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Sorption of urea hydrogen peroxide by co-pyrolysed bone meal and cow dung slowed-down phosphorus and nitrogen releases but boosted agronomic efficiency

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Abstract

Co-pyrolysis of animal manure biomass with bone meal (BM) and soaking of the resultant biochar in urea containing solutions may offer a sustainable and cheap way of formulating slow-release nitrogen (N) and phosphorus (P) fertilisers. This method can lead to optimisation of the carbon sequestration capacity of the biochar, abatement of environmental pollution by P and N and alleviation of the severity of the projected future scarcity of P. A few studies have indicated that sorption can create efficient slow-release fertilisers although all of them utilised charged moieties such as ammonium ions to formulate them and as a result, there is a paucity of data concerning the efficiency of fertilisers formulated using uncharged compounds like urea. It's against that background that we examined the possibility of leveraging co-pyrolysis and sorption with urea containing solutions to formulate slow-release N and P fertilisers along with assessing the agronomic efficiency of the formulated fertilisers through cultivating lettuce in pots for two seasons. Both urea-hydrogen peroxide (UHP) and urea were utilised as N sources. UHP (CDBM-UHP) and urea (CDBM-Urea) containing biochars averagely released 64.40% and 87.00% of the added N, respectively over the 28-day incubation period with the amount of N released decreasing with increasing concentrations of BM in the biochar. Lettuce yields and nutrient use efficiencies of N and P were higher in the CDBM-UHP than in the CDBM-Urea treatments. It's therefore clear that sorption of UHP by BM containing biochar concomitantly slows-down releases of N and P and boosts the agronomic efficiency of the fertilisers.

Keywords: Agronomic efficiency, Biochar, Real nutrient use efficiency, Slow-release fertilisers, Sorption

Introduction

Nitrogen (N) and phosphorus (P) are irreplaceable nutrient elements in the sustenance of agricultural production systems and life in general [1]. Their usage for supporting plant growth has been growing since the green revolution

in the second half of the twentieth century and are highly credited for boosting agricultural productivity and reducing global hunger. However, continuous fertilisation of agricultural fields has resulted in plenty of problems including the exacerbated release of greenhouse gases, particulate matter precursors, underground and surface water pollution, etc., mainly arising from moderately low nutrient uptake by crops [1, 2]. These losses don't bode well for the future supply of P in particular because although N supply is unlimited due to the Haber Bosch process which produces about 100Tg of N per year [3], phosphate rock reserves are finite and thus should be optimally utilised [3, 4].

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Besides the injurious ramifications on environmental quality and human health, the speedy release of P into the soil exacerbates its fixation especially in acidic and highly weathered soils [5]. Of particular importance to this conundrum are animal manures with abnormally high N:P ratios which hamper their sustainable recycling. Whereas the N to P ratios of most plant biomass average to around 8:1, those of animal manure do not exceed 4:1, thus, the application of livestock manure at optimal N crop requirements portends P accumulation in the soil [6]—with possible contamination of groundwater through leaching or eutrophication of open water sources through surface runoff [7, 8]. Although animal manure has historically been a valuable resource in amending soils and providing crop nutrients, the increasingly large scale animal operations confined to small geographic areas have resulted in the generation of enormous quantities of manure far beyond the assimilative potentials of the lands nearby [6, 9]. Therefore, disposal of manure has increasingly become a problem, prompting farmers to stockpile it under uncontrolled conditions something that hastens its decay resultantly magnifying the emissions of ammonia and other harmful gases like methane and nitrous oxide [10, 11].

Pyrolysis, if leveraged can sustainably solve the above-mentioned problems both through shrinking the volumes of the generated animal wastes and more importantly by providing cheap carrier and coating materials for plant nutrient elements in form of biochar, hydrochar and bio-oil which have great capacities to lessen nutrient releases into the environment. The potentialities and or efficacies of different products of pyrolysis in slowing-down releases of plant nutrients especially nitrogen have been widely assessed by several studies which include amongst others Chen et al. [12], Punga et al. [13], Ye et al. [14] and Liu et al. [15]. The results from all those studies confirm that products of pyrolysis are efficient in slowing down the release of easily leachable plant nutrient elements with resultant benefits for environmental quality and agricultural productivity. To slow the release of P from animal manure biochar, studies by Zhao et al. [16] and Lustosa Filho et al. [5] mulled the idea of co-pyrolysing biomass with P sources and found that co-pyrolysing animal manure biomass with P did not only slow down P release but also improved carbon retentions in the resultant biochar. With diminishing phosphate rock (PR) reserves, it's vital to assess the performance of alternative (renewable) sources of P like bone waste.

Formulating slow-release N and P fertilisers from co-pyrolysed bone waste and animal manure can offer a sustainable way of controlling discharges of N and P into the environment from both animal excrement and mineral fertilisers. While several strategies of synthesising

biochar based slow-release N fertilisers (BFs) have been proposed by different studies, the easiest and cheapest of all of them is N fertiliser sorption by biochar. This is because pelletising the formulated fertilisers or wrapping them in superabsorbent polymers increases production costs and can also pose grave environmental problems especially if synthetic polymers are overused. Indeed, previous studies by Yao et al. [17] and Chen et al. [18] found sorption an effective method of producing slow-release fertilisers even though both employed charged rather than the chemically inactive fertiliser forms. Moreover, An et al. [19] suggested that merging biochar and nutrients through sorption is an inapt undertaking because the amalgamation is mainly controlled by the weak van der Waals forces, thus weakening the slow-release capacity of the formulated fertilisers. The present study, therefore, aimed to examine the possibility of formulating slow-release N and P fertilisers both through co-pyrolysis of animal manure biomass (cow dung) with BM and soaking of the resultant biochar in urea and UHP solutions alongside assessing the agronomic efficiency of the formulated fertilisers.

