochar in ANB, hence the benign effect on soil pH.

The increases in the soil EC observed across all the amendments were a result of the compounding effect of the redox reactions and cation and anion exchange capacities of the biochar amendments as Joseph et al. (2010) demonstrated. The higher increments in soil EC observed with the modified biochar amendments concurred with the observations made by previous studies for example by Wang et al. (2021). On the other hand, the lower increments in soil organic carbon observed in soils amended with the modified biochar than those of the soils amended with pristine biochar may be due to the lack of readily releasable labile carbon contained in the PRB. In agreement with several previous studies by Shen et al. (2016), Lee et al. (2019), Luyima et al. (2019), and others, all biochar amendments increased the amount of soil available phosphorus with no statistically significant differences amongst the different amendments. This increase could have resulted from the biochar-induced increases in soil pH which stimulated increases in mobility and availability of phosphorus in the soil (Shen et al., 2016). However, given the fact that not all the biochar amendments increased soil pH, the increase in available phosphorus could be due to the direct release of phosphorus from the biochar itself as Deluca et al. (2009) opined. Another possible explanation for increases in available phosphorus is possibly the biochar-induced proliferation of arbuscular mycorrhizal fungi which formed symbiotic relationships with the crops grown (Shen et al., 2016).

## 5 Conclusions

The N-enriched biochar amendments elicited the largest reductions in the amount of gaseous  $\text{NH}_3$  evolved and produced the highest Chinese cabbage yields. The biochar-induced reductions in the quantity of gaseous  $\text{NH}_3$  emitted had a direct positive impact on the use efficiencies of the applied N which in turn

affected the Chinese cabbage yields. Generally, KHB was inferior over other modified biochars in both agronomic performance of the Chinese cabbage and the reduction of gaseous  $\text{NH}_3$  volatilisations.

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**Data availability** The data sets supporting the conclusions made are included in the article whereas a limited amount of the modified and nitrogen-enriched biochars can be provided to whoever may want to experiment with them upon request to the corresponding author.

#### Declarations

**Conflict of interest** The authors declare no competing interests.

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