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To link to this article DOI: <http://dx.doi.org/10.1016/j.jclepro.2024.144065>

Publisher: Elsevier

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Cocoa pod husk-derived organic soil amendments differentially affect soil fertility, nutrient leaching, and greenhouse gas emissions in cocoa soils

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ARTICLE INFO

Handling editor: Jeng Shiun Lim

Keywords:

Cocoa pod husks

Cocoa soils

Composting

Pyrolysis

Soil fertility decline

Soil greenhouse gas emissions

ABSTRACT

The depletion of soil nutrients and decline in yields on cocoa farms in west Africa over time force farmers to abandon their farms and look for new fertile land, thereby contributing to deforestation. Cocoa pod husks (CPH) are a major farm waste representing considerable export of nutrients from cocoa soils, particularly P and K. Here, the impacts of soil amendment with raw CPH residues, CPH compost, CPH biochar, or a CPH compost-biochar mixture on soil fertility, greenhouse gas (GHG) emissions, and nutrient losses via leaching were assessed in two laboratory experiments using two major soil types used for cocoa cultivation in Ghana (an acidic Ferralsol and an alkaline Nitisol). In Experiment 1, soil nutrient availability and CO₂ and N₂O emissions were quantified, whereas simulation and quantification of nutrient leaching were conducted in Experiment 2. Soil pH increased from 4.8 to 8.6 by 1.4- and 1.1-folds on average in amended Ferralsols and Nitisols, respectively. Soil electrical conductivity increased in soils amended with CPH compost and/or biochar. Addition of raw CPH caused remarkable microbial immobilisation of N and reduced N availability and leaching, whereas CPH compost and/or biochar addition increased soil nitrate availability but reduced soil ammonium availability. Leaching of Ca in Nitisols was reduced when CPH biochar was included in the soil amendment. While soil K availability increased in all amended soils, most notably when CPH biochar was included, soil P and Ca availabilities were greatest where CPH compost was included. Soil total GHG emission (CO₂ plus N₂O) increased in all amended Ferralsols and the Nitisols amended with CPH compost or raw CPH, with the latter remarkably increasing soil CO₂ emission by up to 14.8-folds. Compared to sole CPH compost amendment, CPH compost-biochar mixture amendment reduced soil total GHG emission and N and P leaching. These findings show that composted and/or pyrolysed CPH can be judiciously used to enhance soil fertility in cocoa farms, particularly in acidic soils. Pyrolysed CPH is especially beneficial for reducing soil nutrient leaching and GHG emissions and thus for increasing the sustainability of cocoa production in Ghana and west Africa.

1. Introduction

Long-term soil degradation due to nutrient depletion is a serious problem affecting the productivity of perennial crops. For instance, cocoa farms typically have a productive life span of between 20 and 30 years (sometimes longer) during which soils become depleted of key

nutrients (Snoeck et al., 2016), causing yield declines (Amponsah-Doku et al., 2022). In west Africa, specifically, this has forced cocoa farmers to look for new fertile land with high forest rent, resulting in a shifting cultivation pattern and migration into virgin forest areas. Cocoa cultivation alone has driven over 37% and 13% of forest loss since 2000 in Côte d'Ivoire and Ghana (Kalischek et al., 2023), the world's first and

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second largest cocoa producing countries (Kozicka et al., 2018), respectively. This shifting cultivation practice is clearly unsustainable. As such, strong calls by environmental advocates (Higonnet et al., 2017) has prompted governments and leading cocoa and chocolate companies to make collective commitments to end deforestation associated with cocoa cultivation (Carodenuto, 2019). Achieving this goal, which aligns with the United Nations Sustainable Development Goal 12 (Ensure sustainable consumption and production patterns) (UN, 2024) and the recently enacted European Union's deforestation-free supply chains regulation (with cocoa among seven target commodities) (EU, 2024), will require maintaining and increasing productivity on existing farms, without expansion to new land. To this end, inorganic fertilisers are promoted to replenish soil nutrients in cocoa farms (Ali et al., 2018). However, many smallholder cocoa farmers in west Africa use very little inorganic fertilisers due to high costs or lack of awareness of fertiliser options (Awunyo-Vitor et al., 2022), which threatens efforts to increase yields and sustain production on existing cocoa farms in the region. Therefore, access to low cost, locally available alternative sources of soil nutrients in west Africa stands to help increase and sustain productivity on existing cocoa farms.

Utilisation of farm waste such as cocoa pod husks (CPH) as organic soil amendments can replenish soil nutrients on cocoa farms or complement the use of inorganic fertilisers, representing a low cost and affordable approach to maintaining soil fertility and productivity on cocoa farms. For instance, CPH is particularly rich in P and K (Hougni et al., 2021) and accounts for 52–76% of dry pods or harvest biomass (Muñoz-Almagro et al., 2019). Thus, its utilisation as an organic soil amendment may increase both soil organic matter (SOM) content and soil nutrients. However, most cocoa farmers in west Africa discard the CPH at the sides of the farms after removing the beans and pulp, due to perceived risk that it spreads black pod disease (*Phytophthora* species) (Acebo-Guerrero et al., 2012), the challenge of spreading it on farms, or lack of awareness of its potential use as an organic soil amendment (Awunyo-Vitor et al., 2022).

Due to the high C:N ratio (>25) of raw CPH (e.g., Table 1), its application directly to soils is likely to promote microbial immobilisation of N in soil (Kumar and Goh, 2007) and reduce N availability to the crop. Composting CPH together with N rich feedstocks such as the leaves of leguminous trees or poultry manure may result in a product with a lower C:N ratio, so its application to soils could increase soil N availability to plants and return P and K mined from the soil by the cocoa

plant. An alternative to composting feedstocks is the production of biochar. Biochar can be generated by heating feedstock biomass (usually at 300–700 °C) under conditions of limited or no oxygen, a process called pyrolysis (Wang and Wang, 2019). Pyrolysis reduces N, H, and O contents of the feedstocks due to volatilisation thereby condensing C, which is chemically transformed to aromatic structures, resulting in a C rich char/biochar that is very resistant to decomposition (i.e., chemically recalcitrant) and has a high surface area which is electronegative (Almutairi et al., 2023). Other elements such as P, K, and Ca that remain stable under pyrolysis temperatures also become more concentrated in the mineral ash component of biochar (Zama et al., 2017). Thus, biochar application to soil can increase the total concentration of soil nutrients as well as mediate their availability by increasing soil pH (the 'liming effect') (Ngalani et al., 2023), while also increasing C stocks (Joseph et al., 2021). However, the high electronegative surface area of biochar makes it capable of adsorbing positively charged ions onto its surface, which can lead to physical retention in soil of some forms of nutrients such as ammonium (Zheng et al., 2013), making them unavailable for plant uptake. Nevertheless, this chemical immobilisation of nutrients via sorption onto biochar surfaces may only occur for a short term following biochar application and may lead to a delay in leaching of nutrients from soil (Clough et al., 2013). The leaching of nutrients is another nutrient loss pathway in cocoa soils in west Africa especially in young plantations due to limited root network and ground cover and the high rainfall in the tropical rainforest countries (Van Vliet and Giller, 2017). As such, biochar co-application with N fertilisers, such as N rich compost, could increase soil nutrient retention thereby reducing nutrient leaching.

When organic amendments are applied to soil, they can also affect greenhouse gas (GHG) emissions from soil, including CO₂, N₂O, and CH₄. However, biochar is considered a negative emissions technology (IPCC, 2022). Not only is biochar C recalcitrant, thereby increasing soil C storage, studies have also found that biochars reduce non-CO₂ GHG emissions from soil by 12–50% (Joseph et al., 2021). On the other hand, application to soil of organic amendments with high labile C content, such as raw plant residues, could increase soil CO₂ emission due to their rapid decomposition and the impacts of labile C inputs on SOM C priming (Mwafulirwa et al., 2019). Therefore, CPH based organic soil amendments such as raw CPH residues or compost and biochar made from CPH (sole applications or co-application) could increase total or available soil nutrients but could also differentially affect crop productivity and GHG emissions from soil. Soil amendment with compost and biochar made from CPH can also reduce the spread of black pod disease, due to suppression of *Phytophthora* during composting and pyrolysis temperatures (Doungous et al., 2018). Yet limited work has been conducted on compost and biochar made from CPH as organic soil amendments to improve productivity on cocoa farms.

The objectives of this study were to assess (i) the impacts of soil amendment with raw CPH residues, compost made from a combination of CPH, leaves of leguminous trees, and poultry manure (hereafter called CPH compost), biochar made from CPH (i.e., CPH biochar), and a mixture of CPH compost and CPH biochar (i.e., CPH compost-biochar mixture) on soil fertility (availability of key nutrients such as N, P, K, and Ca in soil, soil pH, soil electrical conductivity (EC), and soil microbial biomass) and soil CO₂ and N₂O emissions in two contrasting cocoa soils from Ghana, west Africa, (ii) the impacts of these CPH based organic soil amendments on microbial N immobilisation and leaching of N, P, K, and Ca in soil following their application with or without urea fertiliser, and (iii) the retention in soil of ¹⁵N-labelled urea N. Three hypotheses were tested: (i) that soil nutrient availability, GHG emissions, and nutrient leaching would increase with CPH compost application but decrease with CPH biochar application, (ii) that application of a CPH compost-biochar mixture would maintain soil nutrient availability but reduce GHG emissions and nutrient leaching, and (iii) that organic soil amendments would increase the retention in soil of ¹⁵N-labelled urea N.

Table 1
Properties of soils and cocoa pod husk (CPH)-derived organic soil amendments used in this study in Experiments 1 and 2 (n = 3).

Property	Soils		Organic amendments		
	Ferralsol	Nitisol	CPH residues	CPH compost	CPH biochar
Total C (%)	2.2 ± 0.1	1.2 ± 0.0	41.7 ± 0.3	28.2 ± 0.9	48.8 ± 8.7
Total N (%)	0.2 ± 0.0	0.1 ± 0.0	0.9 ± 0.0	1.8 ± 0.0	1.4 ± 0.1
C:N ratio	14.5 ± 0.2	13.0 ± 0.2	47.5 ± 0.1	15.7 ± 0.8	34.1 ± 3.4
pH	4.8 ± 0.0	8.6 ± 0.0	nd	9.8 ± 0.1	10.7 ± 0.0
EC (µS/cm)	18.5 ± 0.3	50.4 ± 0.6	nd	6.1 ± 0.4	13.0 ± 0.1
SOM (%)	6.4 ± 0.2	3.7 ± 0.1	na	na	na
P (mg/kg)	nd	nd	1208 ± 7	15510 ± 545	3741 ± 430
K (mg/kg)	nd	nd	34899 ± 454	34831 ± 1089	85849 ± 9145
Ca (mg/kg)	nd	nd	6245 ± 112	57469 ± 4432	16295 ± 4193

EC, electrical conductivity; SOM, soil organic matter; na, not applicable; nd, not determined.

