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Role of Nutrient-Enriched Biochar as a Soil Amendment during Maize Growth: Exploring Practical Alternatives to Recycle Agricultural Residuals and to Reduce Chemical Fertilizer Demand

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Received: 4 May 2019; Accepted: 31 May 2019; Published: 10 June 2019

Abstract: Recycling and value-added utilization of agricultural residues through combining technologies such as anaerobic digestion and pyrolysis could double the recoverable energy, close the nutrient recycle loop, and ensure cleaner agricultural production. This study assessed the beneficial application of biochar to soil to recycle digestate nutrients, improve soil quality, and reduce conventional chemical fertilizer. The addition of digestate-enriched biochar improved soil quality as it provided higher soil organic matter (232%–514%) and macronutrients (110%–230%) as opposed to the unenriched biochar and control treatments. Maize grown in soil amended with digestate-enriched biochar showed a significantly higher biomass yield compared to the control and non-enriched biochar treatments but was slightly lower than yields from chemical fertilizer treatments. The slightly lower yield (20%–25%) achieved from digestate-enriched biochar was attributed to slower mineralization and release of the adsorbed nutrients in the short term. However, digestate-enriched biochar could in the long term become more beneficial in sustaining soil fertility through maintaining high soil organic matter and the gradual release of micronutrients compared to conventional chemical fertilizer. Positive effects on soil micronutrients, macronutrients, organic matter, and biomass yield indicates that enriched biochar could partly replace chemical fertilizers and promote organic farming in a circular economy concept.

Keywords: agricultural residues; anaerobic digestate; nutrient recycle; agroecosystems; corn fertilization

1. Introduction

Traditional open loop agricultural production systems are a major cause of non-point environmental pollution as there is no resource recovery from waste materials such as agro-processing residues, or manure. However, when viewed from a circular economy perspective, these abundant agricultural wastes represent a huge pool of untapped resources that could be converted into bioenergy, bio-fertilizers to maintain soil fertility, and other value-added products. The circular economy concept is currently being promoted worldwide as an innovative approach to total ecosystem management, where products at the end of their service life or waste materials from production processes are valuable resources for the production of renewable, value-added products [1]. In the context of agro-processing and the soil grown food chain, the adoption of the 'circular economy approach' could improve resource use efficiency through value-added utilization of agricultural wastes focused on nutrients and energy recovery.

Anaerobic digestion (AD) is among the popular and widely applied technologies under the concept of the circular economy, which aims to recover bioenergy from excess crop residues, manure, and other organic wastes from agro-processing industries [2]. The AD process recovers energy as biomethane, which is recycled back to cover the company's energy demand whilst the surplus can be supplied to local electricity grids. In addition, at the end of the AD process, the residues (anaerobic digestate) that remain in the reactor can be used as biofertilizer. The anaerobic digestate usually contains high concentrations of bioavailable nutrients, such as ammonium, phosphorus, potassium, magnesium, calcium, and trace elements (Fe, Ca, Mg, K, Zn, Cu, and Mn) in addition to organic matter [3]. Thus, it is a good source of agricultural nutrients [3–5] and serves as a substitute for the costly chemical fertilizers that poverty-stricken rural farmers cannot afford [6].

In the past decade, the use of anaerobic digestate in agricultural systems was deemed sustainable because all the biofertilizer could be assimilated into agricultural production. However, at present, there are growing challenges for sustainable land applications of anaerobic digestate. Firstly, due to increasing numbers of industrialized livestock breeding and feeding operations and the consequent increased number of large-scale biogas plants, excess volumes of anaerobic digestate are produced beyond their agricultural assimilation potential [5–7]. For instance, in China the annual manure generation is over 4 billion tons and the anaerobic digestate generated is approximately 2.3 billion tons of which less than 70% can be recycled back to agriculture due to land limitations [8]. Similarly, in the EU the anaerobic digestate production reached 56 million tons per year in 2010, of which 80% could be recycled back into agriculture [9].

Secondly, due to strict regulations, such as the Nitrates Council Directive 91/676/EEC (EEC, 1991), only a small amount of anaerobic digestate can be applied through land spreading depending on the nutrient levels of the recipient soils. Moreover, it is also forbidden to use anaerobic digestate in non-cropping seasons. Consequently, in typical full-scale scenarios, the handling of the liquid digestate presents numerous challenges that include large storage area requirements and long-distance transportation to target cropping areas, which imparts a negative economic value [10,11]. Therefore, as livestock farms become more separated from the target nutrient sinks (the crop lands), there is a need to shift focus to the alternative utilization of surplus anaerobic digestate other than land spreading.

One of the promising alternatives to improve resource recovery from agricultural wastes after AD treatment is the integration of AD with pyrolysis where a portion of the non-biodegradable material and lignocellulosic agricultural residues can be used to produce additional energy. Simultaneously, the resultant biochar can also be used to adsorb and concentrate the nutrients from the liquid phase of anaerobic digestates and then used as soil amendment and fertilizer. Biochar has a highly porous structure, large surface area, and high cation exchange capacity all of which bestows on it a high sorptive capacity that can be exploited during nutrient recovery [12,13]. Apart from the cation exchange and large surface area, biochar is recalcitrant, which enables large amounts of carbon to be stored in the soil [14]. The combination of the above-mentioned characteristics makes biochar a good candidate for nutrient recycling.

Indeed, several studies have demonstrated that biochar can adsorb nitrogen (as NH_4^+–N, NO_3^-–N, and Urea), phosphorus (as orthophosphate), potassium, and organic matter from different aqueous solutions such as landfill leachates, anaerobic digestates, urine, and livestock wastewater [15–18]. As a soil amendment, biochar has been reported to offer several benefits, which include increased soil texture, soil carbon, nutrient retention, and cation exchange capacity, beside support to microbial diversity that increases mineralization and availability of nutrients in amended soils [19–21]. In a recent study, Fidel et al. [22] evaluated the potential reduction of greenhouse gases (N_2O and CO_2) emissions from biochar-amended soils based on laboratory soil incubations experiments and field scale studies under continuous cropping with four crop systems namely; no-till continuous corn, switch grass, forb mix, low-diversity and high-diversity grass mix. Their results highlighted that biochar had no effect on long term (>60 days) soil CO_2 emissions, but was able to suppress by 27% for the entire growing season of maize growing. The NO_2 reduction potential in continuous cropping systems was in part attributed to decreased soil bulk density and increased the absorption capacity for organic molecules and nutrients by biochar, thereby simultaneously increasing oxygen availability and decreasing the availability of substrates to nitrate and nitrite-reducing microbes.

The proposed use of biochar to concentrate and recycle nutrients from liquid anaerobic digestates can create new markets for the material and could also reduce the land requirement for liquid digestate disposal. Moreover, coupling anaerobic digestion with biochar based nutrient recovery fits into the concept of a circular economy where maximum value can be achieved from the solid and liquid waste streams [23–25]. In this novel context, the AD process extracts biomethane from the biodegradable biomass while the pyrolytic process can extract additional energy in the form of syngas and bio-oils from the solid AD digestate, and non-biodegradable biomass meanwhile, the nutrient enriched biochar could be marketed as a value added soil amendment and biofertilizer.

In ecological engineering literature, there is a growing research interest in using nutrient-enriched biochar as alternative slow release fertilizer [26–28]. However, only a few studies have so far evaluated digestate nutrients adsorption and their recycling through using the enriched biochar as both a soil amendment and alternative fertilizer [12,29–31]. From all the above-mentioned studies, nutrient enriched biochar showed positive benefits in increasing the crop growth and yield. The increase in crop growth and yield was attributed to the increased nutrient retention, whereby biochar adsorbs nutrients and slowly releases them to match the crop uptake rates, hence reducing potential leaching.

While the above reports are promising, there is still no consensus on the "net absolute benefits" of applying biochar for nutrient recovery. This is because biochar addition to soils does not always give consistent yield increases and the plant responses to biochar addition vary widely. In addition, the mechanisms behind the capture and subsequent release of organic or inorganic mineral nutrients by different types of biochar is not sufficiently understood. Some researchers argue that the high sorptive capacity of most biochars, which strongly binds vital nutrient elements, could limit a sufficient supply available for plant absorption [15,32]. Others point to the possible increase in soil toxicity from heavy metals, especially through indiscriminate use of biochar from mixed feedstock for digestate nutrient recovery [33–35]. From the above discussion, it is implied that more studies are needed, especially those that compare plant responses to different enriched biochar materials relative to chemical fertilizers to establish the potential chemical fertilizer substitution values.

