



Co-pyrolysed animal manure and bone meal-based urea hydrogen peroxide (UHP) fertilisers are an effective technique of combating ammonia emissions

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Abstract

Formulating biochar-based nitrogen fertilisers from charred livestock manure and urea, the two largest emitters of ammonia (NH₃) may help to abate particulate matter emitted from agricultural operations. However, animal manure biochar inadequately retains carbon, thus impairing its primary role of carbon sequestration. Co-pyrolysis of animal manure with phosphorus (P) may improve quality of the biochar, but with the phosphate rock reserves expected to vanish soon, a shift to renewable P sources is desirable. Bone waste is laden with P and can be a viable replacement of the phosphate rock. In the current study, we assessed the efficiency of bone waste as a P source in the co-pyrolysis of cow dung and quantified the NH₃ emitting potentials of the biochar-based urea and UHP fertilisers formulated with the co-pyrolysed biochar. Co-pyrolysis of cow dung with bone waste increased yield and carbon retentions of biochar and boosted biochar's capacity to attenuate NH₃ emissions. UHP fertilisers formulated from the co-pyrolysed biochar lessened NH₃ evolutions by as high as 85.93% and were more effective in reducing NH₃ volatilisations than co-pyrolysed biochar-based urea fertilisers.

Keywords Ammonia emissions · Urea hydrogen peroxide · Co-pyrolysis · Fertilisers · Upland and paddy soils

Introduction

Animal excrement and nitrogen (N) fertilisers are by far the largest emitters of NH₃ which through intricate atmospheric reactions forms constituent chemical species of particulate matter (PM) [1, 2] and is thus a vital air pollutant [3, 4]. The general importance of NH₃ emissions to air quality has been underscored by several studies including but not

limited to Tsimpidi et al. [5], Pinder et al. [6], Wang et al. [7], Megaritis et al. [8] and Bessagnet et al. [9] with each of them calling for effective curtailment of NH₃ emissions for the betterment of human health and environment. An overwhelming interest in using biochar to curb NH₃ volatilisations has ensued in recent past, although different studies have come up with contrasting observations.

Mandal et al. [10] found that combined applications of biochar and N fertilisers effectively attenuated NH₃ volatilisations by as high as 77.2% in comparison with N fertiliser applications without any biochar amendments. The observation was later backed by Sun et al. [11] who reported diminished emissions of NH₃ from N fertilisers added to biochar amended soils even though the rates of reduction recorded were way smaller than those reported by the former i.e. the slowdown in NH₃ volatilisations prompted by biochar amendments ranged between a paltry 4.2% and 11.2%. On the contrary, however, studies by Subedi et al. [12], Fan et al. [13], Feng et al. [14] and He et al. [15] registered elevated levels of NH₃ discharge from N fertilisers applied in biochar amended soils.

To ensure optimal slowdown of N release and possibly NH₃ emissions from N fertilisers, studies by Chen et al. [16],

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Punga et al. [17] and Liu et al. [8] for example formulated slow release fertilisers. The former pelletised biochar and urea hydrogen peroxide (UHP) using kaolin as a binding material while both Punga et al. [17] and Liu et al. [8] pre-pended bentonite in the biochar-N fertiliser mixtures. The inclusion of clay in the biochar-based N fertilisers might have been intended to boost the adsorption of N by biochar-based fertilisers due to the high surface areas of clay. Developing a slow release fertiliser from urea and charred livestock manure (the largest emitters of NH_3) may offer a sustainable solution to the pressing issue of PM emissions ensuing from agriculture. However, the very low carbon retention capabilities of high mineral animal manure derived biochar weakens its key role of sequestering carbon.

Studies by Zhao et al. [19] and Zhao et al. [20] espoused that co-pyrolysis of biomass with P improves carbon retentions in biochar which is particularly important for animal manure biochars with exceedingly low carbon retention capabilities. Amidst prognosticated scarcity of the finite phosphate rock (PR) reserves [21, 22], it is appropriate to surmise that renewable P sources such as BM will have a central role in the sustainability of agricultural production systems in the future. Besides supplying P needed for the improvement of biochar quality especially carbon retention, bone char is an efficient adsorbent and thus, co-pyrolysing it with animal manure may enhance the resultant biochar's ability to adsorb added N which may concomitantly reduce NH_3 discharges to the environment. Objectives of this study were to assess the ammonia emitting potentials of biochar-based urea and UHP fertilisers (CCDBFs) formulated out of co-pyrolysed BM and animal manure using cow dung (CD) as a representative for animal manure and to delineate some of the mechanisms which may underlie the gaseous volatilisations.

Materials and methods

Biochar and CCDBFs (CCDB-Urea and CCDB-UHP) production

Dried cow dung and rendered bone waste were each ground and sieved through a 1.8 mm sieve. The sieved materials were blended in varying proportions to obtain final mixtures containing 0%, 5%, 10%, 25% and 50% of BM by weight. The mixtures were rewetted to ensure cohesion amongst the admixed components, dried again and then pyrolysed at 500 °C. Pyrolysis followed packing feedstock into a ceramic container covered with a lid and combusting in a muffle furnace (Lindberg/Blue M) for 2 h. Additionally, bone char (BC) was produced from unmixed bone meal pyrolysed in the same way as adumbrated earlier but at two different temperatures of 500 °C (BC500) and 750 °C (BC750). Another

treatment with triple superphosphate (TSP) as a P source added at a rate of 25% of the mixture was included in the experiment to aid in the comparison of the efficacy of BM with conventional P sources. 3.5 mm extruded activated carbon (AC) was purchased from Duksan chemicals[®], South Korea. Formulation of co-pyrolysed bone meal and cow dung-based UHP fertilisers (CCDB-UHP) followed soaking biochar in a UHP solution for 24 h at room temperature adopting mixing ratios of 5:1, respectively, while the same mixing ratios were adopted for making co-pyrolysed bone meal and cow dung-based urea fertilisers (CCDB-Urea). The mixtures were oven dried at 105 °C for 24 h, cooled and packed for further analysis and usage. 0%, 5%, 10%, 25% and 50% BM containing biochar-based urea fertilisers were denoted as CDB-Urea, CD + BM 5-Urea, CD + BM 10-Urea, CD + BM 25-Urea and CD + BM 50-Urea, respectively, while CDB-UHP, CD + BM 5-UHP, CD + BM 10-UHP, CD + BM 25-UHP and CD + BM 50-UHP symbolised their corresponding CCDB-UHP fertilisers.