Materials and methods

Characterisations of BFs and soil

Rendered bone waste was finely ground into BM, sieved through a 2 mm strainer and mixed with cow dung in two different ratios of 1:1 and 1:3, respectively. The cow dung had also been dried and strained through a 2 mm sieve. The mixtures were pyrolysed at 500 °C and then soaked in urea and UHP solutions to form CDBM-Urea and CDBM-UHP, respectively. The urea and UHP containing fertilisers formulated out of the 1:3 amalgams are denoted as CDBM 1-Urea and CDBM 1-UHP, respectively while CDBM 2-Urea and CDBM 2-UHP represent urea and UHP containing fertilisers, respectively, made out of the 1:1 mixture. Additionally, CDTP-Urea and CDTP-UHP fertilisers formulated out of an admixture containing 75% cow dung and 25% triple super phosphate (TSP) and pyrolysed at 500 °C were included for purposes of comparing BM to a conventional source of P. All the formulated fertilisers were oven dried for 24 h at 105 °C. Both urea and UHP were mixed with co-pyrolysed biochars in ratios of 1:5, respectively.

The total carbon (C) and total nitrogen (TN) of the biochar-based slow-release N fertilisers formulated (BFs) were determined with a C/N analyser, total P in both BFs and soil was extracted by paying strict adherence to the aqua regia method and analysed for orthophosphate following a method espoused by Murphy and Riley [20] after neutralising the supernatant with 4 M NaOH using p-nitrophenol indicator. Available P in BFs was extracted with 2% formic acid (Formic P) and analysed

colourimetrically at 470 nm following the vanadate-molybdate method. Soil extractable P was extracted with Olsen solution, filtered and then assessed for orthophosphate following the ascorbic acid method proposed by Murphy and Rilley [20]. Determination of the total elemental compositions of BFs followed extraction with the perchloric acid (wet ashing) and measurements of the resultant filtrates with ICP-OES. Concentrations of soil mineral elements including K, Ca, Mg and Na were determined with ICP-OES after extraction with 1 N neutral ammonium acetate solution. pH of the BFs was determined in a 1:10 BFs: water suspension. The nutrient compositions and other chemical properties of the BFs are shown in Table 1 below while the properties of the soil used are given in Luyima et al. [32].

Releases of N and P from the BFs

The N and P release potentials of the BFs were conducted through a simple batch experiment which was carried out by mixing two grams of each of the BFs with 200 mL of deionized water and then agitated at 60 rpm on a reciprocating shaker at 25 °C. Two portions of 5 mL each of the suspension (one for N and the other for P analysis) were collected at regular intervals, filtered through 0.45 µm Advantec membrane filters and analysed for N and P. For P release analysis, suspensions were collected at 8, 16, 24, 48, 72, 96, 120, 144, 168, 216, 264, 312, 384, 456, 552 and 672 h while for N analysis, suspensions were collected at 24, 48, 72, 96, 120, 144, 168, 216, 264, 312, 384, 456, 552 and 672 h although the cumulative amounts of both N and P released were graphically presented in days instead of hours. P contents of the filtrated suspensions were analysed following the ascorbic acid method proposed by Murphy and Rilley [20] while the total N concentrations were determined colourimetrically following a method developed by Okalebo et al. [21]. P sources evaluated included CDBM 1, CDBM 2, TSP and BC. Values of

CDBM 1 and CBM 2 were obtained by averaging P concentrations of both urea and UHP containing CDBM 1 and CDBM 2, respectively. Each of the Changes in N and P concentrations as a function of time were fitted using nutrient release kinetic models including zero order, first order, pseudo first, second order, pseudo second, Elovich, power function, and parabolic diffusion models as were documented by Sparks [22] and Zhao et al. [16].

Evaluation of the agronomic efficiency of BFs

To assess the agronomic efficiency of the different BFs, two seasons of pot experiments were conducted with the leaf lettuce. BFs amendments were CDTP-Urea, CDTP-UHP, CDBM 1-Urea, CDBM 1-UHP, CDBM 2-Urea, CDBM 2-UHP while control and treatments where P sources of BC and TSP, each separately added to the pots applied with urea and UHP were also included. Each of the BFs was applied to the soil at a rate of 0.5% (w/w) which translates to 15 metric tons of BFs per hectare (considering a soil with a bulk density of 1.5 g/cm³ and an incorporation depth of 20 cm) and each growing season lasted for 5 weeks after transplanting of two-week-old seedlings. Regular watering and other agronomic practices were carried out to ensure proper growth and development of the planted lettuce. At each harvest, agronomic characteristics of the leaf lettuce including shoot weight, shoot height, root weight, root length, number of leaves, leaf length and leaf width were determined. Additionally, plant uptakes of N and P under the different soil amendments were also assessed to delineate the N and P use efficiencies. Plant sample analysis followed strict adherence to the analytical methods espoused by Kalra [23]. Total nitrogen was determined through the miro-Kjeldahl method while total P was assessed by paying adherence to the nitric-perchloric acid digestion in an open vessel method. The real nitrogen (RNUE) and phosphorus

Table 1 Selected properties of the BFs, TSP and BC

Treatment	pH	Elemental content (%)		C/N ratio	Total P (mg g ⁻¹)	Formic P	K	Ca	Mg
		C	N						
BC	9.98 ± 0.0	14.33 ± 2.6	2.71 ± 0.5	5.29 ± 0.5	150.9 ± 1.4	23.06 ± 4.5	3.25 ± 0.2	313.11 ± 8.4	5.88 ± 0.3
TSP	3.44 ± 0.0	0.21 ± 0.1	0.04 ± 0.0	5.25 ± 0.4	205.6 ± 4.2	34.93 ± 1.0	6.37 ± 0.4	167.08 ± 5.6	6.63 ± 0.0
CDBM 1-Urea	8.53 ± 0.1	35.11 ± 3.1	12.70 ± 0.1	2.76 ± 0.1	85.8 ± 2.9	10.73 ± 0.3	2.53 ± 0.3	216.10 ± 8.1	4.89 ± 0.2
CDBM 1-UHP	8.99 ± 0.0	35.09 ± 2.8	11.93 ± 0.1	2.94 ± 0.0	85.5 ± 3.5	10.72 ± 0.5	2.66 ± 0.1	216.19 ± 7.7	5.00 ± 0.5
CDBM 2-Urea	8.86 ± 0.1	27.01 ± 2.7	13.12 ± 0.2	2.06 ± 0.0	127.8 ± 1.8	16.52 ± 2.9	3.03 ± 0.5	270.81 ± 7.5	5.41 ± 0.1
CDBM 2-UHP	9.02 ± 0.1	27.04 ± 2.5	12.90 ± 0.1	2.10 ± 0.1	128.0 ± 1.7	16.60 ± 3.2	2.98 ± 0.3	270.85 ± 7.9	5.16 ± 0.1
CDTP-Urea	6.05 ± 0.1	37.21 ± 1.9	11.67 ± 0.8	3.19 ± 0.5	122.7 ± 2.0	18.64 ± 1.1	4.20 ± 0.2	180.04 ± 7.3	6.17 ± 0.5
CDTP-UHP	6.17 ± 0.1	37.16 ± 2.2	11.44 ± 0.1	3.25 ± 0.2	123.0 ± 2.3	18.65 ± 0.8	4.18 ± 0.2	180.90 ± 6.8	6.12 ± 0.0.7

BC bone char, TSP triple superphosphate, CDBM 1 75% cow dung + 25% bone meal (3:1 mixture), CDBM 2 50% cow dung + 50% bone meal (1:1 mixture), CDTP 75% cow dung + 25% bone meal.