To fill the knowledge gaps, this study investigates whether nutrients adsorbed by biochar could be available to support maize (*Zea Mays* L.) growth in comparison to mineral fertilizer i.e., Nitrogen, Phosphorus and Potash (NPK). The following specific objectives were pursued: (i) to assess the changes in soil properties and nutrition after nutrient laden biochar amendments; (ii) to evaluate the differences in plant growth in soil premixed with digestate enriched biochar in comparison with unenriched biochar, NPK + biochar, and NPK fertilized soils without biochar; (iii) to determine the difference in plant uptake of nutrients and heavy metals (Zn, Cr, Cu, Fe, and As) following the application of digestate enriched biochar. Based on these specific objectives, two hypotheses were tested: H_1, soil application of biochar enriched with anaerobic digestate nutrients would subsequently increase available N, P, and K concentrations, which would result in equal or higher growth of maize when compared to un-amended soils with pure NPK fertilizer or pure biochar (without unenriched); and H_2, the heavy metals in the digestate will be immobilized and their uptake would be reduced because of the application of enriched biochar materials.

2. Materials and Methods

2.1. Biochar Sources and Their Characterization

In this study, two types of biochar were analyzed. The first was produced from corn cobs (CB) and the other produced from wood obtained from the pruning of fig trees (WB). The biochars were produced using slow pyrolysis at 600 °C with the maximum residence time of 10 h. Biochar was characterized for its physiochemical parameter estimations, which include pH values, electro conductivity (EC), oxidative–reductive potential (ORP), and cation exchange capacity (CEC). In addition, the ash content, fixed carbon content, volatiles content, and elemental composition (C, H, N, and S) were determined based on the ASTM 1892 standard for chemical analysis of charcoal [36]. The biochar surface area was determined based on the N_2 adsorption technique using the Brunauer–Emmett –Teller (BET) method. The biochar functional groups and structural chemical composition were determined with the FT-IR, SEM-EDS, and XRD techniques [36,37]. The details of these analyses can be found in Kizito et al. [38].

The surface acidity and alkalinity of the biochars were determined by Boehm titration [39]. The surface acidity was determined by shaking 0.2 g of biochar with 20 mL of 0.1 N NaOH for 24 h. The slurry was filtered through 0.45 μm syringe filters. An aliquot of 5 mL of the NaOH filtrate was transferred to 10 mL of a 0.1 N HCl solution, which neutralized the unreacted base. The solution was back-titrated with 0.1 N NaOH in the presence of a phenolphthalein indicator. The surface basicity was determined similarly to surface acidity. Here, 0.2 g of biochar was shaken with 20 mL of a 0.1 N HCl solution for 24 h. The slurry was filtered and an aliquot of 5 mL of HCl filtrate was transferred to 10 mL of a 0.1 N NaOH solution, which neutralized the unreacted acid. The solution was back-titrated with a 0.1 N HCl solution. The base or acid uptake of biochar was converted to surface acidity or basicity (mmol/g), respectively.

The determination of water-soluble macronutrients (Ca^{2+}, Mg^{2+}, Na^+, K^+, $NO_3{}^-$, and $PO_4{}^{3-}$) was done following a previously published method by Angst and Sohi [40] with slight modification of shaking time from 4 to 24 h. The prolonged shaking/agitation was done to allow detachment and dissolution of ions from biochar into the water. In brief, 1 g of biochar was added to 20 mL distilled water (20:1 mass ratio) and shaken (150 rmp for 24 h) on a rotating shaker. Two blank samples containing only distilled water were also prepared and shaken together with the biochar samples. After shaking, the mixtures were centrifuged (8500 rmp, 10 min at ambient temperature of 25 ± 1 °C) and filtered through 0.45 μm membrane syringe-driven filters. The filtrate was then used for analysis of dissolved ions by ICP-OES (Optima 7300 DV, Perkin Elmer, Waltham, MA, USA). The biochar water holding capacity (WHC) was done following a method described by [41].

2.2. Biochar Nutrient Saturation

The procedure to concentrate anaerobic digestate nutrients onto biochar was as follows; firstly, the raw biochars (CB and WB) were dried overnight (80 ± 5 °C) to stabilize their moisture contents. Afterwards, a known mass of biochar (particle size 0.5–1 mm) was added to a known volume of digestate, at a biochar/solution ratio of 1:5 (*wt/wt*). This mixture was continuously stirred for 48 h to allow for sufficient sorption of nutrients onto the biochar. The pH was adjusted (using 0.5 M H_2SO_4) and maintained at 6 ± 0.5 for the entire sorption period, to maintain the ammonium and simultaneously stimulate phosphate sorption [38]. The concentrations of the target nutrients ($NH_4{}^+$-N, $PO_4{}^{3-}$, and K^+) and trace elements (Na, Ca, and Mg) in the biochars were determined before and after the sorption period as described in the preceding Section 2.1. Subsequently, the amount of nutrients ($NH_4{}^+$–N, K^+, and $PO_4{}^{3-}$) adsorbed onto the biochar were calculated based on initial and final concentrations in sorbate solution and mass of biochar (details of which are given in the Supplementary Materials). After sorption was complete, the solid and liquid phase were separated by manual sieving through 0.25 mm sieves. The separated solids were air dried to a moisture content of 10% ± 2%, similar to the air-dried soil materials as described in Section 2.3.

2.3. Soil Sampling and Analysis

The soil used in this experiment was extracted from a depth of 15–20 cm from a 3-year fallowed plot on farmland owned by China Agricultural University, located in Shuangzhuan village in the outskirts of Beijing City. The soil was air-dried to a 10% moisture content and sieved to uniform particle size of 2.0 mm. The soil was analyzed (in-situ) for several physiochemical properties: soil texture, CEC, soil organic matter (SOC), total carbon (TC), pH, total nitrogen (TN), inorganic nitrogen (NH_4^+–N and NO_3^-–N), total phosphorus (TP), Olsen phosphorus, formic acid extractible P, exchangeable cations (Ca, Na, K, Mg, Mn, Fe, and Al), and heavy metals (Cu, Zn, Cr, and As). Soil texture was determined by the hydrometer method while pH and EC were measured in 1:5 soil/water (*w/v*). The inorganic N (NH_4^+–N and NO_3^-–N) of the soil samples was extracted with 2 M KCl solution (1:5 *v/v* for 1 h) and the corresponding concentrations were determined colorimetrically using a UV spectrophotometer machine. The contents of the total soil organic carbon (TOC) and TN in the soil were measured by following the Kjeldahl Total Nitrogen protocol according to Spokas et al. [19]. The orthophosphate and formic acid extractable P were determined by colorimetry based on the ascorbic acid and molybdenum blue as per the standard method [42]. Meanwhile, Olsen P was analyzed based on the Olsen method [43] whose details are given in Supplementary Material (Text S1).

To measure the exchangeable cations (Ca, Mg, Na, and K), soil was extracted in acidic (pH = 4.35) 1.0 M ammonium acetate solution and the filtrate was then analyzed using ICP-OES, Optima 7300 DV, Perkin Elmer, Waltham, MA, USA). We also investigated total heavy metal concentrations of biochar, in comparison to the anaerobic digestate and soil.

Heavy Metals Determination in Soil, Biochar, and Corn Biomass

The metal content was analyzed using ICP-OES equipment aforementioned after Nitric acid digestion of the samples following a procedure prescribed by Zheljazkov and Warman [44]. Briefly, 1 g of dried soil/biomass subsamples (biochar or corn) was digested with 15 mL of HNO_3 contained in a 250 mL digestion tube. The sample was first heated for 50 min at 90 °C, then the temperature was increased to 140 °C and maintained at this point for 5 h until a clear solution was obtained. The clear solution was allowed to cool down to room temperature (25 °C), then after, the solution was filtered (Whatman No. 42 filter paper) and the filtrate was diluted to 25 mL with deionized water. From the diluted solution, the total and water available content of K, Cu, Cr, As, and Zn were detected by ICP-OES. Multi-element calibration standards in the concentration range of 10–100 mg L^{-1} were used, Quality control measures were taken to assess contamination and reliability of data by running blanks and drift standards after every five determinations to recalibrate the instrument. Moreover, for all elements, analytical precision (RSD) was typically 1%–5% for individual aliquots ($n = 3$).

2.4. Greenhouse Experimental Setup

A completely randomized block design was used to arrange the growth patterns for the different treatments. The following treatments were studied: (1) soil with un-enriched CB/WB (i.e., no NPK or anaerobic digestate nutrients); (2) soil + biochar (CB/WB) enriched with anaerobic digestate nutrients; (3) soil with biochar (CB/WB) + NPK fertilizer; (4) soil with NPK fertilizer and no biochar added; (5) soil without biochar or NPK fertilizer (Control). A further detailed description of the applied treatments is reported in Table 1. Each treatment, including the control, was replicated three times resulting in a total of 42 pots. Biochar was applied to the soil at two rates of 0.75% and 1.5% (*wt/wt*) corresponding to 10 and 20 t carbon/ha, respectively. The selected biochar application rates were based on a review study by Jeffery et al. [45], who reported that an increase in crop yield can be achieved at biochar dosages in the range of 10 – 20 t/ha of biochar. The quantity equivalent of these biochar applications rates was calculated based on soil density, carbon content of the biochar, the recommended field plough depth of 10 cm, and the amount of digestate nutrients added to the soil. The details of the calculation for biochar added are given in the Supplementary Materials (Supplementary Text S2).