Experimental set up

NH_3 Emissions were measured through two incubation experiments. Firstly, the effects of CD biochar (CDB), AC and BC (BC 500 and BC 750) on NH_3 volatilisations from urea and UHP were investigated by using both paddy and upland soils. That incubation experiment was executed to identify the best experimental conditions for the second and main incubation experiment. Paddy soils were kept under saturated conditions while upland soils were maintained at 60% of the water holding capacity following recommendations by Punga et al. [17] and biochar was added at a rate of 3% of the soil. N in forms of Urea and UHP was applied to the soil at rates of 500 mg per kg of soil paying strict adherence to the mixing procedure adopted by Mandal et al. [10]. Paddy and upland soils were respectively picked from paddy and upland fields, air dried, ground and strained through a 2.0 mm sieve. Upland soil which emitted the highest volumes of NH_3 in the first incubation experiment was selected for usage in the main incubation experiment where NH_3 volatilisation potentials of the different co-pyrolysed BM and CD biochars (CCDB), CCDB-Urea and CCDB-UHP were measured. Both CCDB-Urea and CCDB-UHP fertilisers were added to the soil at rates that maintained the N application rate of 500 mg/kg.

The relationships between each of the surface area (SA), micro-pore volume (MpV) and total pore volume (Vt) of CDB, AC, BC 500, BC 750 and CCDB on NH_3 emissions were also investigated. This followed recommendations by Mandal et al. [10] that the nature and properties of biochar's pores may have direct impacts on NH_3 volatilisations from the soil. Alongside NH_3 volatilisation measurements, mineralisation rates of the CCDBFs were determined and the

relationship between them and cumulative NH₃ volatilisations explicated. This is because the rate at which N fertilisers mineralise may have direct implications on gaseous NH₃ discharges from the soil. Both incubation experiments proceeded at room temperature and each lasted for 28 days.

Measurement of NH₃ volatilisations and N mineralisation rates

Measurement of NH₃ volatilisations followed a procedure espoused by Mandal et al. [10] where NH₃ was captured by 0.2 M sulphuric acid and the unreacted acid titrated with 0.4 M sodium hydroxide. In brief, 100 g of the soil containing different amendments was placed in a 500 ml jar (respiration jar) and scintillation vials (20 ml) containing 10 ml of 0.2 M sulphuric acid were hung inside the jar to capture NH₃ emitted from the soil. Schematic diagram of the experimental set up is shown in Figure S1 in the supplementary file. N mineralisation rates of the CCDBFs were derived from the equation adopted by Thangarajan et al. [23] and given below:

$$N_{mr} = \frac{(N_{ft} - N_{fc}) - (N_{it} - N_{ic})}{fd - fi},$$

where N_{mr} is the net N mineralisation rate (mg/kg of soil per day), N_{ft} and N_{it} are the total mineral N concentration of the amended soil on the final and initial incubation days, respectively, N_{fc} and N_{ic} are the total mineral N concentration of the control on the final and initial incubation days, respectively, while fd and id are the respective final and initial incubation days. Mineral N is the sum of ammonium nitrogen (NH₄⁺-N) and nitrate nitrogen (NO₃⁻-N) concentrations. NH₄⁺-N and NO₃⁻-N concentrations were measured colourimetrically following the analytical methods adopted by Kalra and Crumbaugh et al. [24] after extraction with 2 M KCl.

Biochar and soil analysis

The pH was determined by adding 25 ml of 0.01 M CaCl₂ solution to 5 g of either air dried biochar or soil samples followed by overhead rotation of the mixture for 1 h after which pH of the suspension was measured directly using a pH metre. The EC measurement followed addition of 200 ml of

desalinated water to 20 g of either soil or biochar and shaking for 1 h. The solution was filtered and EC was measured in the filtrate using pH and EC metre. Surface area (SA) of biochar was computed as an equivalence of iodine numbers following proposals by Mianowski et al. [25] and Phuong [26]. The iodine numbers of different biochar samples were determined by paying strict adherence to the ASTM D4607-94 method. Micro-pore volume (MpV) and total volumes (Vt) of biochar were determined from the modelled equations propounded by Nunes and Guerreiro, [27] using both methylene blue and iodine numbers. Biochar carbon (C) and nitrogen (N) were assessed with C/N analyser while mass yields were obtained through direct weighing of the biomass feed stocks and obtained biochar. Soil organic carbon (OC) was determined following the Walkley and Black method with organic matter (OM) computed by multiplying 1.72 with the OC value obtained. Available phosphorus was extracted with Olsen solution and determined colourimetrically for orthophosphate by paying strict adherence to the ascorbic acid method using a UV-Vis spectrophotometer (Evolution 300; Thermo Scientific, Inc.). Soil exchangeable cations including K⁺, Ca²⁺, Mg²⁺ and Na⁺ were measured with ICP-OES (GBC Scientific, Australia) after leaching the samples with 1 N ammonium acetate solution at a neutral pH (7.0). Carbon retentions were calculated from the equation set forth by Zhao et al. [20] and is given below:

$$Carbonretetion(\%) = \frac{C_{pm} \times W_{pm}}{(c_{fb} \times w_{fb}) + (C_{am} \times W_{am})} \times 100,$$

where C_{pm} and W_{pm} are carbon content and weight of the pyrolysed materials, respectively, C_{fb} is carbon content of the feed stock biomass, W_{fb} is the weight of the feed stock biomass, C_{am} is the carbon content of the added material while W_{am} is the weight of the added material. The chemical properties of the soil are presented in Table 1 while those of the biochars are shown in Table 2. Co-pyrolysed biochars were also characterised with scanning electron microscope (results shown in Figure S2) in the supplementary file.