2. Materials and methods

2.1. Overview of the experimental approach

This study was performed in two soil incubation experiments (Fig. 1) that were run independently but with identical treatments, which included two major types of cocoa soils that contrast in soil pH (an acidic Ferralsol and an alkaline Nitisol), four types of CPH-derived organic soil amendments (raw CPH, CPH compost, CPH biochar, and CPH compost-biochar mixture) plus a control treatment without organic soil amendment, and with or without ^{15}N -labelled (10 atom% ^{15}N) urea fertiliser application (Table S1). Experiment 1 was used for measurement of soil fertility parameters and surface soil CO_2 and N_2O emissions, whereas Experiment 2 was used for measurement of soil nutrient leaching, as will be described in detail in the subsequent sections.

2.2. Soil collection

The acidic Ferralsol and alkaline Nitisol used for this study were collected in Ghana from mature cocoa farms of the age 10–15 years old. The Ferralsol was collected from a farm at Sendu in the Elembele district of the Western Region, located within a Wet Evergreen (WE) cocoa agroecological zone, whereas the Nitisol was collected from a farm at Acherensua in the Ahafo Ano District of the Ahafo Region, located within the Moist Semi-Deciduous North West (MSNW) ecotype (Fig. S1). Both locations are characterised as having distinct wet and dry seasons, the latter typically extending from December to February/March. For each soil type, approximately five sub-samples were taken at random across the farm (0–10 cm soil depth), mixed into a composite sample, then sieved through a 4-mm mesh onsite. Soil sampling and initial processing were conducted by the Soil Science Division of the Cocoa Research Institute of Ghana, New Tafo-Akim, Ghana. The sieved soils were then packed securely and transported to the University of Reading, UK, where they were characterised for chemical properties (Table 1) before use in experiments.

2.3. Production of organic amendments

The organic amendments used in this study were produced at the Department of Horticulture of the Kwame Nkrumah University of Science and Technology, Kumasi, Ghana, from CPH feedstock collected from a cocoa farm. For CPH compost production (Video S1), macerated CPH, poultry manure, and *Gliricidia sepium* leaves of chopped size c. 2–5 cm were made into a heap of about 1.5 m^3 with a 12-L plastic container, in layers in a ratio of 5:1:1 respectively. Water was sprinkled on the surface of each layer until the heap was formed and made damp but not soggy. The heap was covered with black polythene sheets. Three 2.5 m hollow side-sliced bamboo sticks with the septa broken through, creating a continuous cavity through the stem, were then inserted from the open top of the heap to reach the base. The cut ends of the bamboo sticks to be inserted into the heap were slanted to avoid the end sitting flat on the base of the heap. These bamboo sticks served as vents, reducing the need for frequent turning. The heap remained covered until the 5th day when the compost moved from the mesophilic phase to the thermophilic phase, at which point the heap was uncovered for turning. Turning was done every 5 days until the temperature dropped (from c. 50°C to c. 39°C), after which it was done fortnightly when the compost entered the cooling phase. The entire process lasted 12 weeks. For CPH biochar production, the barrel-in-barrel method was used. For this, dried CPH feedstock of about 8% moisture content was loaded into an inner steel container (diameter 43 cm, height 78 cm), lowered into an empty oil drum also made of steel (diameter 60 cm, height 97 cm), and covered with a lid with a chimney (height 74 cm, opening width 20 cm). Fuel wood was packed around the outside of the inner steel container with ‘starter material’ that were burned, heating the feedstock until the fire subsided and then the resulting biochar was quenched with water (Rodríguez-Vila et al., 2022). Dried raw CPH residues (uncomposted and unpyrolysed) were also included as an organic amendment. Sub-samples of these organic amendments (raw CPH, CPH compost, and CPH biochar) were transported to the University of Reading, UK, where they were crushed with a pestle and mortar and characterised for chemical properties (Table 1) before experimental setup.

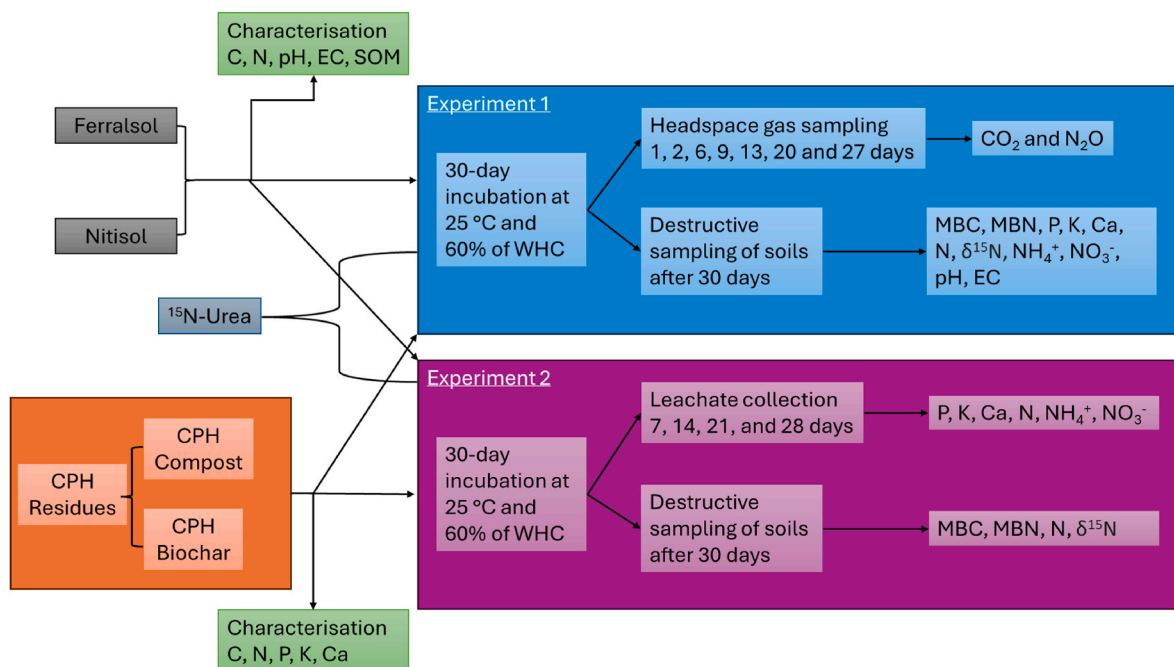


Fig. 1. Block diagram illustrating the input variables (left), incubation conditions and sampling timelines (centre), output data (right), and the relationships of these components between the two experiments. Experiment 1 was used for measurement of surface soil CO_2 and N_2O emissions at set time points, with the first headspace gas sampling at 1 d corresponding to 6 h after the start of soil incubation. Experiment 2 was used for weekly measurement of soil nutrient leaching. CPH, cocoa pod husks; EC, electrical conductivity; SOM, soil organic matter; WHC, water holding capacity; MBC, microbial biomass C; MBN, microbial biomass N.

2.4. Soil incubation

For soil incubation in both experiments, the rates of organic soil amendment, expressed as weight per 100 g soil (Table 2), equivalent to field application rates of 10 and 5 tonnes ha⁻¹ for CPH compost and CPH biochar respectively, were used. The amendment rate of CPH compost was also adopted for raw CPH residues. In Experiment 1, each experimental unit consisted of a wide neck, open glass container of 50 cm³. For Experiment 2, each experimental unit consisted of a microcosm made of a PVC column of approximately 40 cm², fixed with a mesh to the bottom to contain soil while allowing water drainage. For each experimental unit, 100 g dry soil equivalent of the 4-mm sieved soil was thoroughly mixed with or without the CPH-derived organic amendments and packed to a bulk density of 1.3 g cm⁻³ to reflect field bulk density at the soil collection sites. The ¹⁵N-labelled urea was applied as a solution spread across the soil surface at the start of each experiment, at a rate equivalent to 20 kg N ha⁻¹. Packed experimental units were incubated at 25 °C for an experimental duration of 30 days. Each experiment was laid out in a randomised complete block design with four replications (Table S2). Soil water content was maintained at 60% of the water holding capacity with gravimetric addition of deionised water across the soil surface every 2 days, with longer intervals following each leaching event in Experiment 2.

2.4.1. Experiment 1: measurement of GHG emissions and soil fertility parameters

In Experiment 1, total surface soil CO₂ and N₂O effluxes were measured over the entire incubation period, after 6 h and then 2, 6, 9, 13, 20, and 27 days. Shorter sampling intervals were used during the first 13 days considering that studies have shown that GHG emissions from soil following the application of organic amendments are greatest during the first two weeks (e.g., Mwafulirwa et al., 2019). To sample the soil CO₂ and N₂O effluxes, microcosms were placed in glass jars (193 mL headspace) that were sealed air-tight for 1 h. Thereafter, 10 mL air was sampled from the headspace at the start and the end of the jar closure period using a gas syringe and hypodermic needle connected via rubber septa. The air samples were transferred into 12 mL pre-evacuated Labco Exetainer® glass vials for analysis of CO₂-C and N₂O-N concentration values with gas chromatography (Agilent 7890B) (Adekanmbi et al., 2023). Calculation of soil total CO₂-C and N₂O-N efflux rates of each treatment per sampling point was achieved using the CO₂-C and N₂O-N concentration values. These rates were used to calculate cumulative CO₂-C and N₂O-N emissions over the duration of the experiment. Furthermore, cumulative soil total GHG emissions (CO₂ plus N₂O, expressed as CO₂ equivalents) were calculated. The CO₂ equivalents of N₂O were calculated by multiplying the amount of N₂O by its global warming potential (i.e., 298 kg CO₂ equivalent kg⁻¹ N₂O) (IPCC, 2007). The soil in each microcosm was destructively sampled after 30 days of incubation for analysis of soil microbial biomass C (MBC) and N (MBN), soil P, K, Ca, ammonium and nitrate availability, soil pH, soil EC, total soil N concentration, and the δ¹⁵N signature of the soil.

2.4.2. Experiment 2: measurement of nutrient leaching, soil MBC, soil MBN, soil total N, and δ¹⁵N signature of the soil

In Experiment 2, soil leaching was applied to the microcosms at weekly intervals for four weeks. For this, the soil in each microcosm was irrigated with deionised water (100 mL each time), ensuring a slow flow rate and even distribution of water across the soil surface to minimise soil disturbance. Leachates were collected during each leaching event in containers placed below the microcosms. Leachate samples were analysed for P, K, Ca, ammonium, nitrate, and total leached (i.e., dissolved) N concentrations. The soil in each microcosm was destructively sampled after 30 days, following the final leaching event, and analysed for soil MBC, soil MBN, and the total N concentration and δ¹⁵N signature of the soil.

2.5. Analytical methods for soil and organic amendments

SOM content was determined by mass lost after oven-dry samples were combusted in a muffle furnace at 450 °C for 24 h. Approximately 10 g of air-dried 4 mm sieved soil was weighed into a pre-weighed crucible, dried in the oven at 105 °C for 24 h, re-weighed, and then combusted in a muffle furnace at 450 °C for 24 h before the final weight was taken. The SOM content was calculated as the difference between the oven-dry soil and the combusted soil. Soil water holding capacity was determined by completely saturating approximately 50 g of 4 mm sieved soils in water overnight and then draining gravimetrically for 24 h. A representative sub-sample of the drained soil was weighed into a pre-weighed crucible and then mass lost was quantified after drying in an oven at 105 °C for 24 h. The water holding capacity was expressed as the mass of moisture, divided by the mass of the oven-dried soil (multiplying by 100 to convert this into a percentage). The pH and EC of the organic amendments and soil samples were measured using Jenway pH and EC electrodes in the slurry after shaking 10 g of air-dried 4 mm sieved soil with 25 mL of deionised water for 15 min in a 50 mL centrifuge tube placed in an end-over-end shaker at 30 revolutions per minute.