(RPUE) use efficiencies of the applied fertilisers were computed from the equation espoused by Wang and Zhou [24] as follows;

$$RNUE = \frac{N \text{ uptake by plants in the fertilised plot} - N \text{ uptake by plants in the control}}{\text{Fertiliser N} - \text{Residual N}} * 100$$

$$RPUE = \frac{\text{Puptakebyplantsinthefertilisedplot} - \text{Puptakebyplantsinthecontrol}}{\text{TotalPapplied} - \text{RemnantPattheendofthegrowingseason}} * 100$$

For each treatment in the first season except the control, two sets were set up one of which was used for computations of the nutrient use efficiencies in the first growing season while the other was utilised as the control experiment in the second growing season. Therefore, each of the treatments had its control experiment in the second growing season.

Statistical analysis

The data from the pot experiments were subjected to a single factor analysis of variance (ANOVA) using the Microsoft Excel 16 version and the results obtained were subjected to a tukey post hoc test with the p value set at 5% using the studentised q tables. The statistical differences amongst different treatments were denoted by small letters of the English alphabet while the standard deviation on graphs were indicated with error bars.

Results

N and P releases from the BFs

As shown in Fig. 1, CDBM-Urea fertilisers released more N than their CDBM-UHP counterparts. For example, CDTP-Urea cumulatively released 964.52 mg/g of N during the 28-day period of the experiment whereas CDTP-UHP liberated 715.35 mg/g of the soaked N. In the same vein, BFs formulated from cow dung co-pyrolysed with BM released far less N than those made out of cow dung co-pyrolysed with TSP. The amount of N released from the BM containing BFs diminished with increasing BM concentrations in the BFs. For example, CDBM 1-Urea cumulatively freed 841.30 mg/g of N vis-a-vis 804.00 mg/g N obtained from CDBM 2-Urea. Relatedly, the amount of N cumulatively released from CDBM 1-UHP in the 28 days of the experiment stood at 629.42 mg/g while CDBM 2-UHP cumulatively discharged 586.46 mg/g.

Apart from CDTP-Urea whose N release best fitted to both the pseudo first and pseudo second orders ($R^2 = 0.995$), N release from the remainder of the BFs was best fitted to only the pseudo second order of kinetic release as indicated in Table 2. The quantity

of cumulative N obtained at equilibrium (qe) reduced with increasing proportions of BM in the co-pyrolysed biochar and was higher in the CDBM-Urea than in the

CDBM-UHP fertilisers. For example, the obtained qe stood at 997.33 mg/g in the CDTP-Urea but reduced to 914.29 and 866.67 mg/g in CDBM 1-Urea and CDBM 2-Urea, respectively. The lowest qe value of 644.83 mg/g was obtained with CDBM 2-UHP. Similar to N release, P release from all the BFs fitted well to the pseudo second order of release kinetics.

BC released 1.58 mg/g of P over the entire period of the experiment while CDBM 1 and CDBM 2 released lower quantities of 0.42 and 0.79 mg/g P, respectively. On the other hand, TSP cumulatively discharged 299.10 mg/g while CDTP liberated 125.74 mg/g of P as shown in Fig. 2. TSP and BC discharged 77.63 and 82.84%, respectively of the total P cumulatively released over the entire experimental period with in

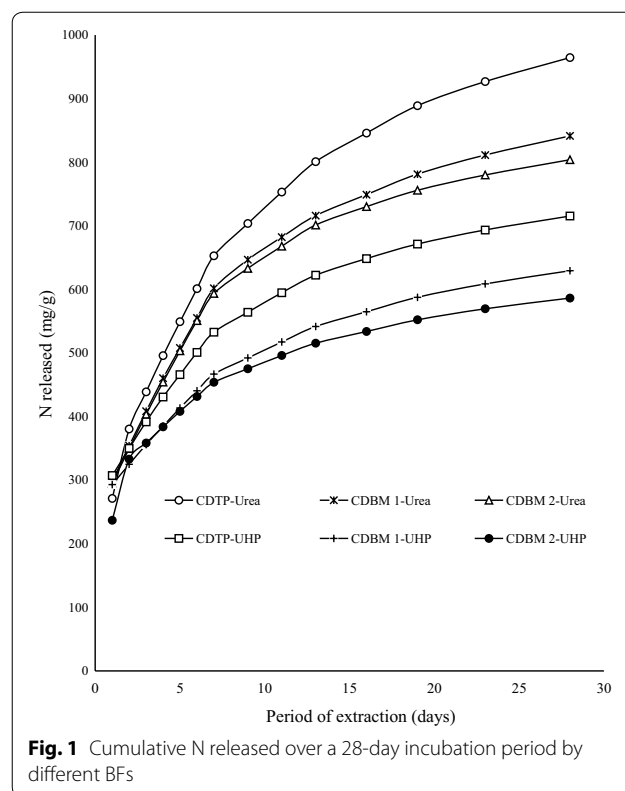


Fig. 1 Cumulative N released over a 28-day incubation period by different BFs

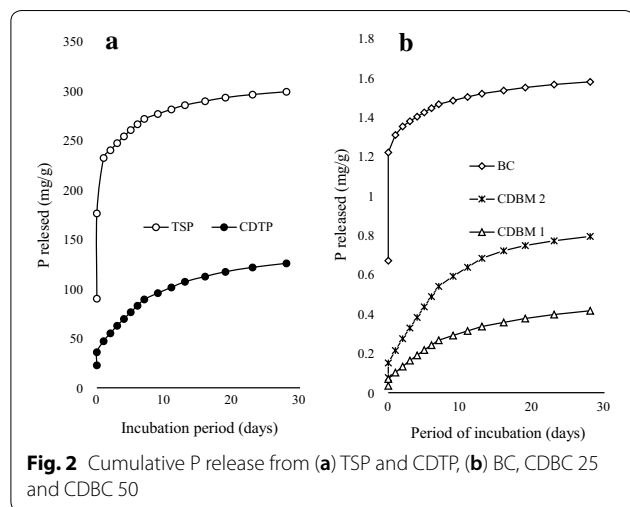
Table 2 Coefficients (R²) of the examined models and the rate constants for N and P release kinetics from co-pyrolsed biochar based fertilisers