Statistical analysis

Data analysis was conducted through Microsoft Excel version 2016 and included (1) a correlation analysis to discern the extent of the relationships between NH₃ volatilisations

Table 1 Chemical properties of the soils used in the experiment

Soil type	pH (CaCl ₂)	EC (dSm ⁻¹)	N (%)	OM (%)	Avail. P (mg kg ⁻¹)	Ca (cmolc kg ⁻¹)	Mg (cmolc kg ⁻¹)	K	Na
Upland	6.12	0.15	0.07	2.79	13.08	6.10	0.38	0.11	0.01
Paddy	5.66	0.26	0.12	4.09	19.87	5.32	0.50	0.23	0.07

OM organic matter, avail. P available phosphorus

Table 2 Selected properties of the resultant biochar

Sample	pH	EC (mS/cm)	MBN (mg/g)	MpV (cm ³ /g)	SA/I ₂ number (mg/g)	V _t (cm ³ /g)	Yield (%)	Carbon (%)	Carbon retention (%)
BC 500	9.88	14.99	11.3	0.0661	113.84	0.170	61.2	12.20	73.20
BC 750	10.67	11.24	13.4	0.0634	108.10	0.173	53.6	9.89	51.97
CDB	10.57	12.91	18.1	0.0545	77.57	0.179	36.9	41.30	47.92
CD+TSP	6.33	13.37	16.4	0.0559	79.31	0.176	51.1	37.11	79.26
CD+BM 5	10.19	13.76	17.7	0.0548	78.03	0.178	39.0	40.40	51.29
CD+BM 10	10.05	13.18	16.3	0.0577	88.00	0.177	41.8	39.70	55.99
CD+BM 25	9.75	10.71	16.0	0.0596	97.05	0.177	45.3	35.01	60.07
CD+BM 50	9.71	9.50	15.8	0.0611	104.11	0.177	49.1	26.81	63.81
AC	NM	NM	23.2	0.2960	938.00	0.275	NM	NM	NM

NM not measured, MBN methylene blue number, EC electrical conductivity, MpV micro-pore volume, SA surface area, V_t total volume

and SA, MpV and V_t of biochar. (2) A linear regression analysis to establish the relationship between NH₃ volatilisations from the soil and rate of N mineralisation. (3) Analysis of variance (ANOVA) on the results for the effect of CCD-BFs on NH₃ evolutions and N mineralisation at 5% level of significance followed by post hoc *t*-tests with studentised *q* tables to quantify the significant differences between the different treatments.

Results and discussion

Effects of co-pyrolysis on biochar properties

As indicated in Table 2, co-pyrolysed biochars had slightly lower pH values than the pure CDB biochars, i.e. pH of CCDB ranged between 10.19 and 9.71 while that of CD+TSP was 6.33 against a pH value of 10.57 registered by CDB. This observation accorded with that of Zhao et al. [19] who noted that co-pyrolysing switch grass and saw dust with BM and TSP decreased pH to 8.45–8.67 and 4.96–5.12, respectively, from 8.56–9.56 in pure biochars. They ascribed the acidic pH of biochar produced from co-pyrolysis of biomass and TSP to the strong acidity of TSP. The slightly lower pH of CCDB biochars than pristine CDB might have been due to the marginally low intrinsic pH of BC, although more investigations may be needed to properly expound the reasons underlying this observation. Additionally, co-pyrolysis of CD with BM augmented resultant biochar's surface area from 77.57 mg/g of CDB to a maximum value of 104.11 mg/g in the CD+BM 50 biochar, with SA values rising along increasing BM contents in the biomass feed stocks. This effect is likely to have stemmed from the high SA of BC itself.

In agreement with a previous study by Zhao et al. [19], co-pyrolysis increased yield of the charred materials and

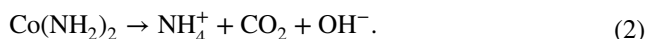
the increments magnified with increasing BM content in the biomass feed stocks pyrolysed. This outcome might have ensued from the recalcitrance of the additives to disintegration upon heating as evidenced from the high yields obtained when BM was pyrolysed. Carbon content reduced to 40.40–26.81% in co-pyrolysed biochars from 41.30% in CDB, an observation that concurred with the results obtained by Zhao et al. [19], Zhao et al. [20] and Lustosa-Filho et al. [28]. The low C content of the additives diluted the carbon concentration of the biomass feed stock, an effect that was carried over to biochars. On the contrary, however, C retentions increased with increasing concentrations of BM in the samples from 47.92% in CDB to a maximum concentration of 63.81% in CD+BM 50 while CD+TSP biochar retained 79.26% of its carbon. The high C retentions may be due to the passivation of carbon brought about by P additives added to biomass which form a durable coating on the surface of biochar preventing C decomposition as delineated by Jiang et al. [29] and Zhao et al. [20] and shown in SEM images (Figure S2) in the supplementary file. The higher efficiency of TSP than BM in retaining biochar C stems from the differences in their P species and availability [20]. For instance, Zhao et al. [20] demonstrated that readily available P supplied by TSP bonded to C and oxygen atoms of the biomass forming hard to break C–O–PO₃ chemical groups which could not be formed with BM.