Soil N (ammonium and nitrate) availability was determined colourimetrically using a Skalar SAN++ Continuous Flow Analyser following extraction of the fresh mass equivalent to 10 g of air-dried 4 mm sieved soil with 50 mL of 1 M KCl solution in a 125 mL polypropylene bottle. Samples were shaken for 30 min on an orbital shaker and then filtered through a Whatman No. 2 filter paper. Nitrate was reduced to nitrite by hydrazinium sulphate and the nitrite (originally present plus reduced nitrate) was determined by diazotising with sulphanilamide and coupling with N-(1-naphthyl)ethylenediamine dihydrochloride to form a highly coloured azo dye which was quantified as absorbance at 540 nm. Ammonium was measured based on the Berthelot reaction. After dialysis against the buffer solution of pH 5.2, the ammonia in the sample was chlorinated to monochloramine, which reacts with salicylate to form 5-aminosalicylate. After oxidation and oxidative coupling, a green coloured complex was formed and quantified as absorbance at 660 nm. Data was expressed as mg per kg of oven-dried soil, after correcting for the moisture content of the soil.

Table 2

Application rates of cocoa pod husk (CPH)-derived organic amendments to soil and their equivalent rates of C, N, P, K, and Ca in Experiments 1 and 2.

Organic soil amendment	Organic amendment application rate (g per 100 g soil)	Equivalent rate for organic amendment C (mg per 100 g soil)	Equivalent rate for organic amendment N (mg per 100 g soil)	Equivalent rate for organic amendment P (mg per 100 g soil)	Equivalent rate for organic amendment K (mg per 100 g soil)	Equivalent rate for organic amendment Ca (mg per 100 g soil)
Raw CPH residues	3.9	1603.9	33.9	4.7	134.4	24.0
CPH compost	3.9	1083.8	69.3	59.7	134.1	221.3
CPH biochar	1.9	936.6	27.3	7.2	164.8	31.3
CPH compost-biochar mix ^a	2.9	1010.2	48.3	33.5	149.5	126.3

^a Compost-biochar mix was derived by mixing half rates of CPH compost and CPH biochar.

To determine soil MBC and MBN, chloroform fumigation-extraction was used according to Vance et al. (1987) and Brookes et al. (1985), respectively. Quantities of fresh 4 mm sieved soil samples equivalent to 12.5 g dry soil were weighed into glass beakers with two beakers per sample. One sample was fumigated in a desiccator under vacuum along approximately 50 mL of ethanol-free chloroform and some anti-bumping granules in darkness for 24 h. The second beaker was treated similarly but remained un-fumigated. Both soil samples were then extracted with 50 mL of 0.5 M K_2SO_4 solution by shaking for 30 min in an orbital shaker and then filtered using a Whatman No. 42 filter paper. The extracts were analysed for total organic C (TOC) on a TOC Analyser (Shimadzu TOC-L) as CO_2 after combustion and oxidation at 680 °C. The extracts were also analysed for total dissolved N colour-metrically (absorbance at 540 nm, based on the hydrazine reduction method described above) on a Skalar SAN++ Continuous Flow Analyser after microwave digestion of 7.5 mL of the extract (0.5 M K_2SO_4) and 7.5 mL of 0.18 M potassium persulfate ($K_2S_2O_8$) at 160 °C for 40 min in a MARS 6 microwave digestion system. MBC and MBN were calculated as the difference between TOC and total dissolved N values of the paired fumigated and non-fumigated extracts using conversion factors k_{EC} of 0.45 (Vance et al., 1987) and k_{EN} of 0.54 (Brookes et al., 1985), respectively.

Ball-milled oven-dried organic amendments and soil samples were analysed for total N concentration by dry combustion of the sample using Flash Dynamic Combustion and quantification using a thermal conductivity detector on an Elemental Analyser (Thermo Flash 2000 EA). Ball-milled oven-dried soil samples at the end of each experiment were also analysed after Flash Dynamic Combustion for $\delta^{15}N$ signature on an Isotope Ratio Mass Spectrometer (Thermo Fisher Scientific, Delta V). The $\delta^{15}N$ values of the soil samples were used to separate the total soil N into two component fractions of urea-derived N (because urea was ^{15}N labelled) and native SOM plus organic amendment N, using a model analogous to the two-source-partitioning equation described by Mwafurirwa et al. (2017) (terms replaced accordingly). Urea-derived N (retained in soil) was expressed as a proportion (%) of the amount of urea N applied at the start of each experiment.

Total concentrations of P, K, and Ca of organic amendments and soils were determined by ICP-OES (PerkinElmer Optima 7300) based on methods described by Rodríguez-Vila et al. (2022). For this, 0.5 g of milled soils or organic amendments were weighed into MARSXpress digestion tubes. This was followed by the addition of 9 mL of nitric acid and 3 mL of hydrochloric acid to soils and digestion with a MARS 6 microwave digestion system at 175 °C following USEPA method 3051, or the addition of 2 mL of ultra-pure water and 8 mL of nitric acid to organic amendments and digestion at 200 °C. After digestion, samples were filtered through Whatman No. 540 filter papers and diluted prior to ICP-OES analysis for P, K, and Ca after calibration with matrix-matched standards.

Leachate samples were filtered and acidified with 5% nitric acid prior to ICP-OES analysis, as described above. Leachate samples were also analysed colourmetrically for ammonium and nitrate on a Skalar SAN++ Continuous Flow Analyser using the methods described above. Total leached (dissolved) N concentration was measured on the Skalar SAN++ Continuous Flow Analyser as nitrate after microwave digestion of 7.5 mL of sample and 7.5 mL of 0.18 M potassium persulfate ($K_2S_2O_8$) at 160 °C for 40 min in a MARS 6 microwave digestion system. The weekly concentrations of elements in leachate samples were used to calculate the cumulative amounts leached over the experiment duration.

2.6. Statistical analyses

Three-way ANOVA was used to test the effects of soil type, organic amendment, and urea application on soil fertility parameters, cumulative soil CO_2 -C and N_2O -N emissions, and cumulative amounts of nutrients leached from soil. For treatments with urea application, two-way ANOVA was used to test the effects of soil type and organic amendment

on urea N retention in soil. Data were checked for significant outlier values, normality, and homogeneity and/or sphericity of variance before conducting ANOVA. Where statistically significant ($P < 0.05$) effects were found among the organic amendments, Tukey's range test was used to assess differences between individual means. Furthermore, path analysis using the structural equation modelling method was conducted to elucidate the direct and indirect effects of key explanatory variables (selected from the measured parameters according to existing knowledge) on cumulative soil CO_2 -C and N_2O -N emissions and urea N retention in soil as response variables. All statistical analyses were conducted in R-4.2.2 (R Core Team, 2022).

3. Results

While the intention is to interpret both experiments together, the results of soil chemical fertility and GHG emissions in Experiment 1 are presented first, followed by the results of nutrient losses, microbial biomass, and urea retention in soil after leaching in Experiment 2. The results section then concludes with the results of path analysis generated with data from both experiments.

3.1. Soil fertility properties and urea N retention in soil at the end of Experiment 1

In Experiment 1 in both the Ferralsols (initial pH 4.8) and the Nitisols (initial pH 8.6), all organic soil amendments (raw CPH, CPH compost, CPH biochar, or a CPH compost-biochar mixture) significantly ($P < 0.05$) increased soil pH (Fig. 2a). Whereas soil pH was increased to 6.4–6.6 in the amended Ferralsols, amended Nitisols were in the pH range of 8.9–9.6. In amended Ferralsols the increases in soil pH were accompanied by significant ($P < 0.05$) reductions in soil ammonium availability, which was greatest in the raw CPH treatment. Soil ammonium availability was low in all Nitisols (Fig. 2b). However, soil nitrate availability was significantly ($P < 0.05$) increased by the addition of CPH compost, CPH biochar, or their mixture in the Ferralsols. The addition of raw CPH significantly ($P < 0.05$) reduced soil nitrate availability in both soil types (Fig. 2c). In soils amended with raw CPH, the reductions in soil available N coincided with marked increases in soil MBN (Fig. 2d) and MBC (Fig. 2e). CPH compost also significantly ($P < 0.05$) increased soil MBN and MBC (Fig. 2). Significant ($P < 0.05$) increases in soil EC were observed in both soil types amended with CPH compost, CPH biochar, or their mixture, but not in soils amended with raw CPH (Fig. 2f). These results indicate the differential effects of the organic amendments on the availability of nutrients in soil. Indeed, total soil K concentration significantly ($P < 0.05$) increased in all amended soils (the highest increase was in soils amended with CPH biochar) (Fig. 3a), whereas total soil P and Ca concentrations were significantly ($P < 0.05$) increased by only the addition of CPH compost or CPH compost-biochar mixture (Fig. 3b and c).

When comparing soil types, total soil K, P, and Ca concentrations at the end of the experiment were overall significantly ($P < 0.05$) higher in the Nitisols than in the Ferralsols (Fig. 3a–c). Overall, urea application significantly ($P < 0.05$) reduced soil pH but increased soil ammonium (especially in the Ferralsols) and nitrate availabilities, soil EC, and soil MBC (especially after the addition of raw CPH) and MBN (Fig. S2). Urea-derived N retained (i.e., recovered) in soil at the end of Experiment 1 did not significantly vary with organic soil amendments (Table 3; data not shown), but was overall higher in the Ferralsols (51.5%) than in the Nitisols (40.7%).