Table 1. Description and abbreviations of the different biochar-soil treatments.

No.	Treatment Nomenclature	Treatment Abbreviation
1	Soil + wood biochar	WB-N
2	Soil + corn biochar	CB-N
3	Soil + wood biochar (digestate enriched)	WB-T
4	Soil + corn biochar (digestate enriched)	CB-T
5	Soil + wood biochar + chemical NPK	WB + NPK
6	Soil + corn biochar + chemical NPK	CB + NPK
7	Soil + chemical NPK	PS + NPK
8	Control (no chemical NPK and no biochar)	Control

The experimental plants were maize (Chinese yellow sweet corn; variety GB4404.1–2008) with a 99.1% germination rate. Commercial PVC gardening pots (height 25 cm, 20 cm top diameter, and 15 cm bottom diameter) were used for growing the maize. Prior to maize sowing, the pots were filled with 6 kg of either plain soil or soil premixed with biochar alone or in combination with digestate nutrients or NPK fertilizer. Thereafter, each pot was weighed and labelled according to the treatment given and its replication number. Finally, all the experimental pots were set up in a greenhouse (at 26 ± 2 °C with a humidity of 70% ± 5%) located in Shuangzhuan demonstration farm. The pots were watered daily and left to stand for 10 days to allow the stabilization of the treatments before planting. Afterwards, three maize seeds were centrally planted per pot (4 cm depth) and after complete germination (≈10 days), the two most vigorous seedlings were retained.

The fertilization plan was done as follows; the pots that received anaerobic digestate-enriched biochar, the control treatment pots, and pots where non-enriched biochar was being tested did not receive any form of additional fertilization. The artificially fertilized treatments (i.e., soil + biochar + NPK and soil + NPK treatments) received an equal amount of basal fertilizer of NPK (10–20–20) administered as; 150 mg N, 100 mg P, and 150 mg K per kg soil based on $(NH_4)_2SO_4$, $Ca(H_2PO_4)_2$, and KCl, respectively, according to the prior soil fertility analysis. In addition to NPK, all pots received an equal dose (10 mg/kg soil) of magnesium as $MgCl_2{\cdot}6H_2O$, zinc as $ZnSO_4{\cdot}7H_2O$, ammonium molybdate as $(NH_4)Mo_7O_{24}$, boron as boric acid (H_2BO_3), manganese as $MnSO_4$, copper as $CuSO_4{\cdot}2H_2O$, and Fe as FE-EDTA (10%). The fertilizer was administered via fertigation at the beginning of the experiment. To avoid leaching, the nutrient solution was supplied in four consecutive quantities of 150 mL per pot. Routine watering cycles were done every 2–3 days to keep soil moisture at 60% (by weight) field capacity. In the due course of experimental monitoring, the pots were randomly re-oriented to ensure an even spread of light and weeding was done on a weekly basis.

2.5. Plant Tissue Analysis

Maize plants were harvested after 56 days to obtain the above ground biomass (AGB) yield by cutting the stalks at 3 cm from the surface of the soil. Simultaneously, soils from each pot were collected (soils with similar treatments pooled together into a single sample) and air dried for further analysis as previously described in Section 2.3. The below ground biomass (BGB) was removed from the soil by wetting of the pot contents, the attached soil and biochar particles were removed by washing the roots in water. The green weight of both AGB and BGB was recorded. Thereafter, the materials were oven dried at 60 °C for 72 h followed by grinding (to 0.1 mm, using a hammer mill) for subsequent tissue analysis. The elemental analysis was completed using a VarioMax CHNS analyzer. Meanwhile the TN and total inorganic nitrogen (TIN) were determined using the Kjeldahl method. Olsen P and exchangeable cations were determined as previously described in Section 2.3. Likewise, plant tissue heavy metal uptake (Cr, As, Cu, and Zn) were analyzed after hot block digestion with 0.5 M nitric acid following the same procedure as previously described in Section 2.3. Finally, the macro nutrient (Ca, Mg, Mn, and Na) and heavy metal (Cr, As, Fe, Zn, and Cu) uptake was calculated by multiplying the total dry biomass weight by the individual ion content [46].

Apparent nutrient recovery (ANR) from all treatments was calculated according to Sadaf et al. [47] using Equation (1):

$$ANR(\%) = \frac{(NC_{Ft} \times DM_{Ft}) - (NC_{Cont} \times DM_{Cont})}{TN_{app}} \times 100, \quad (1)$$

where NC_{Ft} is the nutrient content (mg/g of dry matter) in the fertilized treatment, DM_{Ft} represents the total dry matter from the fertilized treatment, NC_{Cont} is the nutrient content in the control (mg/g of dry matter), DM_{Cont} represents the total dry matter of the control treatment, and TN_{app} (mg/kg) represents the total amount of a particular nutrient applied to the soil.

2.6. Statistical Analysis

The means and standard deviations (±SD) of all three replications are reported. Differences among treatments were evaluated through a one-way analysis of variance (ANOVA) test using Tukey's least significant difference (LSD) in the Sigmaplot software version 20 (Systat, Inc, San Jose, CA, USA). A significance level of 95% was considered for statistical inference.

3. Results and Discussion

3.1. Biochar and Soil Properties

The properties of the biochar and soil used in this study are reported in Table 2. The experimental soil is a clay loam soil with medium-to-high bulk density (1.42 kg/m^3), containing carbon (1.67%), nitrogen (1.12%), total P (0.67%), sulfur (0.21%), and Al^{3+} (1.32%), which indicated low fertility. The two applied biochars showed differences in terms of composition and physical characteristics. Notably, WB exhibited a higher carbon content (90.8%), pH (9.4), surface area (147 m^2/g), and cation exchange (121.2 cmol$_c$/kg) compared to CB. On the other hand, CB exhibited higher water holding capacity (173%) than WB (148.7%) (Table 2).

Since the pyrolysis temperature and conditions were similar for all biochars the difference in pH, surface area, CEC, and mineral content was more likely related to the precursor feedstock [48]. Rehrah et al. [48] studied biochar from different materials and attributed the increased surface area to the high presence of compositional compounds (lignin, cellulose, and hemicellulose) in feedstocks. This could be a plausible explanation for the measured high porosity and specific surface area of WB and CB. Likewise, previous studies have reported biochars derived from wood and other biomass containing lignin, including corncobs and maize stalk, to exhibit high cation exchange and surface area [12,49]. The higher content of ash and minerals in the CB biochar could be attributed to the high concentration of metal ions found in raw corncobs. The pyrolysis of corncobs concentrated the already existent metals, which subsequently accumulated in the ash [16,49]. The high water-holding capacity of CB biochar could be due to the existence of oxygen-containing functional groups (C=O, COOH, and O–H) that tend to bond with water molecules. This suggestion is supported by the FT-IR analysis (see Figure S2 in Supplementary Material) where CB biochar exhibited intense bands (1000–1360 cm) corresponding to oxy groups such as ketone, alcohols, and carboxyl groups [50].

Table 2. Selected physiochemical properties of the studied soil and biochar materials (except for percentages, all values are reported as mean ± SD, *n* = 3).

Parameter	**Soil Sample**	**Raw (Unenriched) Biochar**		**Digestate Enriched Biochar**	
		Corncobs (CB-N)	**Wood (WB-N)**	**Corncobs (CB-T)**	**Wood (WB-T)**
Clay (%)	53.3	-	-	-	-
Silt (%)	28.5	-	-	-	-
Sand (%)	18.2	-	-	-	-
pH (KCl)	6.92 ± 0.34	8.94 ± 0.31	9.8 ± 0.43	8.42 ± 0.2	8.6 ± 0.4
EC (µS.m^{-1})	167 ± 4.2	477 ± 14	431 ± 17	512 ± 22	468 ± 18
Density (g/cm^3)	1.43 ±.013	0.384 ± 0.03	0.499 ± 0.071	n.d	n.d
WHC (% dry wt.)	147.4±	173.4	148.7	177 ± 3.3	159 ± 2.6
CEC (cmol/g)	13.8 ± 4.5	53.6 ± 1.0	121.2 ± 1.1	38 ± 4.2	86 ± 3.6
BET-N_2 (m^2/g)	-	33.4 ± 5.1	147.0 ± 26	n.d	n.d
Total pore volume (mL/g)	-	0.068	0.176	n.d	n.d
Total C (%)	1.67	77.4	90.0	81 ± 3.1	91 ± 1.8
Total N (%)	1.12	1.24	0.41	4.11	3.36
Sulphur (%)	0.21	0.15	0.031	0.27	0.18
Ash (%)	n.d	11.6	4.2	12.4	4.9
C/N	1.49	62.4	219.5	19.7	27
H/C	n.d	0.042	0.23	0.031	0.185
O/C	n.d	0.120	0.069	0.084	0.024
Surface Acidity (mol$_c$/kg)	n.d	1.23 ± 0.3	0.92 ± 0.12	0.87 ± 0.07	0.79 ± 0.1
Na (%)	0.12	0.88	0.13	1.77	0.73
Mg (%)	0.22	0.37	0.24	0.56	0.43
Al (%)	1.32	0.12	0.11	0.14	0.17
Si (%)	0.17	0.74	0.11	0.75	0.14
P (%)	0.67	0.43	0.23	1.89	0.93
K (%)	2.16	3.30	0.91	10.4	5.83
Ca (%)	0.91	0.51	0.12	1.56	0.94
Fe (mg/kg)	46.4 ± 11	234.8 ± 23	6.70 ± 0.8	247.4 ± 21	10.38 ± 1.3
Mn (mg/kg)	58.3 ± 5.4	27.2 ± 3.9	4.33 ± 0.7	29.4 ± 4.2	5.44 ± 1.1
Zn (mg/kg)	6.26 ± 1.3	12.8 ± 1.7	3.47 ± 0.67	13.2 ± 1.8	13.43 ± 2.2
Cu (mg/kg)	5.66 ± 0.9	3.90 ± 0.71	2.44 ± 0.66	8.73 ± 1.1	10.47 ± 1.7
Cr (mg/kg)	1.74 ± 0.1	1.89 ± 0.2	1.21 ± 0.12	1.93 ± 0.44	2.62 ± 0.65
As (mg/kg)	1.10 ± 0.2	1.23 ± 0.3	3.16 ± 0.8	1.43 ± 0.5	3.66 ± 0.74