NH₃ emissions from upland and paddy soils in the first incubation experiment

Although the first incubation experiment was a preliminary one intended to aid in the selection of the right experimental conditions for the main incubation experiment, it helped to quantify NH₃ volatilisations from a range of pyrolysed materials including BC, CDB and AC. From Fig. 2, the cumulative NH₃ volatilisations were higher in the upland soil than

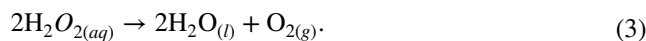
in the paddy one. This could have been due to the higher pH of the upland soil since Mandal et al. [10] demonstrated that gaseous NH_3 loss from the soil increased along increasing soil pH. Another reason for this difference might be the differences in the OM contents of the soils, because Verdi et al. [46] found that applying urea to OM-rich soil led to more NH_3 volatilisations than when urea was applied to low OM containing soil. At cumulative volatilisations of 141.6 mg/kg and 94.6 mg/kg from upland and paddy soils, respectively (Fig. 1a, b), urea-only amendment constituted the greatest loss of applied N of all the treatments. N lost as NH_3 from upland soil accounted for 28.32% of the total quantity of N applied while the loss from paddy soil amounted to 18.92%. The obtained values tallied well with a majority of former studies for instance by Subedi et al. [12], Mandal et al. [10], Feng et al. [14], Sun et al. [11] and others which reported gaseous NH_3 emissions amounting to between 10 and 40% of the applied urea N.

Applying UHP instead of urea faintly subsided NH_3 volatilisations by 15.20% and 18.02% in upland and paddy soils, respectively. Hydrogen peroxide (H_2O_2) protonates in water according to Eq. 1, increasing the concentration of hydrogen ions in soil solution which neutralise OH^- produced when carbamide ($\text{CO}(\text{NH}_2)_2$) hydrolyses as was explained by Bolan et al. [30] and Mandal et al. [10] and shown in Eq. 2;

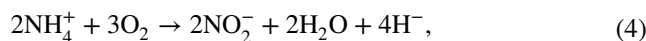


In the absence of OH^- to reduce NH_4^+ to NH_3 as indicated by Bolan et al. [30], gaseous NH_3 emissions subsided

while ammonification and possibly nitrification proliferate. Another fate of H_2O_2 applied along with urea in the biochar-UHP complex in the soil may be dissociation in soil water producing free oxygen radicals and water as shown in the following equation:

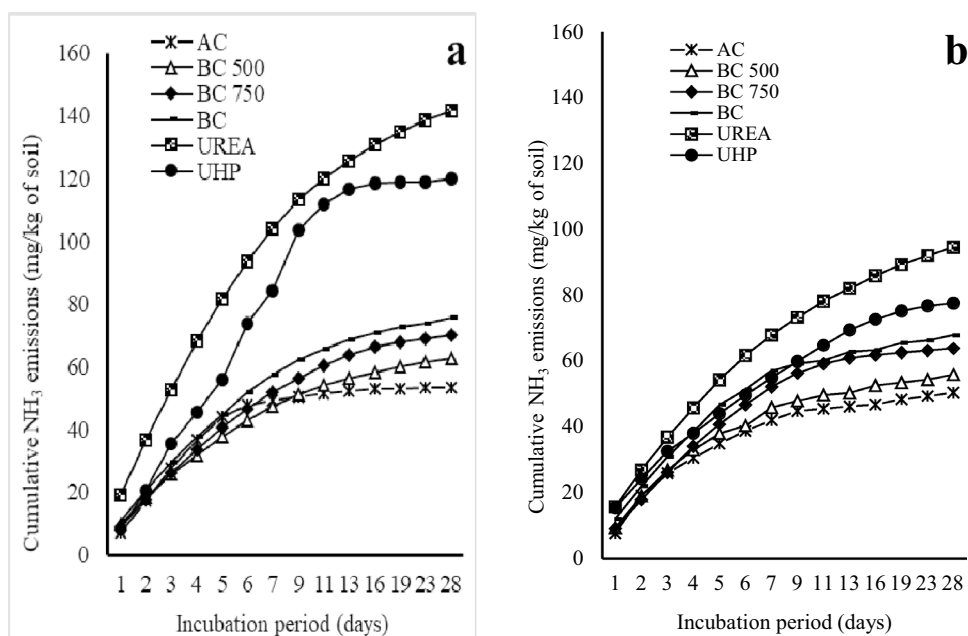


Oxygen released enhances nitrification by oxidising NH_4^+ to NO_2^- and then NO_3^- as demonstrated by McElroy [31] and elaborated in Eqs. 4 and 5. These chemical reactions prevent breakdown of NH_4^+ to NH_3 by OH^- which may offer another explanation for the observed reductions in the gaseous emissions where UHP instead of urea was applied.



From Fig. 1a, and b, CDB, BC 500 and BC750 reduced NH_3 emissions by 46.7%, 55.8% and 50.6%, respectively, when added to upland soil while the reductions in the paddy soil were smaller than in the upland soil and stood at 30.3%, 42.0% and 32.5%, respectively. These observations were in agreement with those made by Mandal et al. [10] and Sun et al. [11] who reported lessened emissions of NH_3 upon biochar additions to the soil. The rates of reductions in the current study were however, lower than those reported by Mandal et al. [10] possibly due to low biochar application rates used but higher than the ones recorded by Sun et al. [11]. Another clear observation was that BC was more efficient in combating volatilisations of NH_3 than biochar

Fig. 1 Cumulative NH_3 emissions from urea and UHP applied to **a** upland and **b** paddy soils with and without AC, BC and CDB amendments