Kinetic models	N in Urea form			N in UHP form			Phosphorus					
	CDTP	CDBM 1	CDBM 2	CDTP	CDBM 1	CDBM 2	TSP	CDTP	BC	CDBM 1	CDBM 2	
Zero order $[A]_t = [A]_0 - k_0t$												
R ²	0.239	0.195	0.218	0.168	0.138	0.209	0.283	0.386	0.197	0.816	0.894	
k ₀	-3.5733	-3.6761	-3.8937	-3.6511	-3.1932	-3.2819	-0.0785	-0.0142	-0.0004	-2 × 10 ⁻⁵	-7 × 10 ⁻⁵	
First order $Log[A]_t = Log[A]_0 - \frac{k_1}{2.303} * t$												
R ²	0.417	0.417	0.523	0.382	0.252	0.356	0.493	0.622	0.387	0.876	0.939	
k ₁	-0.0398	-0.0449	-0.0544	-0.0488	-0.0401	-0.0539	-0.0039	-0.0016	-0.0037	-0.0009	-0.0018	
Pseudo first order $ln(q_e - q_t) = lnq_e - k_{1b} * t$												
R ²	0.995	0.987	0.981	0.976	0.998	0.971	0.924	0.984	0.930	0.979	0.956	
k _{1b}	-0.1079	-0.0787	-0.0825	-0.0659	-0.0952	-0.0675	-0.0050	-0.0035	-0.0052	-0.0029	-0.003	
Second order $\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2t$												
R ²	0.659	0.737	0.873	0.755	0.528	0.587	0.866	0.841	0.707	0.926	0.918	
k ₂	0.0006	0.0008	0.0012	0.0012	0.0010	0.0015	0.0005	0.0002	0.0941	0.0375	1.1084	
Pseudo second order $\frac{t}{q_t} = \frac{1}{k_{2b} * q_e^2} + \frac{1}{q_e} * t$												
R ²	0.995	0.996	0.997	0.996	0.995	0.998	1.000	0.992	1.000	0.991	0.993	
q _e	997.33	914.29	866.67	800.00	654.78	644.83	303.03	135.86	1.59	0.48	0.92	
k _{2b}	0.00025	0.00030	0.00035	0.00041	0.00057	0.00062	0.00019	0.00010	0.05472	0.0165	0.0099	
Elovich $q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt$												
R ²	0.990	0.984	0.984	0.985	0.979	0.980	0.840	0.983	0.762	0.971	0.819	
Power function $lnq_t = lnk + v lnt$												
R ²	0.988	0.985	0.980	0.989	0.991	0.957	0.710	0.976	0.654	0.969	0.966	
Parabolic diffusion $q_t = A + C * t^{1/2}$												
R ²	0.968	0.959	0.946	0.961	0.975	0.972	0.629	0.957	0.559	0.972	0.956	

R² values (in bold) are an important indication of the strength of the fit to the different kinetic models by the tested BF_s fertilisers

[A]_t is the concentration of N or P at time t, [A]₀ is the initial concentration of N or P, q_t is the cumulative concentration of N or P at time t, q_e is the cumulative quantity of N or P obtained at equilibrium of the experiment, [A]_t = q_{t2} - q_{t1} where q_{t2} is the cumulative concentration of N or P at the current sampling and q_{t1} is the cumulative concentration of N or P at the preceding sampling

BC bone char, TSP triple superphosphate, CDBM 1 75% cow dung + 25% bone meal (3:1 mixture), CDBM 2 50% cow dung + 50% bone meal (1:1 mixture), CDTP 75% cow dung + 25% bone meal.



the first 24 h. Additionally, the q_e values of 303.03 and 1.59 mg/g obtained for TSP and BC, respectively were higher than the values obtained with the co-pyrolsed biochars of CDBM 1, CDBM 2 and CDTP whose q_e totalled to only 0.48, 0.92 and 135.86 mg/g, respectively as shown in Table 2.

Agronomic efficiency of BF_s

Apart from the control and treatments where TSP and urea or UHP were separately added to the soil (which either registered losses or no change in yields), the rest of the treatments experienced boosted yields in the second season of the experiment as shown in Table 3. CDTP-UHP produced the most stellar performance in almost all the aspects of crop yields assessed in both the growing seasons and was closely followed by CDTP-Urea amendment. In the second season, the differences in yield between the ordinary urea treatment of TSP + Urea