The abbreviations CB-N, WB-N, CB-T and WB-T represent unenriched corn biochar, wood biochar, enriched corn biochar, and enriched wood biochar respectively. n.d—not determined; EC—electro conductivity; CEC—Cation Exchange Capacity; WHC—Water holding Capacity; ORP—Oxidative Reductive Potential; BET-N_2—Surface Area determined by Brunauer–Emellet–Teller Nitrogen adsorption Method; C/N—Carbon/Nitrogen ration; H/C and O/C—Hydrogen to Carbon ratio and Oxygen to Carbon ratio respectively.

3.2. Recovery of Nutrients via Biochar Sorption

The amount of adsorbed nutrients (mg/g) was determined by the monolayer sorption isotherm and are as follows: WB had 23.6, 19, and 21 mg/g, while CB had 15.3, 23, and 27.2 mg/g for $NH_4{}^+$–N, $PO_4{}^{3\text{-}}$–P , and K^+, respectively. These were in the order of WB > CB. The variations in the adsorbed amounts could be corroborated with the differences between the individual physiochemical properties of the biochars (Table 2). Notably, WB has high porosity and is negatively charged, thus it adsorbed more $NH_4{}^+$ and less $PO_4{}^{3-}$ compared to CB. Furthermore, the lower sorption of K^+ onto both CB and WB was observed and could be due to the high rate of desorption from these biochars due to cation competition at the biochar active sites [31]. The $PO_4{}^{3-}$ and $NH_4{}^+$ sorption mechanisms for these biochars have been reported in our previous studies [17,38].

Based on the adsorbed amounts and the analyzed physicochemical properties such as pH, EC, CEC, fixed carbon, and macro element contents (Table 2), it can be concluded that the studied biochars were good candidates for nutrient recovery in accordance to previous studies [16,18]. From the measured sorption amounts, the theoretical quantity of nutrients adsorbed onto the biochar (per ton of char materials) was calculated to be: 21.4 kg N/ton, 17.2 kg P/ton, and 19.1 kg K/ton for WB; and 13.3 kg N/ton, 20.86 kg P/ton, and 30.8 kg K/ton for CB.

Based on the adsorbed amounts, the potentially added nutrients at the two applied biochar rates of 10 t/ha (0.7% *w/w*) and 20 t/ha (1.4% *w/w*) were calculated. At the lower rate of 10 t/ha, an equivalent biochar mass of 42 g was added to each pot while 85.7 g of biochar per pot was the equivalent applied to attain the 20 t/ha rate. Assuming 100% bioavailability of the adsorbed nutrients in the soil, the added enriched biochar at 10 t/ha represented an NPK fertilizer equivalent of 165 mg N, 133 mg P, and 147 mg K per kg of soil for WB and 107 mg N, 161 mg P, and 190 mg K per kg of soil for CB. At 20 t/ha, the NPK equivalent from applying 85.7 g of digestate enriched biochar per pot (20 t/ha rate) was calculated to be 337 mg N, 271.4 mg P, and 300 mg K per kg of soil for WB and 219 mg N, 329 mg P, and 389 mg K per kg of soil for CB. In theory, based on the adsorbed amounts, the enriched biochar materials added higher ratios of NPK compared to the mineral fertilizer treatments (see Section 2.4).

Previous studies suggest however, that for biochar to make a viable contribution to soil N, P, and K nutrient pools, the nutrients need to be released into the soil solution in concentrations within ranges suitable for plant uptake and increased crop production [20]. Moreover, the rates of nutrient release in different biochar will depend on the nutrient pool in the biochar and the soil conditions [51]. To study this phenomena, desorption experiments (data not shown) were carried out based on distilled water (pH = 7.2 ± 0.2) and results showed that only 60%–68%, 70%–76%, and 75%–80% of the previously adsorbed NH_4^+–N, PO_4^{3-}–P, and K respectively were desorbed. Using desorption in water as a proxy for expected nutrient release in soil, the actual expected NPK equivalents would be 112 mg N, 101 mg P, and 125 mg K and 73 mg N, 122 mg P, and 162 mg K for WB and CB, respectively, at 10 t/ha. Meanwhile, at 20 t/ha, the values would be 229 mg N, 206 mg P, and 255 mg K for WB and 149 mg N, 250 mg P, and 331 mg K for CB.

3.3. Effects of Biochar Amendments on Soil pH, EC, and CEC

Both pH and EC are important parameters that are associated with crop growth. For instance, changes in soil pH have implications on nutrient mineralization and availability (especially N and P) as well as the uptake of base cations such as Ca^{2+}, Mg^{2+}, and K^+ [50]. Additionally, higher EC values are associated with high salinity, a condition that could lead to a decrease in water uptake by plant roots and cause a subsequent nutrient imbalance [52]. In this study, the NPK treatments without biochar slightly reduced the pH by 0.22 when compared to the control but did not significantly increase the EC or CEC (Table 3).

The application of biochar alone or in combination with digestate/NPK increased the soil pH by 0.6–1 points and CEC by >300% (Table 3). The influence of biochar on soil pH, EC, and CEC was higher in WB treatments. Considering the physiochemical properties of the studied biochars (Table 2), the increase in soil pH in amended soils could be due the increased ash accretion and the subsequent dissolution of hydroxides and carbonates [53]. The observed increase in EC in biochar treatments could be attributed to the release of basic cations into the soil [54]. The observed increase in CEC after biochar treatments could be explained by the existence of various chemical functional groups that render the biochar as an active chemical exchange surface [55,56]. According to Zornoza et al. [56], slow pyrolyzed biochars, similar to the ones used in this study, tend to have a greater number of functional groups with the potential to form carboxylic carbon that retains cations on its surface, thus increasing CEC. Furthermore, slow pyrolyzed biochars tend to have relatively high volatile humic matter and when they are applied into the soil, some level of mineralization occurs, which releases charged low molecular weight humic-like substances that could increase CEC [15,57]. Similar studies have reported an increase in EC, CEC, and pH after soil amendment with biochar [45,57]. However, contrary to the results of previous studies [54], the doubling of the biochar load from 10 to 20 t/ha did not significantly increase EC, pH, or CEC.

Table 3. Changes in soil pH, electro conductivity (EC), cation exchange capacity (CEC), macronutrients, and heavy metals as influenced by the different soil biochar amendments (values given as mean ± SD, $n = 3$).