(CDB) possibly due to differences in surface area and pore properties as was propounded by Mandal et al. [10]. Indeed, strong negative correlation coefficients were found between NH_3 volatilisations and MpV (-0.83243), SA (-0.83177) and Vt (-0.77119) of BC, CDB, AC and CCDB. These results of correlation analysis imply that biochar's micro-porosity and surface area take precedence over total volume in influencing the quantity of NH_3 discharge from the soil. The results also augur well with observations made by Subedi et al. [12] who found biochar with a large SA more effective than hydrochar (with a small SA) in abating NH_3 volatilisations. Later on, Feng et al. [14] showed that paddy soils amended with wheat straw biochar produced at 700°C emitted lower quantities of NH_3 than soil that received biochar produced at 500°C , because the latter had lower SA than the former. From Figure S2 (in the supplementary file), SEM images reveal that increasing concentration of BM in the biomass mixture led to creation of porous biochar which may explain the high efficiency of the co-pyrolysed biochars in attenuating NH_3 emissions. Micro-pore volume is particularly important, because Sarkar and Naidu [32] disclosed that a material with a large pore diameter is likely to retain large quantities of water/moisture with accompanying reduction in the amount of NH_4^+ adsorbed. Of all the amendments, AC invoked the highest rates of NH_3 emission reductions standing at 62.40% and 46.72% in upland and paddy soils, respectively. This result was in harmony with that of Wang et al. [33] who found AC more efficient than biochar in adsorbing NH_4^+ from a biogas slurry and attributed its stellar performance to AC's superior SA. This could offer a good explanation to the observations made in this study since AC's SA was at least more than nine-fold that of BC and or CDB.

Besides direct adsorption of NH_4^+ , there are several mechanisms underlying reduced NH_3 emissions observed with biochar amendments as were demonstrated by Mandal et al. [10]. For example NH_3 produced may act as a Brownsted and or Lewis acid accepting a H^+ from the carboxyl groups on the surface of biochar-producing ammonium salts, hence abating gaseous emissions. Additionally, alkaline NH_3 gas can be protonated to NH_4^+ by acidic groups on the surface of biochar and then adsorbed.

Effects of CCDB, CCDB-Urea and CCDB-UHP on NH_3 volatilisations from upland soil

With reference to Fig. 2a, b and c, applying CCDB biochars instead of BC and CDB decreased NH_3 discharges from urea applied to upland soils. Gaseous NH_3 volatilisations in CD + BM 5, CD + TSP, CD + BM 10, CD + BM 25 and CD + BM 50 amended soils reduced by 48.02%, 49.10%, 51.07%, 52.29% and 53.53%, respectively. Similar to the observations made earlier with BC, AC and CDB,

these rates of gaseous reduction were commensurate with the SA, MpV and Vt of the CCDB biochars. This observation is a demonstration that co-pyrolysis of CD (animal manure) with large quantities of BM produces biochar with increased capacities to adsorb NH_4^+ thus reducing NH_3 discharges from soil applied N fertilisers. Relatedly, Zhao et al. [20] demonstrated that biochar produced by co-pyrolysing BM and biomass was more efficient than one produced from a mixture of TSP and biomass in stabilising heavy metals in the soil. Although they attributed their observation to P in hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) that did not react with C during pyrolysis but ended up solubilising to PO_4^{3-} and precipitating heavy metals, elevated SA following the co-pyrolysis may have contributed to that efficiency.

It was also observed that CCDB-Urea and CCDB-UHP were more efficient in reducing gaseous NH_3 emissions than separate applications of fertilisers and CCDB biochars. In comparison to the urea-only amendment, CDB-Urea, CD + TSP-Urea, CD + BM 5-Urea, CD + BM 10-Urea, CD + BM 25-Urea and CD + BM 50-Urea reduced NH_3 volatilisations by 58.47%, 65.50%, 69.15%, 69.77%, 70.84%, and 74.80%, respectively. On the other hand, CDB-UHP, CD + TSP-UHP, CD + BM 5-UHP, CD + BM 10-UHP, CD + BM 25-UHP and CD + BM 50-UHP lessened NH_3 emissions by 71.77%, 73.04%, 76.38%, 79.69%, 83.45%, and 85.93%, respectively. Until now, there has been only a handful of studies into N release potentials of biochar-based N fertilisers, because research into this field is still in a nascent stage. However, the smatterings of data available show that biochar-based N fertilisers are efficient at slowing down N release into the environment.

For example, one of the early studies by Chen et al. [16] discovered that pelletised biochar-based UHP fertilisers reduced leaching of N by up to 74.32% in comparison to UHP only amendment. Later on, Punga et al. [17] found that N containing biochar prills with high biochar and low N contents volatilised lesser gaseous NH_3 than urea. Dong et al. [34] in a bid to develop an efficient slow release biochar-based fertiliser, used different blending ratios of biochar, bentonite, humic acid and a range of adhesive materials and found that the slow release ability of biochar was optimised with 25% biochar, 4% bentonite, and 10% humic acid using modified corn starch adhesive material. Additionally, Liu et al. [18] found that prepending urea to hydrothermally decomposed biomass was more effective than blending biochar and urea in lessening N release into the soil. Shi et al. [35] discovered that urea bound to a blend of biochar and clay minerals reduced N leaching by 70% in comparison to conventional urea and boosted plant growth. Although none of the above-cited studies directly measured gaseous NH_3 emitting potentials of the biochar-based N fertilisers, their inherent slow release abilities may concomitantly slowdown NH_3 volatilisations which