3.2. Soil GHG emissions in Experiment 1

Cumulative soil CO_2 -C emission was significantly ($P < 0.05$) increased by all organic soil amendments in the Ferralsols, whereas in the Nitisols it was significantly ($P < 0.05$) increased by the addition of raw CPH or CPH compost but not CPH biochar or CPH compost-biochar

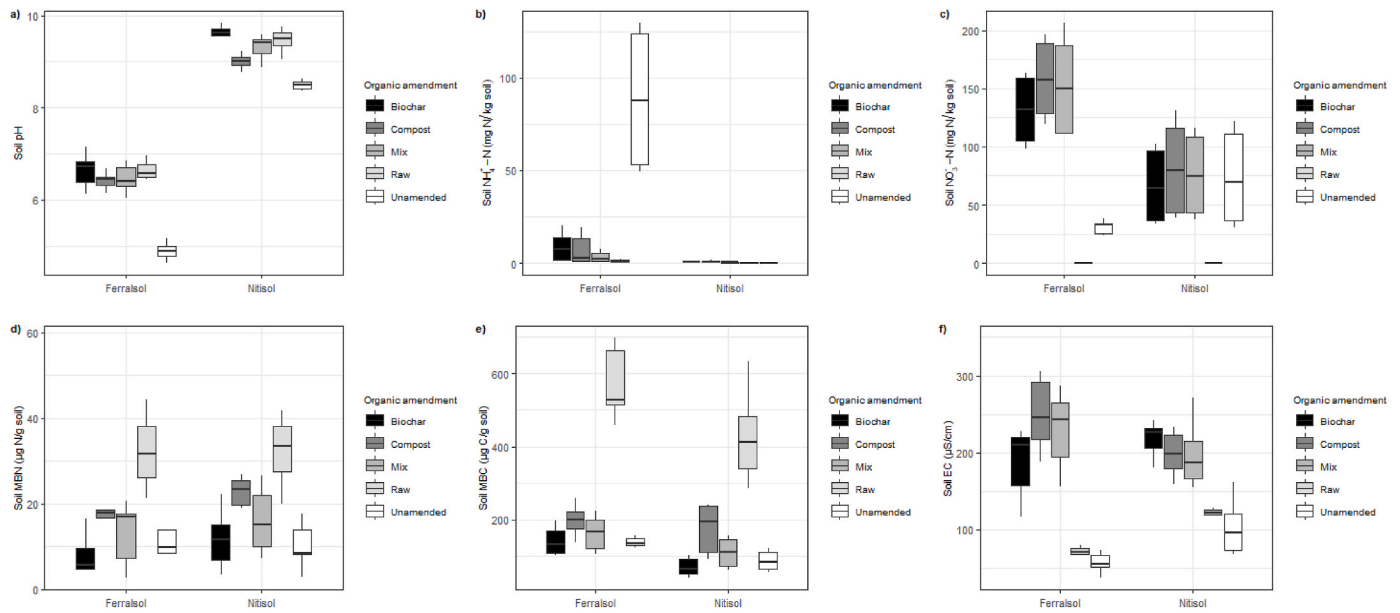


Fig. 2. Effects of cocoa pod husk (CPH)-derived organic soil amendments and soil type on soil pH (a), soil ammonium (b) and nitrate (c) concentrations, soil microbial biomass N (MBN) size (d), soil microbial biomass C (MBC) size (e), and soil electrical conductivity (EC) (f) measured at 30 d in Experiment 1. Mix and Raw represent CPH compost-biochar mixture and raw CPH residues, respectively.

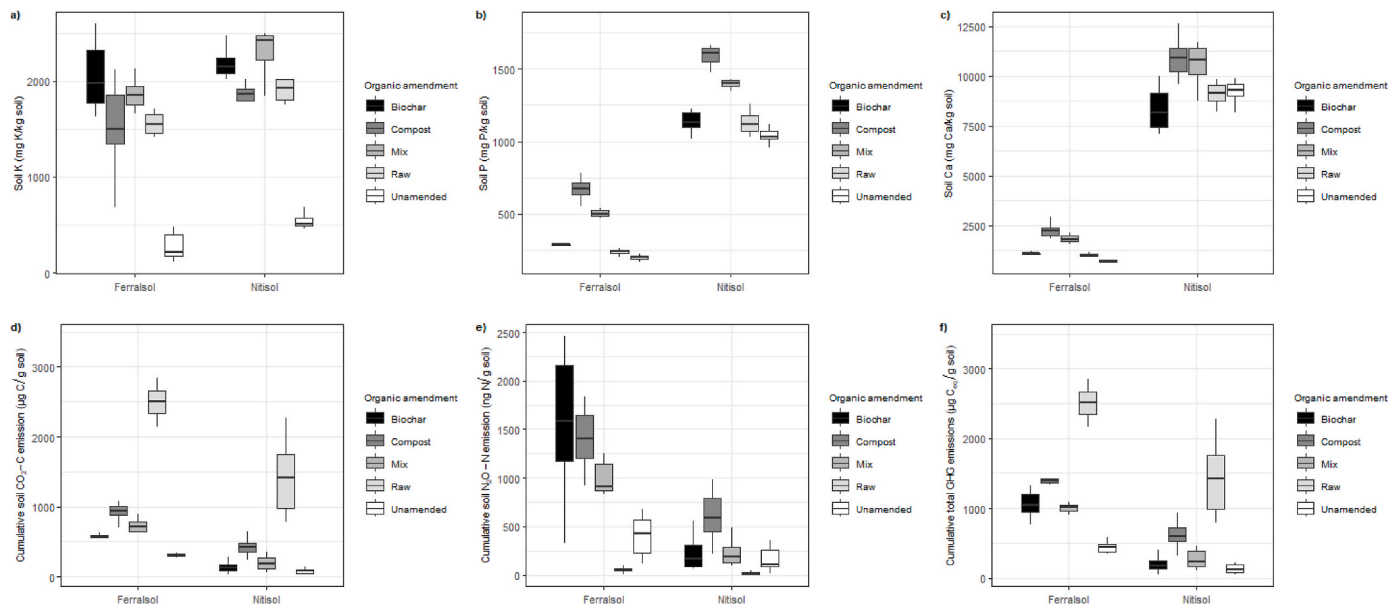


Fig. 3. Effects of cocoa pod husk (CPH)-derived organic soil amendments and soil type on soil K, P, and Ca concentrations (a–c) and cumulative soil CO₂-C (d), N₂O-N (e), and total gaseous (CO₂-C plus N₂O-N) (f) emissions measured in Experiment 1. Total gaseous emissions are presented as CO₂ equivalents (C eq) based on their greenhouse gas warming potential. Mix and Raw represent CPH compost-biochar mixture and raw CPH residues, respectively.

mixture (Fig. 3d). Cumulative soil N₂O-N emission was also not significantly affected by the addition of CPH biochar or CPH compost-biochar mixture in the Nitisols but was significantly ($P < 0.05$) increased by the addition of CPH compost, CPH biochar, or their mixture in the Ferralsols (Fig. 3e). In both soil types, although raw CPH amendment remarkably increased cumulative soil CO₂-C emission (Fig. 3d), it reduced cumulative soil N₂O-N emission (Fig. 3e). The application of CPH compost-biochar mixture resulted in significantly ($P < 0.05$) lower soil GHG emissions (CO₂-C and N₂O-N) than the application of CPH compost alone (Fig. 3d–f).

Both cumulative soil CO₂-C and N₂O-N emissions were overall higher in the Ferralsols (1023 µg C/g soil and 884 ng N/g soil, respectively)

than in the Nitisols (454 µg C/g soil and 254 ng N/g soil, respectively). Emissions were also overall higher from soils with urea application than those without urea application (Figs. S3a and b). Due to the lower soil N₂O emissions compared with the soil CO₂ emissions, the pattern of cumulative soil total GHG emissions (CO₂-C plus N₂O-N, expressed as CO₂ equivalents) between treatments (Fig. 3f) mirrored those of cumulative soil CO₂ emissions. The rates of soil CO₂-C and N₂O-N emissions recorded at different time points over the study duration are provided in Supplementary data S1.

Table 3Variance analysis (*P*-values) of the parameters measured at the end of Experiments 1 and 2.

Expt	Measured parameter	Effects of treatments and their interactions						
		Soil	Urea application	Organic soil amendment	Soil × Urea application	Soil × Organic amendment	Urea application × Organic amendment ^a	Soil × Urea application × Organic amendment ^a
	df	1	1	4	1	4	4	4
1	Soil pH	<.0001	<.0001	<.0001	0.8268	<.0001	.0148	.0447
	Soil NH ₄ ⁺ (mg/kg soil)	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
	Soil NO ₃ ⁻ (mg/kg soil)	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001	<.0001
	Soil EC (μS/cm)	0.2818	<.0001	<.0001	0.1318	<.0001	.0024	.0430
	Soil K (mg/kg soil)	<.0001	0.1139	<.0001	.0134	0.4234	0.2178	0.6037
	Soil P (mg/kg soil)	<.0001	0.8430	<.0001	0.3765	0.3994	0.2455	0.6350
	Soil Ca (mg/kg soil)	<.0001	0.4043	<.0001	0.6633	0.1068	0.8719	0.8794
	Soil MBC (μg/g soil)	<.0001	.0142	<.0001	0.6850	.0356	.0049	0.9623
	Soil MBN (μg/g soil)	0.2419	.0060	<.0001	0.8585	0.5326	0.0883	0.5926
	Cumulative soil CO ₂ -C efflux (μg C/g soil)	<.0001	.0288	<.0001	0.1893	<.0001	.0314	0.9304
	Cumulative soil N ₂ O-N efflux (ng N/g soil)	<.0001	<.0001	<.0001	0.2781	<.0001	.0006	.0232
	Cumulative soil total gaseous emissions (μg C eq/g soil)	<.0001	.0006	<.0001	0.3766	.0001	0.1135	0.5968
	Urea N retained in soil (%)	.0007		0.0588		0.2926		
	Cumulative leached NH ₄ ⁺ (mg/kg soil)	<.0001	<.0001	<.0001	.0043	<.0001	<.0001	.0063
2	Cumulative leached NO ₃ ⁻ (mg/kg soil)	<.0001	0.9965	<.0001	0.8854	<.0001	0.9997	0.7071
	Cumulative leached total dissolved N (mg/kg soil)	<.0001	<.0001	<.0001	0.0772	<.0001	.0002	.0023
	Cumulative leached P (mg/kg soil)	<.0001	0.7642	<.0001	0.6579	<.0001	0.6519	0.9920
	Cumulative leached K (mg/kg soil)	<.0001	0.7768	<.0001	0.6301	<.0001	0.1640	0.9723
	Cumulative leached Ca (mg/kg soil)	<.0001	0.2544	<.0001	0.9028	<.0001	0.8704	0.6228
	Soil MBC (μg/g soil)	<.0001	.0006	<.0001	.0092	<.0001	<.0001	.0012
	Soil MBN (μg/g soil)	.0012	.0070	<.0001	0.4342	.0048	.0009	0.7733
	Urea N retained in soil (%)	<.0001		<.0001		.0067		

Significant *P*-values (*P* < 0.05) are shown in bold. df, degrees of freedom. C eq; CO₂ equivalents; EC, electrical conductivity; MBC, microbial biomass C; MBN, microbial biomass N.

^a Data for the significant effects of the two-way interaction of urea application × organic amendment and three-way interaction of soil type × urea application × organic amendment are presented in detail in [Supplementary Figs. S2–S5](#).