					Macronutrients (g/kg Dry Matter)						Heavy Metals Content (g/kg Dry Matter)				
Treatment *	**pH**	**EC [a]**	**CEC [b]**	**TOC [c]**	**TN [d]**	**TP [e]**	**Ca**	**K**	**Na**	**Mg**	**Fe**	**Cu**	**Zn**	**Cr**	**As**
10 t/ha biochar application															
CB-N	7.7 ± 0.4	289 ± 33	41 ± 7.4	1.86 ± 0.3	0.19 ± 0.01	0.16 ± 0.01	0.13 ± 0.003	0.21 ± 0.03	0.15 ± 0.01	0.11 ± 0.01	81.4 ± 11	1.77 ± 0.3	2.44 ± 0.9	0.61 ± 0.07	0.31 ± 0.03
WB-N	8.1 ± 0.1	317 ± 23	58 ± 13	2.47 ± 0.2	0.11 ± 0.03	0.15 ± 0.03	0.05 ± 0.001	0.16 ± 0.01	0.10 ± 0.03	0.03 ± 0.001	36.9 ± 2.7	0.61 ± 0.05	0.73 ± 0.02	0.12 ± 0.08	0.14 ± 0.05
CB-T	7.6 ± 0.3	299 ± 27	37 ± 6.2	2.18 ± 0.1	0.33 ± 0.06	0.29 ± 0.03	0.16 ± 0.02	0.49 ± 0.01	0.46 ± 0.06	0.33 ± 0.04	93.2 ± 15	6.31 ± 0.6	7.16 ± 1.6	1.89 ± 0.1	1.14 ± 0.1
WB-T	8.3 ± 0.3	346 ± 28	43 ± 5	2.77 ± 0.3	1.21 ± 0.2	0.38 ± 0.00	0.14 ± 0.01	0.42 ± 0.04	0.57 ± 0.05	0.31 ± 0.01	53.1 ± 7.3	2.84 ± 0.9	4.83 ± 0.8	1.21 ± 0.3	1.13 ± 0.1
CB + NPK	7.4 ± 0.24	266 ± 33	42 ± 8.1	1.84 ± 0.1	1.78 ± 0.5	0.36 ± 0.02	0.14 ± 0.001	0.57 ± 0.07	0.43 ± 0.01	0.21 ± 0.03	83.5 ± 13	1.98 ± 0.6	5.11 ± 0.9	0.69 ± 0.05	0.14 ± 0.2
WB + NPK	8.4 ± 0.22	303 ± 21	56 ± 11	2.44 ± 0.4	1.43 ± 0.1	0.29 ± 0.01	0.10 ± 0.002	0.34 ± 0.06	0.13 ± 0.001	0.15 ± 0.03	59.3 ± 6.9	1.83 ± 0.07	1.17 ± 0.2	0.11 ± 0.007	0.89 ± 0.05
20 t/ha biochar application															
CB-N	8.1 ± 0.3	346 ± 25	49 ± 5.7	8.59 ± 1.1	0.33 ± 0.03	0.18 ± 0.04	0.11 ± 0.01	0.39 ± 0.06	0.23 ± 0.01	0.13 ± 0.05	100.6 ± 33	2.33 ± 0.7	2.76 ± 1.1	0.81 ± 0.04	0.21 ± 0.005
WB-N	8.5 ± 041	374 ± 33	60 ± 11	11.3 ± 0.8	0.14 ± 0.02	0.15 ± 0.01	0.04 ± 0.04	0.04 ± 0.001	0.15 ± 0.009	0.04 ± 0.001	48.7 ± 9.3	0.94 ± 0.07	1.42 ± 0.3	0.48 ± 0.02	0.2 ± 0.005
CB -T	7.8 ± 0.4	288 ± 21	42 ± 6.4	9.87 ± 1.4	0.53 ± 0.01	0.49 ± 0.05	0.21 ± 0.01	1.51 ± 0.4	0.51 ± 0.02	0.23 ± 0.05	110.1 ± 26	8.77 ± 1.7	6.55 ± 1.8	1.84 ± 0.5	0.95 ± 0.01
WB-T	8.0 ± 0.2	383 ± 35	66 ± 9.2	11.9 ± 1.2	1.19 ± 0.1	0.55 ± 0.01	0.18 ± 0.01	1.23 ± 0.5	0.35 ± 0.4	0.14 ± 0.01	69.3 ± 4.9	3.73 ± 0.8	6.6 ± 0.4	1.79 ± 0.6	0.25 ± 0.03
CB + NPK	7.8 ± 0.1	253 ± 14	42 ± 6.7	9.11 ± 0.8	0.34 ± 0.07	0.34 ± 0.04	0.13 ± 0.02	1.99 ± 0.05	0.21 ± 0.01	0.21 ± 0.03	129.5 ± 7.4	6.65 ± 1.5	6.93 ± 1.3	0.88 ± 0.006	0.32±
WB + NPK	8.6 ± 0.3	296 ± 26	58 ± 9.1	11.2 ± 0.6	0.23 ± 0.03	0.23 ± 0.01	0.10 ± 0.004	1.44 ± 0.44	0.13 ± 0.03	0.16 ± 0.02	63.3 ± 9.2	3.27 ± 0.3	7.16 ± 0.7	0.31 ± 0.06	0.24 ± 0.07
Soil + NPK	7.3 ± 0.4	178 ± 22	11.6 ± 4.7	1.18 ± 0.3	0.89 ± 0.4	0.89 ± 0.07	0.12 ± 0.01	2.43 ± 0.81	0.15 ± 0.01	0.35 ± 0.04	78.2 ± 10	7.16 ± 0.8	11.67 ± 2.3	1.66 ± 0.1	1.13 ± 0.2
Plain Soil	6.9 ± 0.3	167 ± 4.2	13.8 ± 4.5	1.17 ± 0.5	0.12 ± 0.006	0.07 ± 0.000	0.09 ± 0.001	0.26 ± 0.021	0.12 ± 0.03	0.09 ± 0.01	47.4 ± 5.6	5.66 ± 1.1	6.24 ± 1.1	1.74 ± 0.2	1.1 ± 0.08

* CB-N, WB-N; CB + NPK, WB + NPK; CB-T, WB-T and soil + NPK refer to unenriched corncobs, and wood biochar treatments; corncobs and wood biochar added together with NPK; corn cobs, and wood biochar enriched with nutrients from anaerobic digestate and soil mixed with NPK fertilizer respectively (details in Table 1). [a] EC is the electro-conductivity (μS/cm) is electro conductance which reflects the total dissolved solids; [b] CEC (cmol$_c$/kg) is Cation Exchange Capacity; [c] TOC (%) represents total organic carbon; [d] TN represents Total Nitrogen and this parameter was measured as ((TIN = NH_4^+–N, NO_3^-) + Total Organic Nitrogen); [e] TP represents Total Phosphorus measured as (PO_4^{3-} + Organic P).

3.4. Effect of Digestate-Enriched Biochar on Soil Nutrients

3.4.1. Soil Organic Carbon

The changes in soil organic carbon (SOC) and macronutrients including total nitrogen (TN), total inorganic nitrogen (TIN), and the total P, Ca, K, and Mg according to the different soil amendments are presented in Table 3 and Supplementary Table S2. From the data, addition of biochar alone or in combination with digestate nutrients/NPK significantly ($p < 0.001$) increased the SOC over the control and unamended NPK treatments. For instance, at 20 t/ha of biochar load, digestate-enriched biochar increased SOC by 231.9% and 370% in CB and WB treatments, respectively, compared to 224.8% and 188% achieved with unenriched WB and CB treatments, respectively (Table 3). Given that the amount of carbon added to the soil for each biochar was the same, the differences in SOC among the different types of biochar can be attributed to the rate of carbon mineralization. To this end, the superior increase in SOC for digestate-enriched biochar treatments could be attributed to the sorption of liable organic matter in the digestate that is released into the soil [50]. The observed increase in SOC in this study, is corroborated in previous studies reported by Kasozi et al. [15] and Bruun et al. [32,58] who attributed it to the increased release and microbial mineralization of organic carbon compounds entrained in the porous structure of biochar.

The positive increase in SOC and macronutrients upon soil amendment with digestate-enriched biochar materials indicates that coupling anaerobic digestion and pyrolysis could be an important step in improving and maintaining long term fertility [59]. Moreover, in the present study the increase in SOC also resulted in synergistic benefits such as reduced bulk density and increased plant-availability of Ca, K, P, and Na (see Supplementary Table S2). The increase in SOC following the addition of biochar to soil has been reported to raise the C:N ratio, which in turn could affect N mineralization, especially in low fertility soils [14]. In their meta-analysis review on actual benefits of soil amendment with biochar, Jeffery et al. [45] reported that application of biochars with low nutrient content, results in negative effects on crop production. These findings suggest that the use of enriched biochar can simultaneously improve both SOC, N content, and P content thus providing a more sustainable soil fertility benefit. Practical benefits of biochar increasing SOC and maintaining soil fertility have been demonstrated under field conditions in tropical African soils in Zambia, where an increase in maize yield of 234% was achieved [60] and in Nigeria were NPK enriched biochar amendment increased rain fed rice by >100% [61]. In both studies the authors partly attributed the increase in yield to the positive soil property improvement such as increased SOC, reduced bulk density, and increased water retention.

3.4.2. Soil Nitrogen and Phosphorus

The soils amended with digestate-enriched biochar showed higher concentrations of both water extractable P and Olsen P compared to the soils amended with unenriched biochars and the control; however, it was lower than soils amended with NPK (Figure 1). Compared to the control and unenriched biochar materials, application of digestate-enriched biochar increased TP by 170% and 450% for WB and CB, respectively. Surprisingly, the increase in biochar load did not increase extractable P in the amended soils. The amount of extractable P was reduced at the higher biochar loading of 20 t/ha for all biochar treatments (Figure 1). The decrease in available P was 32% and 47% after application of CB and WB, respectively. Our results are contrary to those reported from a recent study in acidic soils [62]. According to Pandit et al. [62], plant available phosphorous was increased from 23.4 to 84.1 mg/kg as the biochar load increased from 0.5% to 2%, representing an increase of 72.17%. In the present study, the observed reduction in extractable P with an increase in biochar load could be a result of immobilization due to strong sorption onto the biochar surface.