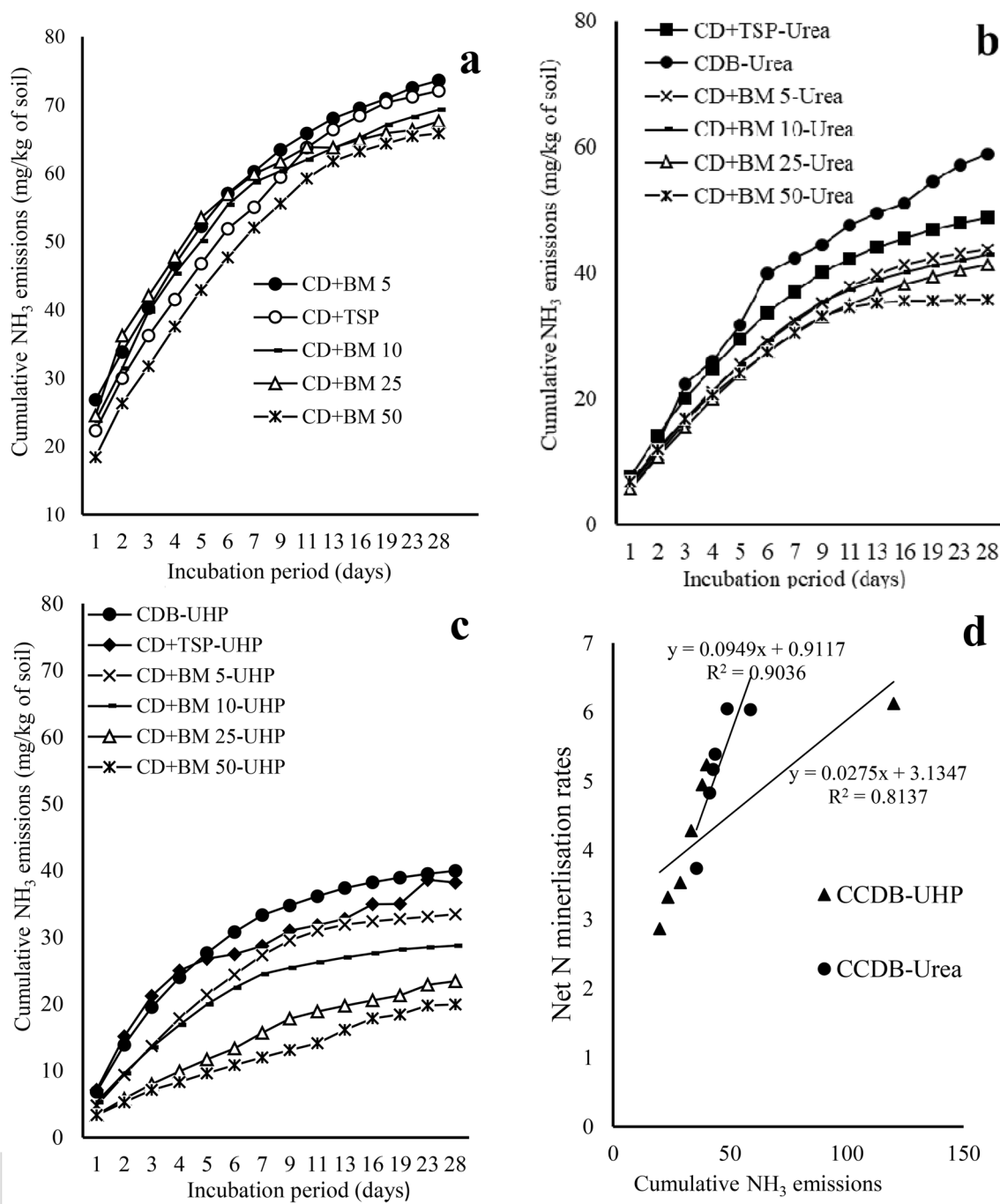


Fig. 2 NH₃ volatilisations from **a** CCDB, **b** CCDB-Urea and **c** CCDB-UHP amended soils, and **d** regression relationship between net N mineralisation and gaseous NH₃ emissions

may explain the low emitting capacities of the CCDB-Urea and CCDB-UHP fertilisers observed in the current study. That line of argument is supported by the strong coefficients of linear regression (Fig. 2d) obtained between the cumulative gaseous NH₃ emissions and rates of mineralisation of CCDB-Urea ($r^2 = 0.8137$) and CCDB-UHP ($r^2 = 0.9036$). This is because rates of N mineralisation are

quantified from inorganic forms of N available in the soil which are potent sources of NH₃ and thus, a reduction in the rate of their release the soil portends reductions in the quantities of NH₃ emitted to the atmosphere. Quantities of volatilised N decreased along increasing BM content in the CCDB, CCDB-Urea and CCDB-UHP which indicates

that biochar's SA plays a crucial role in adsorbing NH_4^+ as indicated by Subedi et al. [12] and Feng et al. [14].

Mineralisation of different CCDB-Urea and CCDB-UHP fertilisers

CCDB-Urea and CCDB-UHP amended soils registered lower concentrations of NH_4^+ -N and NO_3^- -N than both urea and UHP amended soils throughout the incubation period as shown in Fig. 3. The observation accorded with previous studies by Mandal et al. [10] and Dong et al. [34] which reported scaled down mineralisations of N applied to soil with biochar amendments or in form of biochar-based fertilisers. In the current study, levels of mineralised N (NH_4^+ -N and NO_3^- -N) were lower in UHP and CCDB-UHP amended soils than in urea and CCDB-Urea, respectively, which might have stemmed from the lower rates of N release by UHP in comparison to urea as was demonstrated earlier. Another observation was that increasing concentrations of NO_3^- -N followed decrements in the concentrations of NH_4^+ -N in all the treatments possibly because of the direct formation of NO_3^- -N from NH_4^+ -N which was in agreement with the deductions made by Mandal et al. [10].

There are several reasons that may account for the reduced concentration levels of inorganic N observed in the CCDB-Urea and CCDB-UHP fertilisers. Adsorption of NO_3^- and NH_4^+ may be the leading mechanism accounting for the decrease because several studies have confirmed biochar's high affinity for the inorganic N forms. For example, a study by Taghizadeh-Toosi et al. [36] found biochar very efficient in adsorbing NH_4^+ -N, although the adsorbed N was highly bioavailable. Another study by Sarkhot et al. [37] discovered that biochar was an efficient adsorbent for NH_4^+ -N from dairy manure. Tian et al. [38] found both poultry litter and hardwood biochars effective adsorbents of NH_4^+ from storm water. Similarly, Kammann et al. [39] reported improved plant growth using co-composted biochar and suggested that the improvement was due to NO_3^- -N capture by biochar during composting. The captured NO_3^- -N is strongly held up by biochar and not sufficiently extractable with the standard methods as indicated by Haider et al. [40] who had to repeat the extractions several times to be able to effectively remove the captured NO_3^- . Haider et al. [41] also found that biochar applied to a sandy soil greatly retained NO_3^- -N in the top soil preventing it from leaching to lower soil layers.