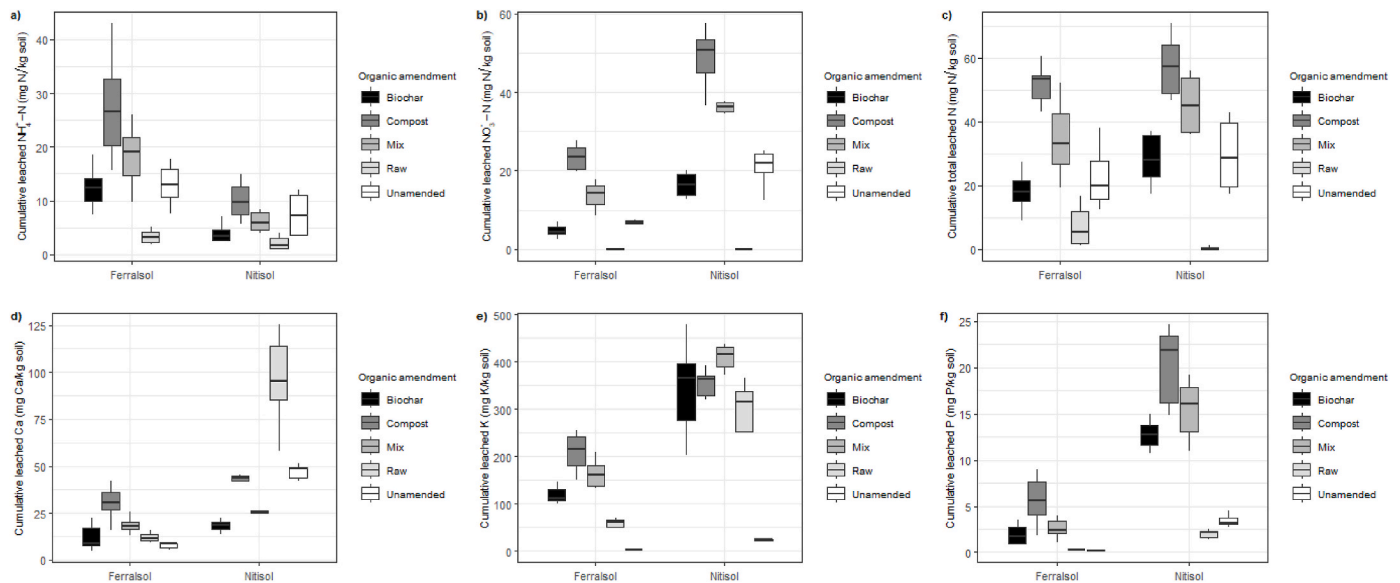


Fig. 4. Effects of cocoa pod husk (CPH)-derived organic soil amendments and soil type on cumulative leachate ammonium (a), nitrate (b), total (dissolved) N (c), Ca (d), K (e), and P (f) measured in Experiment 2. Mix and Raw represent CPH compost-biochar mixture and raw CPH residues, respectively.

3.3. Nutrient leaching from soil in Experiment 2

Soil amendment with raw CPH significantly ($P < 0.05$) reduced cumulative leached ammonium and nitrate and total leached N in both soil types (Fig. 4a–c). However, soil amendment with CPH compost or CPH compost-biochar mixture significantly ($P < 0.05$) increased cumulative leached nitrate and total leached N in both soil types and cumulative leached ammonium in the Ferralsols (Fig. 4a–c). Amendment with CPH biochar did not significantly affect N leaching in either soil type. Soil amendment with CPH biochar or CPH compost-biochar mixture also caused significant ($P < 0.05$) reductions in cumulative leached Ca in the Nitisols (Fig. 4d). Cumulative leached Ca was not significantly affected by soil amendment with CPH biochar in the Ferralsols and CPH compost in the Nitisols, but was significantly ($P < 0.05$) increased by soil amendment with raw CPH, CPH compost, or CPH compost-biochar mixture in the Ferralsols and raw CPH in the Nitisols (Fig. 4d). All organic amendments significantly ($P < 0.05$) increased cumulative leached K in both soil types (Fig. 4e). Amendment-induced cumulative leached P was observed in both soil types after the addition of CPH compost, CPH biochar, or their mixture (Fig. 4f). Soil amendment with raw CPH significantly ($P < 0.05$) reduced cumulative leached P in the Nitisols, but did not significantly affect cumulative leached P in the Ferralsols (Fig. 4f). Application of a CPH compost-biochar mixture significantly ($P < 0.05$) reduced soil N, P, and Ca leaching relative to application of sole CPH compost (Fig. 4). Urea application did not significantly affect cumulative leached nitrate (Table 3), but overall it significantly ($P < 0.05$) increased cumulative leached ammonium and total leached N as expected (Fig. S4). The data of nutrient leaching at different time points over the study period are provided in Supplementary data S2.

3.4. Soil MBN and MBC and urea N retention in soil after leaching in Experiment 2

In Experiment 2, after soil leaching, the patterns of soil MBC and MBN between treatments (Fig. S5) were generally similar to those observed in Experiment 1. In treatments with urea application in Experiment 2, urea-derived N retained in the Nitisols was significantly ($P < 0.05$) and remarkably increased by soil amendment with raw CPH (Fig. 5). Soil amendment with raw CPH or CPH compost did not significantly affect urea N retention in the Ferralsols and Nitisols, respectively, whereas urea N retention was significantly ($P < 0.05$) reduced by soil amendment with CPH compost, CPH biochar, or CPH compost-biochar mixture in the Ferralsols and CPH biochar or CPH compost-biochar mixture in the Nitisols (Fig. 5).

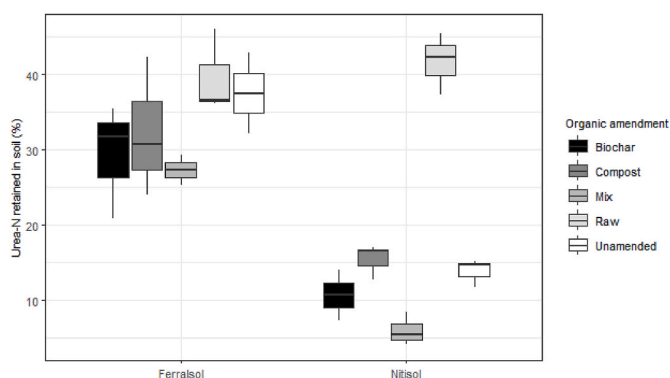


Fig. 5. Effects of cocoa pod husk (CPH)-derived organic soil amendments and soil type on urea N retention in soil after leaching in Experiment 2. Mix and Raw represent CPH compost-biochar mixture and raw CPH residues, respectively.

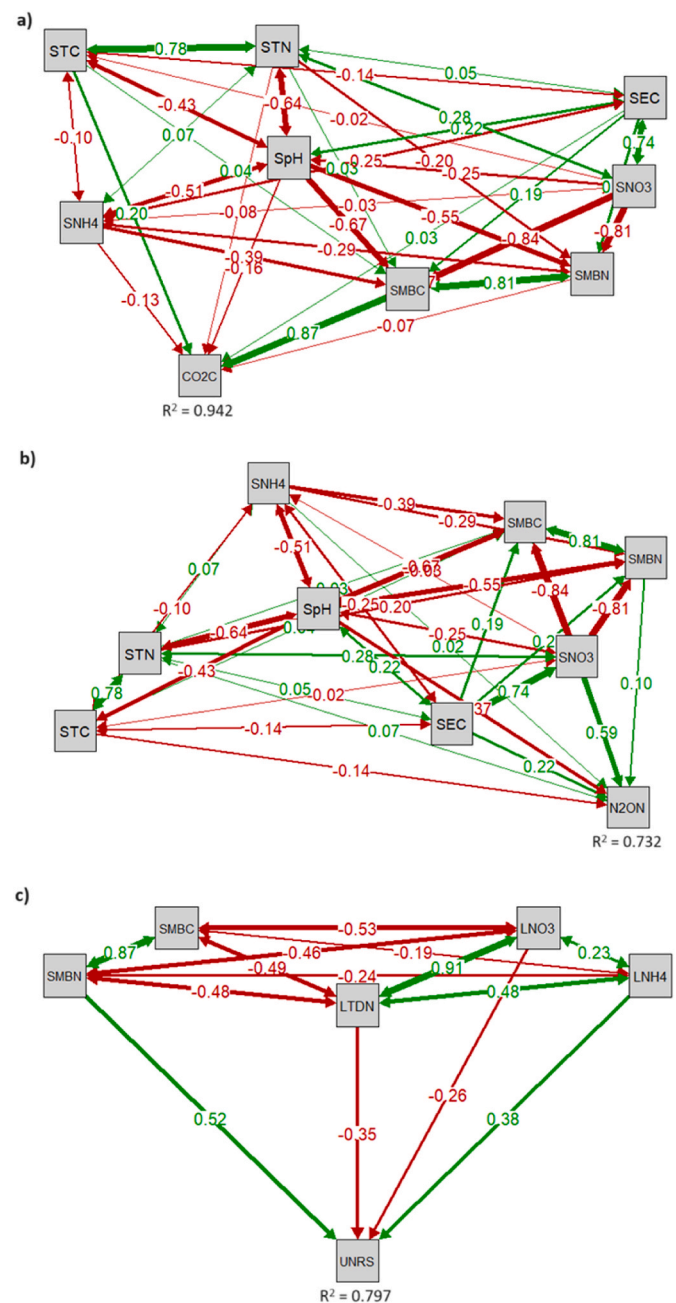


Fig. 6. Path diagrams estimating the direct and indirect relationships between cumulative soil CO₂-C emission in Experiment 1 (a), cumulative soil N₂O-N emission in Experiment 1 (b), and urea N retained in soil after leaching in Experiment 2 (c) versus selected explanatory variables. Single and double headed arrows indicate causal relationships and covariance, respectively. The labels on the lines are standardised coefficient estimates analogous to relative regression weights. Green and red lines represent positive and negative relationships, respectively. The thickness of the lines shows the relative strength of the relationships. The proportion of variance explained (R^2) for each model appears below the response variable. CO₂C, cumulative soil CO₂-C emission (response variable); N₂ON, cumulative soil N₂O-N emission (response variable); UNRS, urea N retained in soil (response variable); SMBC, soil microbial biomass C; SMBN, soil microbial biomass N; SpH, soil pH; SEC, soil electrical conductivity; STC, soil total C; STN, soil total N; SNO₃, soil NO₃-N; SNH₄, soil NH₄⁺-N; LNO₃, cumulative leachate NO₃-N; LNH₄, cumulative leachate NH₄⁺-N; LTDN, cumulative leachate total dissolved N. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.5. Path analysis of soil CO₂ and N₂O emissions and urea N retention in soil

In Experiment 1, path analysis revealed that cumulative soil CO₂-C and N₂O-N emissions were mainly associated with soil MBC size and soil nitrate concentration, respectively, showing positive relationships (Fig. 6a and b). In Experiment 1, path analysis also showed that soil MBN and MBC were mainly associated (negatively) with soil nitrate concentration (Fig. 6a and b). Furthermore, in treatments with urea application path analysis showed that none of the tested parameters had a marked effect on urea N retention in soil in Experiment 1 (data not shown), but in Experiment 2 urea N retention in soil after leaching was mainly affected by soil MBN showing a positive relationship (Fig. 6c). In Experiment 2, path analysis also showed strong positive covariance between cumulative leached nitrate and cumulative total leached N and negative covariance between cumulative leached nitrate and soil MBC (Fig. 6c).