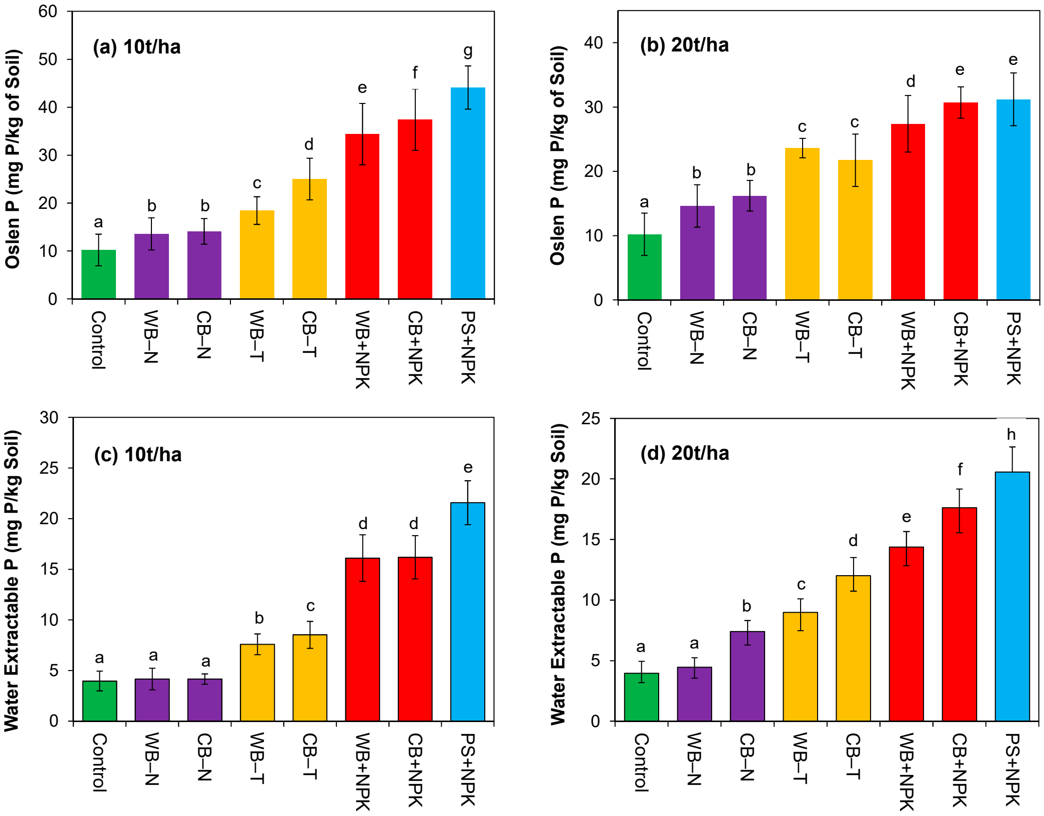

Figure 1. (**a**) Soil available phosphorus (Olsen P) at 10 ton biochar per hectare. (**b**) Soil available Phosphorus (Olsen P) at 20 ton biochar per hectare. (**c**) Water extractible Phosphorus at 10 ton biochar per hectare. (**d**) Soil available water extractible phosphorus at 20 ton per hectare measured after 55 days of soil incubation (27 ± 2 °C) with different biochar and mineral fertilizer; Nitrogen, Phosphorus and Potash (NPK) treatments. The values are presented as means ± SE, $n = 3$ and the different letters inside a bar of each treatment represents significant differences between various treatments following analysis of variance (ANOVA) test (post hoc Tukey test, $p < 0.05$).

Soil TN concentrations were affected by the applied biochar type and the biochar application rates (Table 3). In the unenriched biochar treatments, the highest TN was observed in soil amended with CB, which was expected since the concentration of nitrogen in the CB was much greater than WB (Table 3 and Supplementary Table S2). Compared to the control, applying 10 t/ha of digestate-enriched CB increased TN by 137% while WB increased TN by 50%. Similar to the trend observed with SOC and TP, the digestate-enriched biochars increased soil TN when compared to their unenriched forms with NPK. However, both digestate-enriched biochar and biochar + NPK treatments resulted in a lower increase in soil TN when compared to pure NPK treatments.

Soil TIN was low in all unenriched biochar treatments and ranged from 2.29 to 8.90 mg/kg (WB at 10 t/ha). The low increase in TIN from biochar applications has been reported in other studies [63,64]. However, contrary to the results of previous studies, in this study, the application of digestate-enriched biochar slightly increased ($p < 0.01$) the content of TIN in the soil, which indicates a slightly higher rate of mineralization. The rate of N mineralization was significantly higher in treatments with digestate-enriched biochar in comparison to their unenriched forms, but lower than that observed in biochar + NPK and only NPK treatments (Figure 2). For the digestate-enriched biochar, the rate of N mineralization increased with an increase in the biochar load from 10 to 20 t/ha, while a decreased trend was observed for unenriched biochar and biochar + NPK treatments. The rate and amount of N mineralization did not significantly ($p > 0.05$) increase with an increase in unenriched biochar loading except for WB treatments with NPK fertilizer.

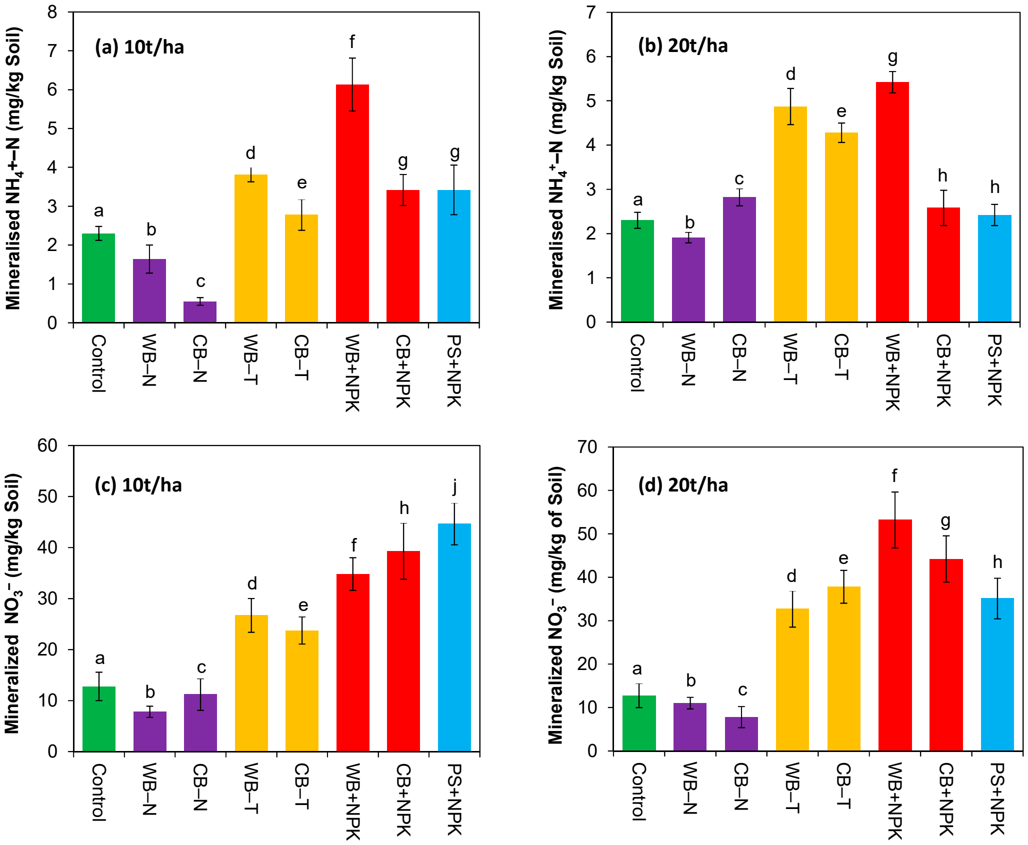

Figure 2. (**a**) Mineralized ammonium ($NH_4{}^+$–N) at 10 ton biochar per hectare. (**b**) Mineralized ammonium ($NH_4{}^+$–N) at 20 ton biochar per hectare. (**c**) Mineralized nitrate ($NO_3{}^-$–N) at 10 ton biochar per hectare. (**d**) Mineralized nitrate ($NO_3{}^-$–N) at 20 ton biochar per hectare measured after 55 days of soil incubation (27 ± 2 °C) with different biochar and NPK treatments. The values are presented as means ± SE, $n = 3$ and the different letters inside a bar of each treatment represents significant differences between various treatments following ANOVA test (post hoc Tukey test, $p < 0.05$).