Another weighty reason for the reduced concentrations of inorganic N pools observed in the current study may be N immobilisation. N immobilisation tends to increase with increasing C: N ratios and thus, adding biochar C is likely to proliferate immobilisation of N by soil micro-organisms [42, 43]. That is because fresh biochars may contain appreciable quantities of labile C that can be readily consumed by soil microbes leading to temporary immobilisation of N in

the soil. Indeed, Bruun et al. [44] demonstrated that biochar which contained a large fraction of labile C immobilised more N than the one with low concentration of labile C. N immobilisation following biochar addition to soil has been shown to slowdown leaching of NO_3^- by Ippolito et al. [45]. The decreased release of inorganic N was the precursor for the reduced net N mineralisation of CCDB-Urea and CCDB-UHP fertilisers added to soil. For example, net N mineralisation rates slowed down from $8.233 \text{ mg kg}^{-1} \text{ day}^{-1}$ in urea amended soil to the lowest value of $3.74 \text{ mg kg}^{-1} \text{ day}^{-1}$ in CD+BM 50-Urea amendment. A similar trend was observed in the CCDB-UHP amendments where net mineralisation rates reduced from $6.12 \text{ mg kg}^{-1} \text{ day}^{-1}$ in UHP amended soils to the lowest value of $2.86 \text{ mg kg}^{-1} \text{ day}^{-1}$ recorded in the CD+BM 50-UHP amendment as shown in Fig. 4 below.

The observed decreases in net N mineralisation rates concurred with previous studies by Dempster et al. [42] and Castaldi et al. [43] who reported reduced net mineralisation rates of N in biochar amended soils. N mineralisation rates are derived from the concentrations of NH_4^+ -N and NO_3^- -N in the soil and hence slowed down mineralisation rates of the biochar fertilisers ensued from reduced release of the inorganic N forms. Therefore, the same reasons given for reduced releases of mineral N hold for the mineralisation rates. Strong linear relationships obtained between cumulative NH_3 volatilisations and mineralisation rates (Fig. 2d) indicate that reduced N mineralisation is a crucial pathway through which biochar-based fertilisers and or biochar attenuate NH_3 volatilisations to the atmosphere.

Conclusion

The results demonstrate that BM (bone waste) is capable of replacing PR as a source of P in the co-pyrolysis of biomass for improved carbon retention and biochar yield although a higher dosage of BM may be required to produce a similar effect achievable with lower dosages of conventional P sources. That was evidenced when biomass mixed with 25% TSP produced a 14.2 percentage increase in biochar yield while the same mixing ratio with BM only elicited an 8.4 percentage rise in biochar yield. The results also confirm dependence of gaseous NH_3 emissions on biochar's surface area, micro-porosity and even total volume indicating the importance of adsorption in the abatement of NH_3 volatilisations. The decreasing NH_3 volatilisations along increasing bone meal concentration in CCDB is because bone char generally has a higher adsorption capacity than animal manure biochar. Therefore, BM included in the biochar feed stock helps to boost resultant biochar's adsorption potential of N concomitantly checking NH_3 emissions.

The study also confirms that applying biochar-based N fertilisers is more effective in controlling NH_3