Table 3 Yield components

Growing seasons	Treatments	Shoot weight (g/pot)	Shoot length (cm)	No. of leaves (per plant)	Leaf width (cm)	Leaf length (cm)	Root weight (g)	Root length (cm)
Season 1	CDTP-Urea	78.45 ± 5.34f	22.30 ± 1.04e	16.00 ± 1.00c	6.90 ± 0.17f	15.67 ± 1.15d	15.97 ± 0.06e	19.00 ± 0.46e
	CDTP-UHP	82.53 ± 3.88g	23.60 ± 0.44f	15.00 ± 1.73bc	7.73 ± 0.51g	16.33 ± 0.58d	16.53 ± 0.46f	20.50 ± 0.82f
	CDBM 1-Urea	71.87 ± 1.63de	19.13 ± 1.2c bc	15.33 ± 0.58bc	5.90 ± 0.62e	14.50 ± 0.50c	14.03 ± 0.03d	17.10 ± 0.75d
	CDBM 1-UHP	74.20 ± 2.11e	20.50 ± 0.50d	15.00 ± 1.00bc	5.33 ± 0.58c	14.80 ± 0.20c	14.10 ± 0.30d	17.70 ± 0.36d
	CDBM 2-Urea	67.63 ± 1.52cd	17.80 ± 0.95c bc	13.00 ± 0.00b	5.63 ± 0.15de	13.33 ± 0.42b	12.89 ± 0.25bc	15.70 ± 0.53c
	CDBM 2-UHP	71.00 ± 2.00d	18.20 ± 0.36bc	14.00 ± 1.00b	5.10 ± 0.10c	13.00 ± 0.30b	13.07 ± 0.11c	15.90 ± 0.10c
	TSP + Urea	58.00 ± 0.98b	17.00 ± 0.20b	19.00 ± 2.00d	4.33 ± 0.15b	16.00 ± 0.36d	12.44 ± 0.50b	13.50 ± 0.50b
	TSP + UHP	62.33 ± 2.42c	17.40 ± 0.70b	16.00 ± 2.65c	4.95 ± 0.06c	15.60 ± 0.20cd	12.63 ± 0.21bc	13.40 ± 0.44b
	BC + Urea	63.60 ± 0.69c	17.9 ± 0.53c bc	14.67 ± 0.50bc	4.37 ± 0.12b	14.37 ± 0.47c	13.22 ± 0.33c	13.7 ± 0.35b
	BC + UHP	64.81 ± 1.60c	18.6 ± 0.79c	15.33 ± 0.35bc	5.50 ± 0.25d	14.83 ± 0.55c	13.46 ± 0.48c	13.67 ± 0.65b
	Control	37.16 ± 1.25a	9.50 ± 0.62a	6.00 ± 1.00a	3.67 ± 0.35a	5.67 ± 0.25a	3.99 ± 0.46a	5.30 ± 0.72a
Season 2	CDTP-Urea	102.20 ± 1.75f	26.53 ± 1.34d	21.67 ± 1.53d	8.17 ± 0.21d	14.93 ± 0.90de	26.26 ± 0.73dcd	20.00 ± 1.73cd
	CDTP-UHP	123.30 ± 2.34h	27.90 ± 1.01e	28.00 ± 1.00f	9.57 ± 0.51e	15.70 ± 0.36e	29.50 ± 1.32e	20.53 ± 1.36d
	CDBM 1-Urea	99.37 ± 1.12ef	25.23 ± 0.93cd	18.67 ± 0.58c	7.33 ± 0.64cd	14.67 ± 0.58d	24.18 ± 2.37cd	20.30 ± 0.36cd
	CDBM 1-UHP	109.98 ± 3.77g	26.00 ± 1.00d	25.33 ± 1.53e	8.90 ± 0.85e	15.43 ± 0.51e	24.45 ± 1.08cd	20.07 ± 0.67cd
	CDBM 2-Urea	96.71 ± 2.06e	24.50 ± 0.72c	19.00 ± 1.73c	7.30 ± 0.53cd	14.37 ± 1.00d	23.08 ± 1.76c	19.10 ± 0.85c
	CDBM 2-UHP	100.84 ± 2.26ef	26.40 ± 0.60d	19.33 ± 0.58c	7.77 ± 0.25d	15.60 ± 0.87e	23.21 ± 0.82c	19.57 ± 1.26cd
	TSP + Urea	51.36 ± 3.24b	21.97 ± 0.95b	16.67 ± 0.58b	5.93 ± 0.12b	11.23 ± 0.25b	10.71 ± 0.45b	13.00 ± 0.87b
	TSP + UHP	62.88 ± 1.97c	22.70 ± 0.66b	17.00 ± 1.00b	6.37 ± 0.55bc	13.03 ± 0.35c	12.05 ± 0.83b	14.63 ± 0.32b
	BC + Urea	89.27 ± 5.14d	23.10 ± 0.36b	19.33 ± 0.58c	6.90 ± 0.36c	14.13 ± 0.86de	24.64 ± 0.62cd	19.90 ± 1.15cd
	BC + UHP	93.33 ± 2.10de	24.87 ± 0.57c	21.00 ± 1.00d	7.13 ± 0.32cd	15.00 ± 0.30de	25.08 ± 1.08d	19.73 ± 1.76cd
	Control	36.62 ± 2.02a	8.83 ± 0.29a	9.67 ± 0.58a	4.40 ± 0.17a	6.73 ± 0.46a	3.23 ± 0.18a	5.27 ± 0.47a

The letters (a–h) denote the significant differences between the different treatments based on the result of the Tukey posthoc test

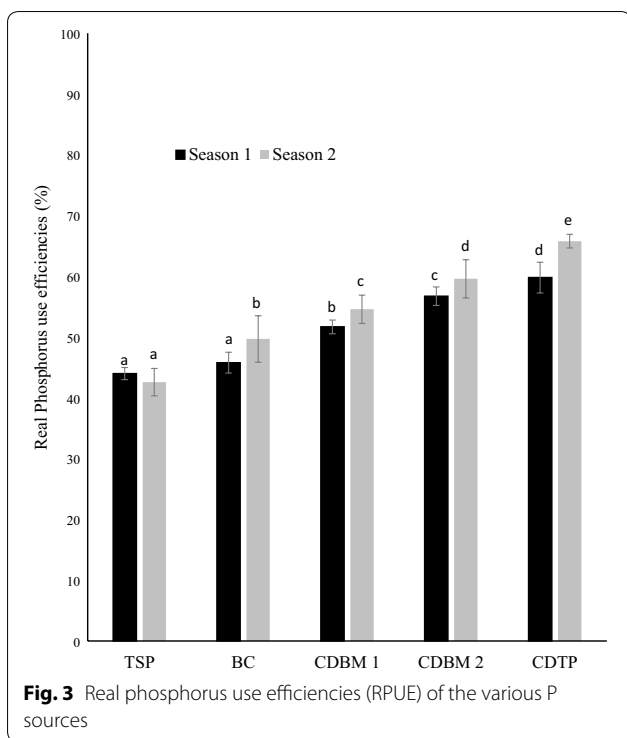
BC bone char, TSP triple superphosphate, CDBM 1 75% cow dung + 25% bone meal (3:1 mixture), CDBM 2 50% cow dung + 50% bone meal (1:1 mixture), CDTP 75% cow dung + 25% bone meal.

and the best performing BF amendment of CDTP-UHP was 71.94 g implying that the latter outperformed the former by a factor of more than two. Besides economic yield, BFs also produced the longest and heaviest roots of all the treatments. For example, while the TSP + Urea treatment produced 12.44 g and 13.50 cm of root weight and root length, respectively, the corresponding BF fertiliser amendment of CDTP-Urea produced 15.97 g and 19.00 cm of root weight and root length, respectively which translates to respective 10.32 and 40.74 percentage increments.