4. Discussion

4.1. CPH-derived organic soil amendments differentially affect soil fertility parameters in cocoa soils

Nutrient availability in soil is a major determinant of soil fertility and is greatly affected by soil pH (McCauley et al., 2009). Most soil nutrients are optimally available to plants within the 6.5–8.0 pH range (McCauley et al., 2009). In this study in Experiment 1, increases in soil pH in the amended acidic Ferralsols (initial pH 4.8) and alkaline Nitisols (initial pH 8.6) to 6.4–6.6 and 8.9–9.6, respectively, suggest that CPH based organic amendments can be used to ameliorate soil pH mediated nutrient unavailability in acidic cocoa soils, whereas their application to alkaline cocoa soils could have adverse effects on nutrient availability. The amelioration of acidic cocoa soils is important considering their wide occurrence as illustrated by Quaye et al. (2021) for cocoa agro-ecological zones of Ghana. In this study in Experiment 1, the increases in soil pH accompanied by increases in soil nitrate availability with the addition of CPH compost, CPH biochar, or their mixture in acidic Ferralsols show that applying composted and/or pyrolysed CPH, rather than raw CPH residues, is especially necessary to increase N availability in acidic cocoa soils. The observed increases in soil nitrate availability after the addition of CPH compost and/or biochar were likely due to the transformation of ammonium into nitrate, via nitrification (Baggs, 2011), as it can be deduced from the corresponding reductions in soil ammonium availability. Other studies have also shown increased nitrification rates in soils that received applications of raw plant residues (e. g., Mwafurirwa et al., 2021) or biochar (e.g., Zhang et al., 2021), often attributed to impacts on the abundance of nitrifying microbes (e.g., Zhang et al., 2021). On the other hand, in Experiment 1, the addition of raw CPH to both soil types caused reductions in soil nitrate availability accompanied by marked increases in soil MBN, implying considerable microbial immobilisation of nitrate N, which could reduce soil N availability to cocoa plants. That the patterns of soil MBC and MBN between treatments in Experiment 2 were similar to those observed in Experiment 1 suggests that leaching simulation did not cause marked effects on soil microbial biomass size and N immobilisation by the microbes. That both soil ammonium and nitrate concentrations at the end of Experiment 1 were overall lower in the Nitisols than in the Ferralsols may be explained by the difference between these soil types in the initial total soil N contents (Table 1), nitrification, or that the high pH of the Nitisol may have caused greater soil N losses in this soil via ammonia volatilisation (Park et al., 2020).

The interpretation that microbial immobilisation of nitrate N occurred in this study is supported by a strong negative association between soil MBN and soil nitrate concentration as revealed by path analysis. Greater microbial N immobilisation in soils amended with raw CPH was driven by microbial growth, as it can be inferred from marked

increases in soil MBC in this treatment in both soil types and experiments (since MBC is an indicator of microbial growth, as 50% of the microbial biomass is C; Egli, 2009). It is likely that the rapid microbial growth in soils amended with raw CPH was due to the release of labile C from raw CPH into soil, which was preferentially and rapidly utilised by microbes (Paterson et al., 2008), and increased microbial demand for N, because of the high C:N ratio of the raw CPH. Indeed, raw CPH likely had a high amount of labile C compared with the composted or pyrolysed CPH. On the other hand, CPH biochar likely had the least amount of labile C as biochar is particularly known to be recalcitrant (Cheng et al., 2008), consistent with the lack of observed effects of CPH biochar on soil MBC and MBN. That soil MBC was higher in the Ferralsols than in the Nitisols could be due to the relatively high initial SOM content of the former supporting a greater microbial population.

Soil EC is an effective measure of the total amount/availability of nutrients in soil (Baldi et al., 2020). Both too low and too high nutrient availability (e.g., >2000 $\mu\text{S cm}^{-1}$ as in saline soils) can be unsuitable for plant growth. In Experiment 1 the increases in soil EC after the addition of CPH compost, CPH biochar, or their mixture (from initial EC of 18.5 and 50.4 $\mu\text{S cm}^{-1}$ to 205–249 and 196–219 $\mu\text{S cm}^{-1}$ in the Ferralsols and Nitisols, respectively) therefore demonstrate the benefits of these soil amendments for soil fertility. For this reason, and because of greater microbial N immobilisation in soils amended with raw CPH, it could be considered that the addition to soil of composted or pyrolysed CPH (or their mixture) would enhance overall soil fertility in cocoa farms. The addition of CPH compost was particularly beneficial for soil P and Ca availability, while the addition of CPH biochar had the greatest benefit on soil available K. These effects were likely influenced by the concentrations of K, P, and Ca in the organic amendments (Table 1). Indeed, the likely reason that all organic amendments increased soil available K concentrations is because CPH is particularly rich in K (Table 1; Houghni et al., 2021).

The greater soil ammonium and nitrate availability (in Experiment 1) and soil MBN and MBC (in both experiments) in treatments with urea application were expected, due to the transformation of urea increasing soil bioavailable N (Gao et al., 2022). In Experiment 1, urea application decreased soil pH and increased soil EC, likely because of the production of H⁺ ions during nitrification and an increase in total soil available N (nitrate plus ammonium ions), respectively.

4.2. Effects of CPH-derived organic soil amendments on GHG emissions in cocoa soils

The findings of this study demonstrate that soil amendment with raw CPH induces higher total GHG emissions (CO₂ plus N₂O) in cocoa soils, whereas soil amendment with pyrolysed CPH results in fewer emissions and could be used as a strategy to minimise emissions when applying CPH-based organic soil amendments. Total GHG emissions (CO₂ plus N₂O) and CO₂-C emission, which showed similar patterns due to the larger CO₂-C fluxes than the N₂O-N fluxes in this study when compared on equal scale of CO₂ equivalents, were highest in both soil types with the addition of raw CPH. The overall patterns of soil CO₂-C and N₂O-N emissions observed between treatments in this study can be ascribed to the initial quality (i.e., chemical composition) of the organic amendments. For instance, the likely high initial labile C content of raw CPH caused not only its rapid utilisation/decomposition by soil microbes but possibly also positive priming of native SOM C, thereby increasing both soil MBC and CO₂-C emission. On the other hand, biochar C is recalcitrant, consistent with low impact on soil microbes and the observed no change or weaker impact on cumulative soil CO₂-C emission from soils amended with CPH biochar. The observed lower cumulative soil N₂O emission in soils amended with raw CPH, compared to no amendment, may be due to microbial N immobilisation reducing soil bioavailable N forms, the substrates of nitrification and denitrification processes that produce N₂O (Baggs, 2011). The overall higher soil CO₂-C and N₂O-N emissions observed in the Ferralsols than in the Nitisols is in line with

the high initial total C, total N, and SOM contents of the Ferralsol compared with the Nitisol used in this study. Also, the increases in soil CO₂-C and N₂O-N emissions with urea application may be because of urea increasing soil bioavailable N following its transformation, thereby supporting microbial processes that produce CO₂ (Keuskamp et al., 2013) and N₂O (Baggs, 2011).

The positive relationship between soil MBC and CO₂-C emission, revealed by path analysis, could be due to microbial biomass or population size affecting the total amount of CO₂-C derived from microbial respiration and microbial decomposition of C compounds (Li et al., 2020). On the other hand, the positive relationship between soil nitrate concentration and N₂O-N emission could be explained by two potential pathways. First, that N₂O-N was mainly produced via nitrification, and thus it was co-produced with nitrate. Second, that N₂O-N was mainly produced via denitrification, and thus its production decreased as increased microbial utilisation/immobilisation of nitrate N reduced soil nitrate concentration and subsequently denitrification. The observed strong negative association between soil nitrate concentration and soil microbial biomass attributes (MBN and MBC) support the latter hypothesis.

4.3. Effects of CPH-derived organic soil amendments on nutrient leaching from cocoa soils

Cumulative leached ammonium and nitrate varied between the Ferralsols and Nitisols likely due to inherent differences in soil pH. This is because soil pH affects microbial transformation of ammonium to nitrate (Zebbarth et al., 2015) and thus the concentrations of these N forms in soil. Overall, the pattern of cumulative total leached N was similar to that of cumulative leached nitrate, because nitrate leaching was greater overall compared with ammonium leaching. Nitrate leaches faster via soil percolating water, which not only reduces available N in soil but also has negative consequences in the environment, such as eutrophication (Singh and Craswell, 2021) and contamination of drinking water (Tariqi and Naughton, 2021). Ammonium can resist leaching through adsorption to negatively charged surfaces on clays and organic matter (Juang et al., 2001). The greater contribution of nitrate, compared with ammonium, to total N leaching in this study is also the reason for the strong positive association between cumulative leached nitrate and total leached N shown in the path analysis. In soils amended with raw CPH, lower N leaching was observed alongside remarkably greater soil MBN, suggesting that this treatment reduced N leaching by promoting microbial N immobilisation. The greater cumulative leached N in soils amended with CPH compost and CPH compost-biochar mixture, compared to unamended soils, may be due to the high addition rates of organic amendment N for the compost treatments (Table 2), and thus may be mainly related to direct leaching of N released from compost.

The observed pattern of P leaching between treatments can be explained by the addition rates of organic amendments P (Table 2). For example, treatments with CPH compost and raw CPH had the highest and lowest addition rates of organic amendment P and caused the strongest and weakest effects, respectively, on cumulative leached P. CPH biochar, however, had the highest addition rate of organic amendment K (Table 2) but showed intermediate effect on cumulative leached K compared with the other treatments. This shows that CPH biochar caused relatively low K leaching when considering the organic amendments K addition rates. Similarly, when considering the K addition rates, soils amended with raw CPH also had relatively low K leaching compared with soils amended with CPH compost or CPH compost-biochar mixture. Ca leaching decreased after the addition of CPH biochar to the Nitisol. The observed higher cumulative leachate P, K, and Ca in the Nitisols than in the Ferralsols can also be explained by the difference in soil pH affecting nutrient mobility (McCauley et al., 2009), as soil pH was higher in the Nitisols than the Ferralsols.

4.4. Urea N retention in soil as affected by CPH based organic soil amendments

In treatments with urea fertiliser application, the observed greater urea N retention after leaching in the Nitisol amended with raw CPH (Experiment 2) was possibly because of microbial immobilisation of urea-derived N, likely due to raw CPH inducing greater microbial utilisation of urea N in this soil owing to its low initial soil N concentration (Table 1). This interpretation is supported by the path analysis, which showed that urea N retention in soil after leaching was strongly and positively associated with soil MBN. The observed weak relationship between urea N retention in soil and soil MBN in Experiment 1 was likely because of lower N losses in this experiment in the absence of leaching. Therefore, while increased microbial N immobilisation in soils amended with high C:N ratio raw plant residues has been reported previously (e.g., Reichel et al., 2018), this study reveals that microbial immobilisation of inorganic fertiliser (such as urea) N following soil amendment with raw plant residues (such as raw CPH) is particularly high in soils with low native soil N and even greater in soils subjected to leaching. Although in the long term the N immobilised in microbial biomass would be recycled into soil from the microbial necromass (Cui et al., 2020), how much of the recycled N will be in available forms in soil for plant uptake, or even re-immobilised by microbes, is unclear. The decreases in urea N retention in the Ferralsols amended with CPH compost, CPH biochar, or CPH compost-biochar mixture and the Nitisols amended with CPH biochar or CPH compost-biochar mixture may be due to the observed increases in soil pH leading to increased urea N losses via ammonia volatilisation (Zhenghu and Xiao, 2000). Further studies including measurement of soil N losses via ammonia volatilisation are needed to confirm this.