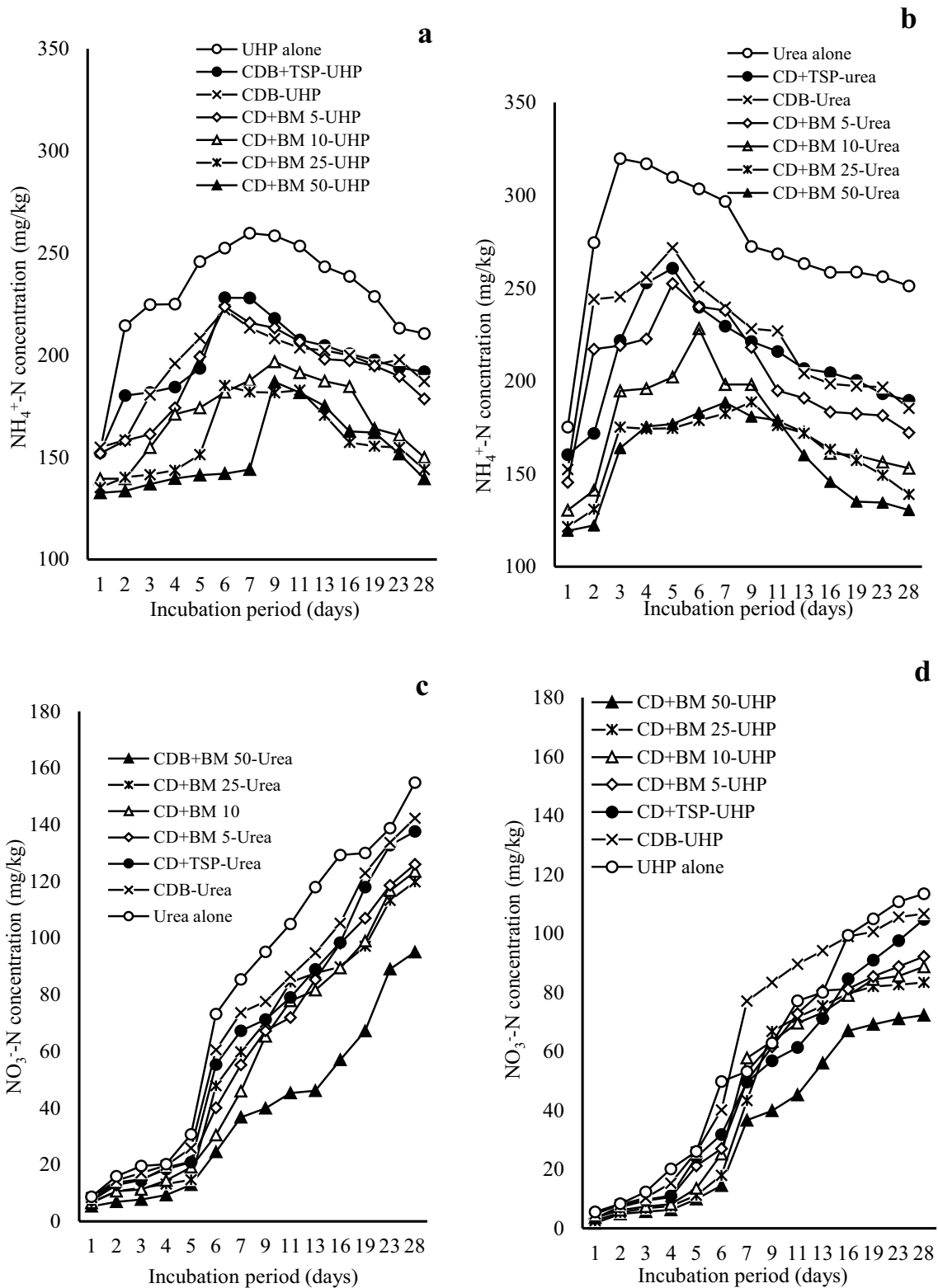
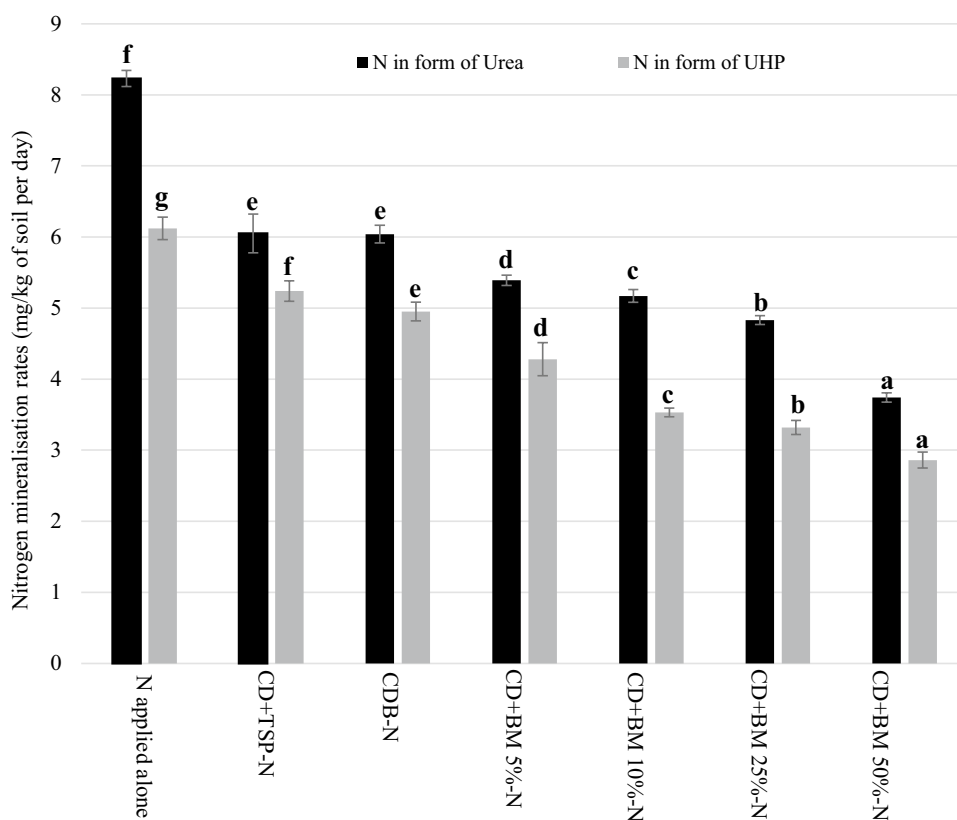


Fig. 3 $\text{NH}_4^+\text{-N}$ concentrations in the **a** CCDB-UHP and **b** CCDB-Urea amended soils, and $\text{NO}_3^-\text{-N}$ concentrations in the **c** CCDB-Urea and **d** CCDB-UHP amendments

Fig. 4 Net N mineralisation rates of CCDB-Urea and CCDB-UHP



volatilisations than separate applications of biochar and N fertilisers. CCDB-UHP attenuated gaseous NH_3 evolutions by as high as 85.93%, while the highest rate of reduction achieved from CCDB-Urea stood at 74.80% in comparison to urea. Therefore, CCDB-UHP was more efficient than CCDB-Urea in controlling NH_3 volatilisations from the soil and is recommended as a replacement for conventional urea. Attenuation of N mineralisation is a prominent pathway through which both CCDB-Urea and CCDB-UHP reduced NH_3 emissions from the soil. However, slowed down net mineralisation rates of the applied N observed in both CCDB-Urea and CCDB-UHP may also hinder proper plant growth. Therefore, experiments are needed to elucidate the agronomic efficiencies of the different CCDB-Urea and CCDB-UHP.

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Author contributions All authors contributed to the study conception and design. LD collected data, conducted the laboratory and statistical analyses and wrote the manuscript while JL helped him with procuring the required materials and in some aspects of data collection and analysis. TKO and JS supervised the experiment and offered technical guidance throughout the entire research period.

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