It could be possible that with increased biochar loading in the soil, the available $NH_4{}^+$–N could be reduced due to the increased sorption from the soil. However, the amount of mineralized ammonium and nitrate in the soil increased after soil amendment with biochar + NPK treatments, which contradicts previous findings by Taghizadeh-Toosi et al. [65] who reported significantly lower $NO_3{}^-$ concentrations with increasing biochar additions from 15 to 30 Mg biochar/ha. In the present study, the observed increase in mineralization following soil amendment with digestate-enriched biochar could be attributed to increased organic matter along with more adsorbed ammonium. The increased organic matter could facilitate microbial colonization that could in turn oxidize the adsorbed ammonium [65].

3.4.3. Soil Extractible Macronutrients (Ca, Na, K, and Mg)

Apart from SOC, TN, and TP, the application of digestate-enriched biochar also has a greater increase in Ca, Mg, and Na compared to the control and unenriched biochars (Table 3 and Supplementary Table S2). Most remarkably, the addition of CB added more total P, K, Ca, and Mg compared to the control and pure NPK treatments. Soil total K concentrations in biochar amended soils ranged from 0.16 to 0.57 g/kg at 10 t/ha. At 20 t/ha the K concentration ranged from 0.04 to 2.78 g/kg (Table 3). Unenriched WB caused a deficit (−37%) in soil K, based on the control. However, when WB was enriched with digestate nutrients and used as a soil amendment, it increased soil K by 62% and by 373% at 10 and 20 t/ha, respectively. Conversely, the application of enriched CB (CBT) at 10 t/ha increased soil K by 58% and 151% and 20 t/ha, respectively. Whilst the unenriched CB (CBN) increased total K by

51%. Interestingly, digestate-enriched biochar treatments significantly ($p < 0.005$) increased available soil K compared to NPK + biochar treatments.

Soil total sodium (Na), calcium (Ca), and magnesium (Mg) were also increased with the application of digestate-enriched biochar compared to the unenriched biochar and control treatments. The Na concentrations ranged from 0.10 to 0.57 g/kg at 10 t/ha and 0.120 to 0.84 g/kg at 20 t/ha (Table 3). The Mg concentrations from biochar amendment ranged from 0.030 to 0.33 g/kg and 0.04 to 0.35 g/kg at 10 and 20 t/ha, respectively. The Ca concentrations ranged from 0.050 to 0.19 g/kg and 0.04 to 0.54 g/kg in biochar amended treatments at 10 and 20 t/ha, respectively. The control contained 0.26, 0.12, 0.09, and 0.09 g/kg for K, Na, Mg, and Ca, respectively. The measured concentrations and percentage increment over the control in pure NPK treatments were 0.12 g/kg (32%), 0.243 g/kg (833%), 0.15 g/kg (12%), and 0.350 g/kg (289%) for Ca, K, Na, and Mg, respectively. On the other hand, the measured Ca, K, Na, and Mg concentrations and percent increment of biochar and NPK combinations over the control (No biochar and no NPK) were 0.140 (52%), 0.57 (119%), 0.43 (26%), and 0.21 g/kg (71%) for CB; and 0.10 (13%), 0.34 (31%), 0.13 (8%), and 0.15 g/kg (26%) for WB.

In comparison, the application of digestate-enriched biochar resulted in the higher availability of K, Ca, and Mg compared to biochar + NPK treatments, NPK treatments, and the control. This result implies that using digestate-enriched biochar resulted in a more complete recycle of a wide variety of nutrients compared to artificial fertilizers. Previous studies [54,62,66] corroborate this finding, it has been reported that the application of biochar adds a variety of nutrients compared to pure mineral fertilizers. Previous studies have also reported an antagonistic relationship between Ca and K, i.e., an increase in the concentration of potassium often limits the uptake of calcium [67]. Based on this proposition, the low uptake of Ca in pure NPK treatments could be attributed to the high K concentration in the mineral fertilizer.

*3.5. Effect of Biochar Amendment on Maize (*Zea Mays*) Growth and Nutrition*

3.5.1. Effect on Biomass Yield

During the whole growth period, plant height increased in the order NPK > biochar + NPK > digestate + biochar > unenriched biochar > control. Maize biomass also responded differently ($p \leq 0.001$) to the two biochar types and their NPK combinations. In general, the application of digestate-enriched biochar produced significantly ($p < 0.05$) higher below-ground biomass (BGB) and above-ground biomass (AGB) compared to the unenriched biochar. The increase in biochar load from 10 to 20 t/ha, resulted in a significant increase ($p < 0.05$) in biomass for maize grown in soil amended with digestate-enriched biochar and biochar + NPK treatments than in treatments with unenriched biochar and soils with only NPK.

The highest AGB (0.28 kg/pot) was achieved with pure NPK treatments while the lowest amount of AGB (0.11 kg per pot) was achieved in soils amended with unenriched fig tree wood biochar (WB) treatments. The percent increase in AGB was in the order of PS + NPK > CB + NPK > WB + NPK > CB-T > WB-T > CB-N > WB-N (Figure 3). Meanwhile, the application of digestate-enriched biochar at both 10 and 20 t/ha had an equal or higher increase in BGB compared to treatments with NPK.

Similar results were reported by Mete et al. [27], Lima et al. [68], Sadaf et al. [47] where NPK treatments gave higher maize biomass and soybean yield, compared to biochar or biochar in combination with NPK. In a recent study, in [61] an increase in yield and N uptake in rain-fed rice yield in two contrasting soils was reported, following the application of rice husk biochar combined with chemical NPK.

Our results are in sharp contrast to what was reported by Schulz and Glaser [26], who compared the effects of biochar to organic and inorganic fertilizers on soil quality and the growth and yield of oats (*Avena sativa* L.) under tropical conditions (26 °C and 2600 mm annual rainfall) in an infertile sandy soil. The authors reported that chemical NPK fertilizer treatment (111.5 kg N/ha, 111.5 kg P/ha, and 82.9 kg K/ha) yielded the lowest plant biomass (0.14 mg/ha, which was ≈25% lower than the yield from biochar or compost treatments). The results of Schulz and Glaser [26] could partly be because they used a sandy soil and intensive irrigation regimes (100 mL of water per day per 113 cm^2). Under these conditions nearly all the applied inorganic N could be leached out after application.

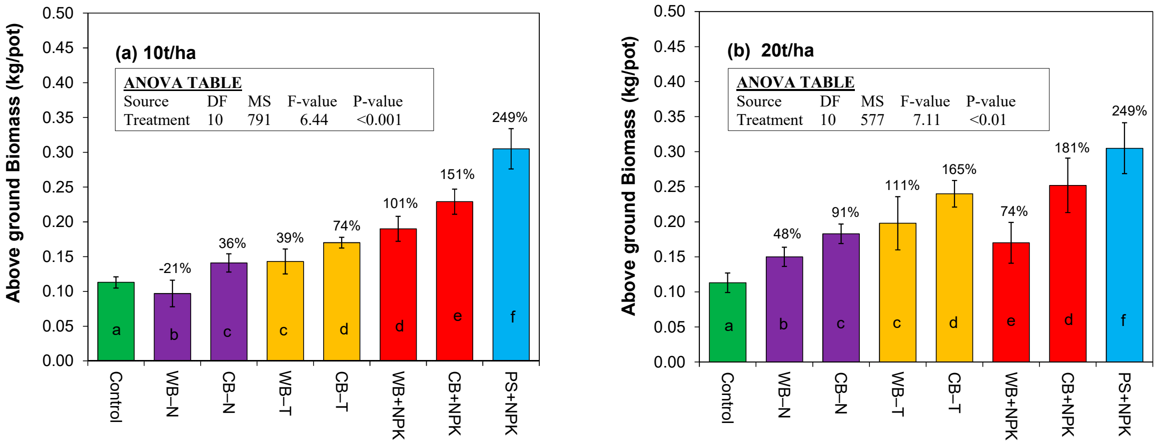

Figure 3. (**a**) Effect of different biochar and/or NPK combinations on aboveground maize dry biomass at 10 ton biochar per hectare. (**b**) Effect of different biochar and/or NPK combinations on aboveground maize dry above ground biomass at 20 ton biochar per hectare The values are presented as means ± SE, $n = 3$ and different letters inside a bar of each treatment represents significant differences between various treatments following ANOVA test (post hoc Tukey test, $p < 0.05$). The percentage values above the bars denote the relative change in dry biomass production in the presence of biochar and/or NPK, as compared to the control receiving no biochar and no NPK.