Apart from TSP treatment that registered a decreased RPUE in the second season, application of the remainder of the biochar amendments led to increased phosphorus use efficiencies by plants in the second season. In both seasons, the phosphorus use efficiency was higher in the CDTP amendment followed in the decreasing order by CDBM 2, CDBM1, BC and TSP as presented in Fig. 3. In the first growing season, the RPUE by lettuce stood at 59.8% of the phosphorus applied in the form of CDTP while the

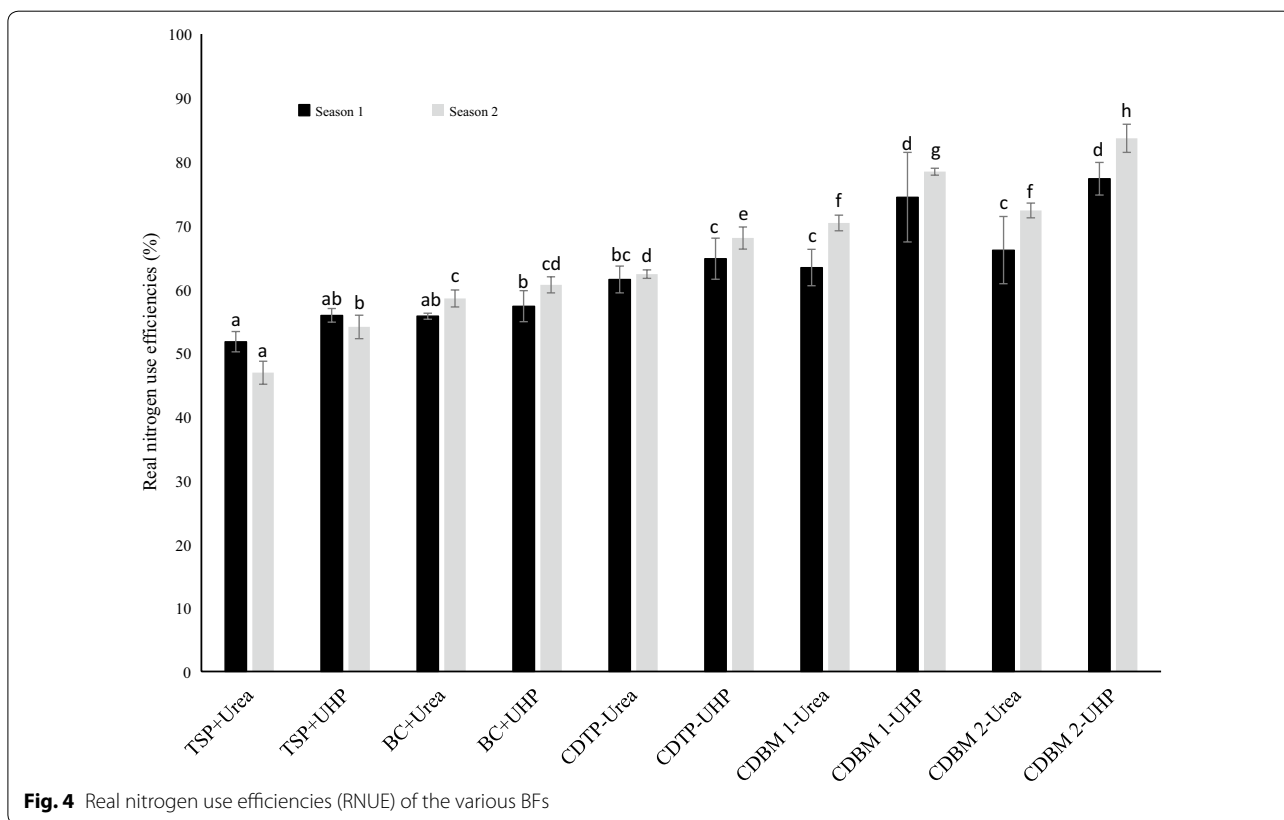
use efficiencies of CDBM 2, CDBM 1, BC and TSP stood at 56.73, 51.70, 45.80 and 44.00%, respectively. The largest improvement in RPUE in the second season came from CDTP which increased by 6 percentage points to 65.80%. This was followed by BC which registered a 3.9% percentage point increment to 49.70% whereas CDBM 2 and CDBM 1 amendments recorded respective percentage point increases of 2.87% and 2.90%. The RPUEs of TSP and BC were not significantly different in the first season even though the BC amendment posted a higher RPUE value.

In terms of nitrogen use efficiency, the lowest RNUE in both seasons came from the TSP + Urea amendment as shown in Fig. 4. The RNUE of TSP + Urea stood at 51.73% in the first season but decreased by 4.86 percentage points to 46.87% in the second lettuce growing season. Applying TSP together with UHP instead of urea (TSP + UHP) improved the RNUE to 55.86% in the first growing season and although it reduced by 1.80 percentage points to 54.06% in the second season, the value obtained in the second season was 7.19 percentage points



higher than that obtained with TSP + Urea. The RNUE achieved with TSP + UHP amendment was not significantly different from that obtained with BC + Urea in the first season but the latter produced an RNUE better than the former in the second season. Apart from the TSP + Urea and TSP + UHP amendments which elicited decrements in the RNUE in the second season, the remainder of the amendments/treatments produced increases in RNUE in the second season. The increments in RNUE in the second season were generally higher in the BM containing BFs than in their TSP containing counterparts. The largest augmentation came from CDBM 1-Urea with a 7.00 percentage point increase whilst CDBM 2-UHP, CDBM 2-Urea and CDBM 1-UHP produced 6.33, 6.23 and 4.00 percentage point increases, respectively of the RNUE in the second season.

As shown in Fig. 4 above, the UHP containing BFs generally recorded higher RNUE values than their urea containing counterparts. For example, CDTP-UHP amendment effected an RNUE of 64.76% in the first season against a value of 61.50% produced with CDTP-Urea and the trend was observed across all other amendments and the two experimental seasons. The highest RNUE values of 77.30% and 83.63% in the first and second seasons, respectively were achieved with CDBM 2-UHP



amendment. This was followed by CDBM 1-UHP which produced RNUE values amounting to 74.40 and 78.40% in the first and second seasons, respectively. The RNUEs were generally higher in the BM containing BFs than in the TSP containing BFs and the values increased with increasing concentrations of BM in the BFs.