4.5. Implications for practitioners

Taken together, the above findings show that composted and/or pyrolysed CPH can be used to enhance soil fertility on cocoa farms, particularly in acidic soils. Furthermore, these findings show that pyrolysed CPH is especially beneficial for reducing soil nutrient leaching and GHG emissions and thus for increasing the sustainability of cocoa production in west Africa. Therefore, promotion of CPH pyrolysis and application across west Africa as a soil amendment, particularly in acidic soils, is recommended. Reduction of GHG emissions from soil due to application of pyrolysed CPH could also provide opportunities for carbon credits (Adhikari et al., 2024).

5. Conclusion

The findings of this study are summarised in Fig. 7. These findings suggest the following: (i) CPH-derived organic soil amendments could be used to improve nutrient availability in acidic cocoa soils by increasing soil pH, whereas their application to alkaline cocoa soils could have adverse effects on nutrient availability. (ii) The application of raw CPH promotes microbial immobilisation of nitrate N in cocoa soils, but applying CPH compost, CPH biochar, or their mixture could increase nitrate availability in acidic cocoa soils. (iii) CPH organic soil amendments, most notably CPH biochar, are effective in increasing soil K availability, with amendment with CPH compost or CPH compost-biochar mixture also effective in increasing soil P and Ca availabilities. Thus, judicious use of CPH compost, CPH biochar, or their mixture can enhance soil fertility in cocoa farms, thereby addressing the challenge of declining soil fertility and yields on cocoa farms in west Africa. (iv) The addition of pyrolysed CPH could be used as a strategy to reduce GHG emissions (CO₂ plus N₂O) from cocoa soils receiving CPH amendments, especially in Nitisols, thereby supporting climate-smart cocoa production. (v) As soil microbial immobilisation of N, total N leaching, and N₂O emissions were all principally associated with soil nitrate concentration, additional measures and/or research on soil

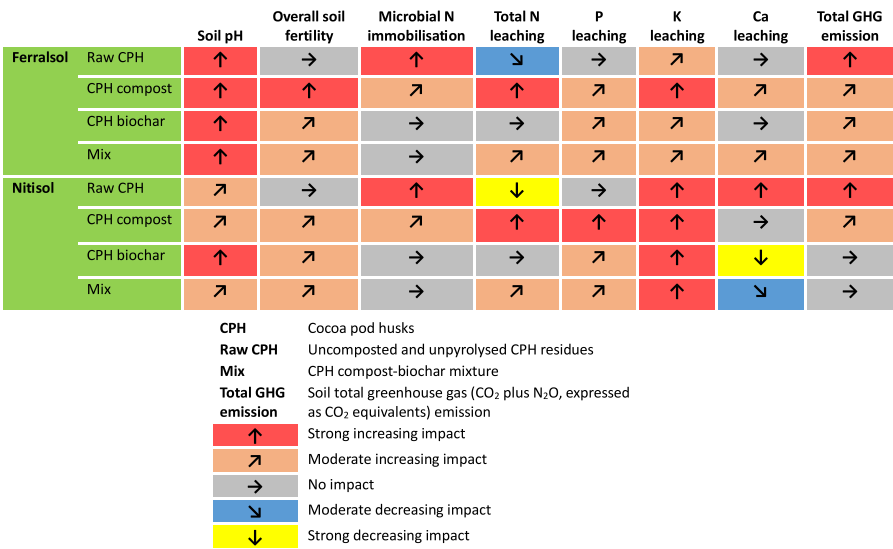


Fig. 7. Infographic summary of the impacts of cocoa pod husk-derived organic soil amendments on soil pH, overall soil fertility (as inferred from the soil electrical conductivity data), soil microbial N immobilisation, nutrient (N, P, K, and Ca) leaching, and greenhouse gas emission as observed in this study in two cocoa soils (an acidic Ferralsol and an alkaline Nitisol) from west Africa.

nitrate management in cocoa soils receiving CPH amendments, such as composted CPH, would be crucial to both increase plant N uptake and reduce the negative impacts of nitrate on the environment.

A long-term field trial was established in Ghana in 2021 to test under field conditions the CPH-derived organic soil amendments used in this study, which will address the short duration limitation of this study. A life cycle assessment and a techno-economic analysis for the use of CPH-derived organic soil amendments in cocoa production in different countries in west Africa are recommended. This controlled laboratory study using an acidic soil and an alkaline soil from Ghana provides a case study for soil pH differences that are also common in other cocoa producing countries in west Africa.

CRediT authorship contribution statement

Lumbani Mwafulirwa: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Tom Sizmur:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Andrew Daymond:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Laura Atuah:** Writing – review & editing, Resources, Funding acquisition, Conceptualization. **Amos Kojo Quaye:** Writing – review & editing, Resources, Funding acquisition, Conceptualization. **Sean Coole:** Methodology, Investigation, Conceptualization. **Steve Robinson:** Writing – review & editing, Funding acquisition, Conceptualization. **John Hammond:** Writing – review & editing, Funding acquisition, Conceptualization. **Godfred Awudzi:** Writing – review & editing, Funding acquisition, Conceptualization. **Dadson Awunyo-Vitor:** Writing – review & editing, Funding acquisition, Conceptualization. **Owusu Domfeh:** Writing – review & editing, Funding acquisition, Conceptualization. **Paul Hadley:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Acknowledgements

This work received funding from the UK Global Challenges Research Fund through the Biotechnology and Biological Sciences Research Council. Thanks go to A Dudley, M Obrien, and A Dodson for their technical support, and the handling editor and anonymous reviewers for their constructive comments to improve the paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2024.144065>.

Data availability

The data used for this study is held in a University of Reading repository and can be made available on request.

References

Acebo-Guerrero, Y., Hernández-Rodríguez, A., Heydrich-Pérez, M., El Jaziri, M., Hernández-Lauzardo, A.N., 2012. Management of black pod rot in cacao (*Theobroma cacao* L.): a review. *Fruits* 67 (1), 41–48. <https://doi.org/10.1051/FRUITS/2011065>.

Adekanmbi, A.A., Dale, L., Shaw, L., Sizmur, T., 2023. Differential temperature sensitivity of intracellular metabolic processes and extracellular soil enzyme activities. *Biogeosciences* 20 (11), 2207–2219. <https://doi.org/10.5194/BG-20-2207-2023>.

Adhikari, S., Moon, E., Paz-Ferreiro, J., Timms, W., 2024. Comparative analysis of biochar carbon stability methods and implications for carbon credits. *Sci. Total Environ.* 914, 169607. <https://doi.org/10.1016/j.scitotenv.2023.169607>.

Ali, E.B., Awuni, J.A., Danso-Abbeam, G., 2018. Determinants of fertilizer adoption among smallholder cocoa farmers in the Western Region of Ghana. *Cogent Food Agric.* 4 (1). <https://doi.org/10.1080/23311932.2018.1538589>.

Almutairi, A.A., Ahmad, M., Rafique, M.I., Al-Wabel, M.I., 2023. Variations in composition and stability of biochars derived from different feedstock types at varying pyrolysis temperature. *Journal of the Saudi Society of Agricultural Sciences* 22 (1), 25–34. <https://doi.org/10.1016/j.jssas.2022.05.005>.

Amponsah-Doku, B., Daymond, A., Robinson, S., Atuah, L., Sizmur, T., 2022. Improving soil health and closing the yield gap of cocoa production in Ghana – a review. *Scientific African* 15, e01075. <https://doi.org/10.1016/J.SCIAF.2021.E01075>.

Awunyo-Vitor, D., Daymond, A., Quaye, A., Awudzi, G., Atuah, L., Mwafulirwa, L., Hammond, J., Turnbull, C., Lahive, F., Coole, S., Robinson, S., Hadley, P., 2022. Cocoa farmers' awareness and usage of compost and biochar as soil amendments in Ghana. A Paper Presented at the VIII International European Congress on Social Sciences, December 4–5, 2022, Faculty of Humanities and Social Sciences, University of Rijeka, Rijeka, Croatia. https://www.academia.edu/93107828/_FULL_TEXT_BOOK.