Discussions

Slow releases of N and P from BBFs

Several former studies have illuminated biochar's high affinity for the different forms of N which concomitantly reduces their release. A case in point is a study by Cai et al. [25] which revealed that biochar derived from agricultural wastes exhibited high affinity for ammonium ions with the absorptivity increasing with decreasing pyrolysis temperatures. The adsorbed ammonium ions were strongly held by biochar to the extent that the desorbed fractions ranged from less than 10% to about 30% of the adsorbed quantities with biochars pyrolysed at higher temperatures desorbing more ammonium ions than those pyrolysed at low temperatures. They attributed their observations to the oxygen functional groups of COOH, C=O, COC present on the biochar surface which tightly hold ammonium ions through electrostatic interactions and hydrogen bonding.

Biochar's ability to adsorb nitrates has also been well documented by Prost et al. [26], Kammann et al. [27], Ventura et al. [28], Haider et al. [29] and others. In fact, a study by Haider et al. [30] indicated that the adsorbed nitrates are held tightly that the standard extraction methods underestimate them and that extractions must be repeated several times before all the captured nitrates can be released. That aforementioned affinity for the different forms of N observed in the above mentioned studies may explain the slow release behaviour of the urea soaked in the biochar of the present study because urea dissolution in water produces ammonium ions that might have been adsorbed through the mechanisms mentioned above. A Fourier transform infra-red spectrum of a UHP containing biochar fertiliser taken by Chen et al. [12] revealed existence of more C-O moieties than in pure biochar indicating that the hydrogen peroxide carried along with urea in the UHP complex oxidised the carbonised surfaces, thus enhancing the biochar's adsorption ability. This might offer an explanation for the better slow release of N obtained with CDBM-UHP as compared to the CDBM-Urea fertilisers. This is because charged ions such as ammonium and nitrate, formed at the disintegration of the UHP complex might have been subsequently absorbed by the superb adsorption sites caused by the peroxide.

Even though research into BFs is still in a fledgling state, the few available studies overwhelmingly substantiate the

slow release capabilities of the fertilisers with the level of efficiency of the slow release capacities heavily dependent on the preparation methods used. For example, Liu et al. [15] indicated that a fertiliser produced by mixing biochar and urea through grinding slowed N release by less than 10% in the first 28 days of the experiment while formulating the same mixture under a sealed reactor led to a slight increase in the slow release capacity of the resultant fertiliser. Additionally, halving the urea concentration while doubling the biochar content and adding bentonite to the mixture in the sealed reactor produced a fertiliser that released only 86.7% of N which accentuated an improvement in the slow release potential of the produced fertiliser. The study explicated that the most efficient slow release fertilisers were produced when polyvinyl alcohol was added to urea, bentonite and biochar in the sealed reactor with the amount of N released decreasing with increasing biochar, bentonite and polyvinyl alcohol concentrations and decreasing urea content in the mixture.

The results of the Liu et al. [15] experiment demonstrate therefore, that mere mixing of biochar with urea has little impact on slowing N release and that more means of improving urea absorptivity into biochar should be explored if the slow release potentials of the generated fertilisers are to be maximised. Basing on that line of thought, it's surprising that mere soaking of biochar in UHP solutions undertaken in the current study produced more efficient slow release N fertilisers than the hydrothermal decomposition route espoused by Liu et al. [15]. This is because the most effective slow release fertiliser of CDBM 2-UHP in the current study contained more urea (16.67%) than the most effective fertiliser formulated by Liu et al. [15] whose urea content amounted to only 7.4%, but the former cumulatively released only about 58.65% of the added N while the cumulative N released by the latter stood at 61.3% over the same 28-day experimental period.

It's worthy noting that the biochar based slow release fertilisers employed in almost all the former studies have included clay minerals especially bentonite – with a purpose of improving the slow release capacities of those fertilisers as was confirmed by An et al. [19]. Shi et al. [31] for example included both bentonite and sepiolite in their biochar-based urea fertiliser formulation and reported that the biochar based urea fertiliser leached only about 60% of the added N against 85% leached from the pure urea over a 30-day experimental period. Puga et al. [13] also prepended bentonite to their formulated BFs, albeit it didn't play any role in slowing down N release from the formulated fertilisers. The study indicated that BFs with BC/N ratios of between 5 and 10 solubilised an average of about 64% of the added N while those with BC/N

ratios ranging between 1 and 2 solubilised an average of 88% of N implying that it's only biochar to nitrogen ratios (BC/N) that influenced N release from the BFs. The results obtained in the present study were inferior to those Puga et al. [13] attained because the BC/Urea (UHP) ratios of 5 adopted in the present study translate to BC/N ratios of 13 but the average quantities of N solubilised from the urea and UHP containing BFs were about 87% and 64.4% of the added N, respectively. However, CDBM 1-UHP and CDBM 2-UHP solubilised 62.94% and 58.56% of added N, respectively which were less than the best average value of 64% obtained by Puga et al. [13].

In another relatedly similar study, Chen et al. [12] added kaolin to the biochar based urea hydrogen peroxide and found that N release from the formulated biochar-based UHP fertilisers decreased along increasing concentrations of kaolin in the fertilisers because high kaolin quantities resulted in a high density of the fertilizer granules produced leading to exceptional resistance to the migration of the nutrients from inside to the particle surface. However, although our study never included any clay in the formulation process of the BFs, the results obtained especially with UHP and biochar with large proportions of BM were satisfactory. The reduction in the amounts of N released along increasing concentrations of BM in the co-pyrolysed biochar used to formulate the BFs may be as a result of increase in surface area properties. As was observed in our recently concluded study (manuscript has just been accepted for publication) by Luyima et al. [32], large proportions of bone meal in the co-pyrolysed biomass led to production of porous biochar exemplified by the mat-like images obtained from the scanning electron microscopy (SEM). Both urea and UHP solutions might have been soaked up into those innumerable pores thus limiting their release into the solution.

The slow release nature of P observed in the co-pyrolysed biochars of the current study accorded well with the previous studies by Zhao et al. [16] and Lusta Filho et al. [5]. In a relatedly similar circumstance, Wang et al. [33] indicated that pyrolysing poultry litter slowed down P release in comparison to un-pyrolysed poultry litter because charring transformed labile P in raw biomass to phosphate minerals in biochar that were not extractable in water even though they were proton-releasable (H^+) in weak acids. The slow release of P from the co-pyrolysed materials observed could have been due to the binding of the soluble phosphorus contained in both TSP and BM by alkali and other phosphate binding metals like Ca, Mg, Fe, Al, etc. which build up as materials pyrolyse. Indeed, Lusta Filho et al. [5] through an XRD analysis confirmed formations of different P forms that were insoluble in water even after 10 days of extraction of the biochar

produced through co-pyrolysis of poultry litter with different phosphates.

Agronomic efficiency of the BFs

The better lettuce yields observed in BFs amendments than in pure mineral fertiliser amendments are in agreement with formerly concluded studies by Lusta Filho et al. [5], Chen et al. [12], Shi et al. [31], Liao et al. [34] and others. The improved agronomic efficiency observed with the application of BFs can be attributable to the slow release nature of the BFs because lessened rates of N release check on leaching and gaseous emissions of N while slow release of P prevents its fixation in the soil. The end result is that both N and P are released over an extended period of time along the entire life cycle of the plants and in quantities commensurate with the requirements of the growing plants which leaves no room for excesses in the soil. In their study, Liao et al. [34] found that the BFs improved nitrogen use efficiency and productivity of rape seed oil by increasing microbial activity which accelerated N cycling, concomitantly increasing N availability to crops. An early study by Li et al. [35] discovered that the potential of transformation of ammonium N to nitrate N as typified by the soil potential nitrification rates is affected by the abundance of the nitrifying micro-organisms in the soil. Subsequently Liao et al. [34] observed higher soil potential nitrification rates in the soils amended with the BFs than in those amended with urea indicating that BFs lead to the proliferation of nitrifying microbes which rapidly convert ammonium N to plant available nitrate N hence checking on gaseous loss of N resultantly improving N use efficiency.

The inferior performance of CDBM-Urea in comparison to the CDBM-UHP might have stemmed from the ability by the latter to sustain N supply over an extended period since Shen et al. [36] and Simonin et al. [37] indicated that the abundance of N oxidising microbes especially ammonia oxidising bacteria and nitrobacter (nitrite-oxidising bacteria) increases with N input. In fact, Liao et al. [34] reported elevated populations of ammonia oxidising bacteria in the soil amended with BFs as compared to other treatments. Besides N, Simonin et al. [37] reported that elevated C input levels increased the abundance of both ammonia oxidising bacteria and nitrobacter whereas Liao et al. [34] observed an increase in the abundance of ammonia oxidising bacteria. In the current study, we observed increases in soil organic carbon in the BFs amended pots, an observation that accorded with that of Liao et al. [34] and which might help to explain the higher RNUE and yields in these treatments than in the pots that were amended with the conventional mineral fertilisers.

Soil pH increased possibly owing to the residual basicity of most of the BFs used which might have created microsites in the soil where P adsorption was decreased as was explicated by Lusta Filho et al. [5]-which may also explain the improved RPUE observed. The roots produced with BFs amendments were denser and longer than those produced with pure P sources of TSP and BC possibly because the slow release of P led to its efficient utilisation by the growing plants. The dense and long roots thus facilitated improved access to nutrients by the growing lettuce which might have in turn contributed to the higher yields obtained with BFs than with the conventional fertilisers. The decreases in yield and RPUE observed in the second season can be attributable to the acidic nature of TSP which acidified the soil over time and hence, might have caused increases in P adsorbing metals such as iron, aluminium, etc. Confirming this notion is a study by Shen et al. [38] who observed a relatively strong negative linear relationship between decreases in soil pH and the above-ground yield of *Lotus pedunculatus cv barsille*. Another possible pathway through which BFs increased RPUE could have been through supporting the growth of arbuscular mycorrhizal fungi (AMF) as was adumbrated by Shen et al. [38]. Proliferation of AMF under biochar amended soils has been well documented by several previous studies and has been pointed out as one of the causes of the improved P availability observed in those treatments. AMF is particularly important for plant acquisition of P because phosphate ions have low mobility in the soil and often elude capture by plant roots as was delineated by Smith and Read [39]. However, further studies to confirm these mechanisms with BFs are needed due to the dearth of data in that regard, even though that was not the objective of the current study.

Conclusions

The results of this study indicate that efficient N slow-release fertilisers can be produced simply through capitalising on the biochar's great sorption power. Additionally, co-pyrolysis of animal manure biomass with BM improves the sorption capacity and boosts carbon retention of the resultant biochar along with supplanting the demand for the finite PR. Although CDBM 2 N fertilisers (CDBM 2-Urea and CDBM 2-UHP) were slightly more effective than CDBM 1 N fertilisers (CDBM 1-Urea and CDBM 1-UHP) in slowing-down N release, the CDBM 1 N fertilisers were agronomically more efficient than CDBM 2 N fertilisers and are thus recommended because they strike a good balance between N slow-release and agronomic efficiency. On the other hand, CDTP N fertilisers of CDTP-Urea and CDTP-UHP induced higher yields than any other amendment but their abysmally

low nutrient use efficiencies render them an environmental risk and unprofitable to farmers. The bottom line, therefore, is that co-pyrolysis of animal biochar with BM (especially in 3:1, respectively) and subsequent soaking in UHP solution create sustainable slow-release N and P fertilisers with elevated carbon retention capacities. However, the mechanisms underlying the observed attenuated rates of N release from the CDBM-Urea and CDBM-UHP fertilisers as well as their long term agronomic efficiency under field conditions require further explication in future studies.

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Authors' contributions

All authors contributed to the study conception and design. LD and JS collected data, conducted the laboratory and statistical analyses and wrote the manuscript, S-AW helped in data collection whenever we needed extra manpower while J-HL helped him with procuring the required materials and in some aspects of data collection and analysis. S-JP and T-KO supervised the experiment and offered technical guidance throughout the entire research period. All authors reviewed the written manuscript before submission to the journal for publication. All authors read and approved the final manuscript.

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Availability of data and materials

The data sets supporting the conclusions made are included in the article while a limited amount of BFs fertilisers can be provided to whoever may want to experiment with them upon request.

Competing interests

All authors declare that they have no competing interests.

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