- Baggs, E.M., 2011. Soil microbial sources of nitrous oxide: recent advances in knowledge, emerging challenges and future direction. *Curr. Opin. Environ. Sustain.* 3 (5), 321–327. <https://doi.org/10.1016/j.cosust.2011.08.011>.
- Baldi, E., Quartieri, M., Muzzi, E., Nofrieri, M., Toselli, M., 2020. Use of in situ soil solution electric conductivity to evaluate mineral N in commercial orchards: preliminary results. *Horticulturae* 6 (3), 39. <https://doi.org/10.3390/horticulturae6030039>.
- Brookes, P.C., Landman, A., Pruden, G., Jenkinson, D.S., 1985. Chloroform fumigation and the release of soil nitrogen: a rapid direct extraction method to measure microbial biomass nitrogen in soil. *Soil Biol. Biochem.* 17 (6), 837–842. [https://doi.org/10.1016/0038-0717\(85\)90144-0](https://doi.org/10.1016/0038-0717(85)90144-0).
- Carodenuto, S., 2019. Governance of zero deforestation cocoa in West Africa: new forms of public-private interaction. *Environmental Policy and Governance* 29 (1), 55–66. <https://doi.org/10.1002/EET.1841>.
- Cheng, C.-H., Lehmann, J., Thies, J.E., Burton, S.D., 2008. Stability of black carbon in soils across a climatic gradient. *J. Geophys. Res.: Biogeosciences* 113 (G2). <https://doi.org/10.1029/2007JG000642> n/a–n/a.
- Clough, T.J., Condon, L.M., Kammann, C., Müller, C., 2013. A review of biochar and soil nitrogen dynamics. *Agronomy* 3 (2), 275–293. <https://doi.org/10.3390/AGRONOMY3020275>.
- Cui, J., Zhu, Z., Xu, X., Liu, S., Jones, D.L., Kuzyakov, Y., Shibistova, O., Wu, J., Ge, T., 2020. Carbon and nitrogen recycling from microbial necromass to cope with C:N stoichiometric imbalance by priming. *Soil Biol. Biochem.* 142, 107720. <https://doi.org/10.1016/j.soilbio.2020.107720>.
- Doungous, O., Minyaka, E., Longue, E.A.M., Nkengafac, N.J., 2018. Potentials of cocoa pod husk-based compost on Phytophthora pod rot disease suppression, soil fertility, and Theobroma cacao L. growth. *Environ. Sci. Pollut. Control Ser.* 25 (25), 25327–25335. <https://doi.org/10.1016/j.fbp.2024.08.010>.
- Egli, T., 2009. Nutrition, microbial. In: *Encyclopedia of Microbiology*. Elsevier, pp. 308–324. <https://doi.org/10.1016/B978-0-12373944-5.00083-3>.
- EU, 2024. Regulation on deforestation-free products. https://environment.ec.europa.eu/topics/forests/deforestation/regulation-deforestation-free-products_en.
- Gao, J., Luo, J., Lindsey, S., Shi, Y., Wei, Z., Wang, L., Zhang, L., 2022. Effects of soil properties on urea-N transformation and efficacy of nitrification inhibitor 3, 4-dimethylpyrazole phosphate (DMPP). *Soil Sci. Plant Nutr.* 68 (1), 228–237. <https://doi.org/10.1080/00380768.2021.2021784>.
- Higonnet, E., Bellantonio, M., Hurowitz, G., 2017. Chocolate's dark secret - how the cocoa industry destroys national parks. https://www.mightyearth.org/wp-content/uploads/2017/09/chocolates_dark_secret_english_web.pdf.
- Hougni, D.-G.J.M., Schut, A.G.T., Woittiez, L.S., Vanlauwe, B., Giller, K.E., 2021. How nutrient rich are decaying cocoa pod husks? The kinetics of nutrient leaching. *Plant Soil* 463 (1–2), 155–170. <https://doi.org/10.1007/s11104-021-04885-1>.
- IPCC, 2007. *Climate Change 2007: The Physical Science Basis*. Cambridge Univ., Press, Cambridge, UK. <https://www.ipcc.ch/report/ar4/wg1/>.
- IPCC, 2022. Strengthening and implementing the global response. *Global Warming of 1.5°C* 313–444. <https://doi.org/10.1017/9781009157940.006>.
- Joseph, S., Cowie, A.L., Van Zwieten, L., Bolan, N., Budai, A., Buss, W., Cayuela, M.L., Graber, E.R., Ippolito, J.A., Kuzyakov, Y., Luo, Y., Ok, Y.S., Palansooriya, K.N., Shepherd, J., Stephens, S., Weng, Z., Lehmann, J., 2021. How biochar works, and when it doesn't: a review of mechanisms controlling soil and plant responses to biochar. *GCB Bioenergy* 13 (11), 1731–1764. <https://doi.org/10.1111/GCBB.12885>.
- Juang, T.C., Wang, M.K., Chen, H.J., Tan, C.C., 2001. Ammonium fixation by surface soils and clays. *Soil Sci.* 166 (5), 345–352. <https://doi.org/10.1097/00010694-200105000-00005>.
- Kalischek, N., Lang, N., Renier, C., Daudt, R.C., Addoah, T., Thompson, W., Blaser-Hart, W.J., Garrett, R., Schindler, K., Wegner, J.D., 2023. Cocoa plantations are associated with deforestation in Côte d'Ivoire and Ghana. *Nature Food* 4 (5), 384–393. <https://doi.org/10.1038/s43016-023-00751-8>.
- Keuskamp, J.A., Schmitt, H., Laanbroek, H.J., Verhoeven, J.T.A., Hefting, M.M., 2013. Nutrient amendment does not increase mineralisation of sequestered carbon during incubation of a nitrogen limited mangrove soil. *Soil Biol. Biochem.* 57, 822–829. <https://doi.org/10.1016/j.soilbio.2012.08.007>.
- Kozicka, M., Tacconi, F., Horna, D., Gotor, E., 2018. Forecasting Cocoa Yields for 2050. *Bioversity International, Rome (Italy)*. <https://cgspace.cgiar.org/handle/10568/93236>.
- Kumar, K., Goh, K.M., 2007. Nitrogen release from crop residues and organic amendments as affected by biochemical composition. *Commun. Soil Sci. Plant Anal.* 34 (17–18), 2441–2460. <https://doi.org/10.1081/CSS-120024778>.
- Li, S., Wang, S., Fan, M., Wu, Y., Shanguan, Z., 2020. Interactions between biochar and nitrogen impact soil carbon mineralization and the microbial community. *Soil Tillage Res.* 196, 104437. <https://doi.org/10.1016/j.still.2019.104437>.
- McCauley, A., Jones, C., Jacobsen, J., 2009. *Soil pH and Organic Matter*. Montana State University. <https://www.certifiedcropadviser.org/files/certifications/certified/education/self-study/exam-pdfs/38.pdf>.
- Muñoz-Almagro, N., Valadez-Carmona, L., Mendiola, J.A., Ibáñez, E., Villamiel, M., 2019. Structural characterisation of pectin obtained from cacao pod husk. Comparison of conventional and subcritical water extraction. *Carbohydrate Polymers* 217, 69–78. <https://doi.org/10.1016/J.CARBPOL.2019.04.040>.
- Mwafurirwa, L.D., Baggs, E.M., Russell, J., Morley, N., Sim, A., Paterson, E., 2017. Combined effects of rhizodeposit C and crop residues on SOM priming, residue mineralization and N supply in soil. *Soil Biol. Biochem.* 113, 35–44. <https://doi.org/10.1016/j.soilbio.2017.05.026>.
- Mwafurirwa, L., Baggs, E.M., Morley, N., Paterson, E., 2019. Ryegrass root and shoot residues differentially affect short-term priming of soil organic matter and net soil C-balance. *Eur. J. Soil Biol.* 93. <https://doi.org/10.1016/j.ejsobi.2019.103096>.
- Mwafurirwa, L., Paterson, E., Cairns, J.E., Daniell, T.J., Thierfelder, C., Baggs, E.M., 2021. Genotypic variation in maize (Zea mays) influences rates of soil organic matter mineralization and gross nitrification. *New Phytol.* 231 (5), 2015–2028. <https://doi.org/10.1111/nph.17537>.
- Ngalani, G.P., Kagho, F.D., Peguy, N.N.C., Prudent, P., Ondo, J.A., Ngameni, E., 2023. Effects of coffee husk and cocoa pods biochar on the chemical properties of an acid soil from West Cameroon. *Arch. Agron Soil Sci.* 69 (5), 744–758. <https://doi.org/10.1080/03650340.2022.2033733>.
- Park, S.M., Kim, S.U., Hong, C.O., 2020. Effect of reducing ammonia volatilization from the arable soil with iron sulfate. *Korean Journal of Soil Science and Fertilizer* 53 (4), 405–414. <https://doi.org/10.7745/KJSSF.2020.53.4.405>.
- Paterson, E., Osler, G., Dawson, L.A., Gebbing, T., Sim, A., Ord, B., 2008. Labile and recalcitrant plant fractions are utilised by distinct microbial communities in soil: independent of the presence of roots and mycorrhizal fungi. *Soil Biol. Biochem.* 40 (5), 1103–1113. <https://doi.org/10.1016/j.soilbio.2007.12.003>.
- Quaye, A.K., Doe, E.K., Attua, E.M., Yiran, G., Arthur, A., Dogbatse, J.A., Konlan, S., Nkroma, Y.D., Addo, D., 2021. Geospatial distribution of soil organic carbon and soil pH within the cocoa agroecological zones of Ghana. *Geoderma* 386, 114921. <https://doi.org/10.1016/J.GEODERMA.2020.114921>.
- R Core Team, 2022. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing. <https://www.R-project.org/>.
- Reichel, R., Wei, J., Islam, M.S., Schmid, C., Wissel, H., Schröder, P., Schlöter, M., Brüggemann, N., 2018. Potential of wheat straw, spruce sawdust, and lignin as high organic carbon soil amendments to improve agricultural nitrogen retention capacity: an incubation study. *Front. Plant Sci.* 9. <https://doi.org/10.3389/fpls.2018.00900>.
- Rodríguez-Vila, A., Atuah, L., Abubakari, A.H., Atorqui, D.W., Abdul-Karim, A., Coole, S., Hammond, J., Robinson, S., Sizmur, T., 2022. Effect of biochar on micronutrient availability and uptake into leafy greens in two urban tropical soils with contrasting soil pH. *Front. Sustain. Food Syst.* 6, 821397. <https://doi.org/10.3389/FSUFS.2022.821397/BIBTEX>.
- Singh, Bijay, Craswell, E., 2021. Fertilizers and nitrate pollution of surface and ground water: an increasingly pervasive global problem. *SN Appl. Sci.* 3 (4), 518. <https://doi.org/10.1007/s42452-021-04521-8>.
- Snoeck, D., Koko, L., Joffre, J., Bastide, P., Jagoret, P., Snoeck, D., Bastide, P., Koko, L., 2016. *Cacao Nutrition and Fertilization*, pp. 155–202. https://doi.org/10.1007/978-3-319-26777-7_4.
- Tariqi, A.Q., Naughton, C.C., 2021. Water, health, and environmental justice in California: geospatial analysis of nitrate contamination and thyroid cancer. *Environ. Eng. Sci.* 38 (5), 377–388. https://doi.org/10.1089/EES.2020.0315/SUPPL_FILE/SUPP_DATASI.DOCX.
- UN, 2024. Goal 12: ensure sustainable consumption and production patterns. https://sdgs.un.org/goals/goal12#targets_and_indicators. (Accessed 28 March 2024).
- Vance, E.D., Brookes, P.C., Jenkinson, D.S., 1987. An extraction method for measuring soil microbial biomass C. *Soil Biol. Biochem.* 19 (6), 703–707. [https://doi.org/10.1016/0038-0717\(87\)90052-6](https://doi.org/10.1016/0038-0717(87)90052-6).
- Van Vliet, J.A., Giller, K.E., 2017. Chapter five - mineral nutrition of cocoa: a review. In: Sparks, D.L. (Ed.), *Advances in Agronomy*, vol. 141. Academic Press, pp. 185–270. <https://doi.org/10.1016/bs.agron.2016.10.017>.
- Wang, J., Wang, S., 2019. Preparation, modification and environmental application of biochar: a review. *J. Clean. Prod.* 227, 1002–1022. <https://doi.org/10.1016/J.JCLEPRO.2019.04.282>.
- Zama, E.F., Zhu, Y.-G., Reid, B.J., Sun, G.-X., 2017. The role of biochar properties in influencing the sorption and desorption of Pb(II), Cd(II) and As(III) in aqueous solution. *J. Clean. Prod.* 148, 127–136. <https://doi.org/10.1016/j.jclepro.2017.01.125>.
- Zebbarth, B.J., Forge, T.A., Goyer, C., Brin, L.D., 2015. Effect of soil acidification on nitrification in soil. *Can. J. Soil Sci.* 95 (4), 359–363. <https://doi.org/10.4141/cjss-2015-040>.
- Zhang, L., Jing, Y., Chen, C., Xiang, Y., Rezaei Rashti, M., Li, Y., Deng, Q., Zhang, R., 2021. Effects of biochar application on soil nitrogen transformation, microbial functional genes, enzyme activity, and plant nitrogen uptake: a meta-analysis of field studies. *GCB Bioenergy* 13 (12), 1859–1873. <https://doi.org/10.1111/gcbb.12898>.
- Zheng, H., Wang, Z., Deng, X., Zhao, J., Luo, Y., Novak, J., Herbert, S., Xing, B., 2013. Characteristics and nutrient values of biochars produced from giant reed at different temperatures. *Bioresour. Technol.* 130, 463–471. <https://doi.org/10.1016/J.BIORTECH.2012.12.044>.
- Zhenghu, D., Xiao, H., 2000. Effects of soil properties on ammonia volatilization. *Soil Sci. Plant Nutr.* 46 (4), 845–852. <https://doi.org/10.1080/00380768.2000.10409150>.