In this study, a loamy clay soil was used and the superior performance with chemical NPK fertilizer in the short term (first growth cycle) could be linked with the increased bioavailability of mineral ions in the soil compared to when biochar is present. In Figure 2, faster rates for N and P mineralization were observed for soils amended with NPK, which indicates increased availability of mineral ions. Comparatively, in the presence of biochar, the release of mineral ions could be slower and more dependent on the microbial access and mineralization of the bound nutrients [32]. In addition, bearing in mind that this study was short term, perhaps the mineral fertilizers supplied more bioavailable nutrients when compared to the slower release from enriched biochar. The slower mineralization in biochar amended soil is also beneficial because in the long run it can reduce rapid flushing of nutrients that could easily leach out [14,62]. Post-harvest soil analysis revealed that in pure NPK treatments the residual nutrients were lower, perhaps indicating that performance could be short lived due to a flush release of nutrients. The proposition that slow nutrient release in biochar treatments could be more beneficial in the long term is supported by previous studies. For instance, Hewage [69] reported that the total AGB of maize increased during four consecutive cropping seasons after one-time application of biochar at 5 t/ha with no additional NPK fertilizer to Gleyic Podzol with its poor physical properties and low TOC content.

3.5.2. Effect on Nutrient and Heavy Metal Uptake

Given that both the anaerobic digestate and biochar used in this study contained some heavy metals and macronutrients (Table S1 in Supplementary Material), the potential transfer to the soil via biochar amendment and the tissue uptake was investigated. The distribution of the selected metals (Cr, Zn, Cu, and As) and macronutrients (Ca, Mg, K, Fe, and TP) in soil, as well as their subsequent tissue uptake under the different treatments are displayed in Table 4.

Table 4. Nutrient and heavy metal uptake in plant tissues as influenced by different treatments. The values given as mean ± SD, *n* = 3 and mean differences were analyzed using ANOVA testing and Fisher least significant difference (LSD at $p = 0.05$).

Treatment [a]	**Nutrient Uptake (mg/kg DM)**					**Heavy Metal Uptake (mg/g DM)**				
	TN	**TP**	**K**	**Ca**	**Mg**	**Cu**	**Zn**	**Cr**	**As**	**Fe**
10 t/ton biochar application										
Control [b]	213 ± 22 ^{a}	41 ± 6.7 ^{a}	256 ± 34 ^{a}	43 ± 6.1 ^{a}	61 ± 4.3 ^{a}	2.60 ± 0.5 ^{a}	2.93 ± 0.81 ^{a}	0.57 ± 0.08 ^{a}	0.46 ± 0.03 ^{a}	18.96 ± 2.1 ^{a}
Soil + NPK	528 ± 27 ^{b}	154 ± 8.2 ^{b}	890 ± 44 ^{b}	178 ± 13 ^{b}	230 ± 11 ^{b}	3.29 ± 0.9 ^{b}	5.49 ± 0.9 ^{b}	0.55 ± 0.04 ^{a}	0.48 ± 0.07 ^{a}	31.28 ± 3.2 ^{b}
CB-N	251 ± 16 ^{c}	67 ± 5.2 ^{c}	470 ± 21 ^{c}	56 ± 7.7 ^{c}	78 ± 8.9 ^{c}	0.81 ± 0.4 ^{c}	1.15 ± 0.3 ^{c}	0.20 ± 0.03 ^{b}	0.13 ± 0.05 ^{b}	48.84 ± 5.1 ^{c}
WB-N	193 ± 5.7 ^{a}	51 ± 5.1 ^{e}	187 ± 6.7 ^{e}	26 ± 4.5 ^{e}	21 ± 3.7 ^{d}	0.28 ± 0.07 ^{d}	0.34 ± 0.04 ^{e}	0.04 ± 0.04 ^{d}	0.06 ± 0.003 ^{c}	22.14 ± 3.1 ^{a}
CB-T	344 ± 24 ^{e}	88 ± 7.4 ^{d}	636 ± 37 ^{f}	47 ± 7.1 ^{a}	91 ± 6.3 ^{e}	2.90 ± 0.9 ^{b}	3.37 ± 0.7 ^{a}	0.62 ± 0.03 ^{a}	0.48 ± 0.08 ^{a}	55.92 ± 4.6 ^{c}
WB-T	277 ± 21 ^{c}	81 ± 5.9 ^{d}	368 ± 33 ^{h}	64 ± 7.2 ^{c}	57 ± 4.4 ^{a}	1.31 ± 0.3 ^{f}	2.27 ± 0.8 ^{a}	0.40 ± 0.1 ^{a}	0.48 ± 0.06 ^{a}	31.86 ± 4.3 ^{b}
CB + NPK	372 ± 29 ^{g}	121 ± 11 ^{e}	590 ± 37 ^{f}	98 ± 10 ^{e}	116 ± 12 ^{f}	0.91 ± 0.09 ^{c}	2.40 ± 0.6 ^{a}	0.23 ± 0.09 ^{b}	0.06 ± 0.003 ^{c}	50.1 ± 7.6 ^{c}
WB + NPK	322 ± 24 ^{e}	101 ± 7.8 ^{d}	455 ± 36 ^{c}	63 ± 8.3 ^{c}	57 ± 9.2 ^{a}	0.84 ± 0.06 ^{c}	0.55 ± 0.07 ^{e}	0.03 ± 0.007 ^{d}	0.37 ± 0.06 ^{e}	35.58 ± 5.4 ^{b}
F-value	68.45	23.56	73.81	34.93	59.32	51.47	38.94	12.67	27.38	71.84
P-value	0.043	0.054	0.038	0.05	0.045	0.048	0.049	0.068	0.053	0.0045
LSD [d]	4.12	1.76	5.72	3.31	4.01	3.43	3.11	0.54	0.89	7.78
20 t/ton biochar application										
CB-N	288 ± 19 ^{a}	90 ± 5.7 ^{a}	532 ± 44 ^{a}	76 ± 12 ^{a}	100 ± 14 ^{a}	1.07 ± 0.2 ^{a}	1.30 ± 0.3 ^{a}	0.27 ± 0.07 ^{a}	0.09 ± 0.02 ^{a}	40.24 ± 5.6 ^{a}
WB-N	178 ± 13 ^{c}	56 ± 4.7 ^{c}	230 ± 34 ^{c}	37 ± 3.5 ^{c}	43 ± 4.1 ^{c}	0.43 ± 0.07 ^{c}	0.67 ± 0.1 ^{c}	0.16 ± 0.05 ^{a}	0.08 ± 0.02 ^{a}	19.48 ± 4.1 ^{c}
CB-T	492 ± 33 ^{d}	121 ± 14 ^{b}	789 ± 82 ^{d}	128 ± 15 ^{b}	136 ± 9.3 ^{b}	4.03 ± 0.6 ^{d}	3.08 ± 0.7 ^{b}	0.61 ± 0.1 ^{b}	0.40 ± 0.09 ^{c}	44.04 ± 3.7 ^{a}
WB-T	367 ± 22 ^{e}	81 ± 8.6 ^{a}	745 ± 56 ^{e}	110 ± 9.1 ^{d}	76 ± 5.5 ^{d}	1.72 ± 0.2 ^{f}	3.10 ± 0.4 ^{b}	0.59 ± 0.08 ^{c}	0.11 ± 0.05 ^{a}	27.72 ± 4.7 ^{d}
CB + NPK	528 ± 42 ^{f}	147 ± 17 ^{d}	861 ± 77 ^{f}	144 ± 9.0 ^{b}	139 ± 11 ^{b}	3.06 ± 0.5 ^{d}	3.26 ± 0.5 ^{b}	0.29 ± 0.09 ^{d}	0.13 ± 0.03 ^{a}	37.4 ± 3.0 ^{e}
WB + NPK	478 ± 42 ^{d}	114 ± 10 ^{b}	969 ± 66 ^{b}	79 ± 5.7 ^{a}	84 ± 6.3 ^{a,d}	0.35 ± 0.07 ^{c}	3.37 ± 0.6 ^{b}	0.10 ± 0.04 ^{a}	0.10 ± 0.04 ^{a}	25.32 ± 4.3 ^{d}
F-value	61.71	66.78	71.34	51.85	33.63	53.78	67.87	11.79	9.54	23.41
P-value	0.035	0.049	0.027	0.031	0.044	0.032	0.049	0.067	0.086	0.050
LSD (0.05)	4.32	6.25	8.57	7.71	6.9	8.32	3.3	0.09	0.067	2.7

The values given as mean ± SD, *n* = 3 and mean differences were analyzed using a Two Way ANOVA test and Fisher Least Significant Difference (LSD) at $p = 0.05$. [a] CB–N, WB–N; CB + NPK, WB + NPK; CB–T, WB–T and soil + NPK refer to unenriched corncobs and wood biochar treatments; corncobs, and wood biochar added together with NPK; corn cobs, and wood biochar enriched with nutrients from anaerobic digestate and soil mixed with NPK fertilizer respectively (see Table 1). [b] Control—Plain soil without NPK fertilizer and no biochar amendment. [c] DM—dry matter, [d] LSD—least significant difference at 5% level of significance.

In general, macronutrient (TP, K, Ca, Fe, and Mg) concentrations were significantly ($p < 0.05$) influenced by type and rate of biochar application in the soil. As opposed to WB, all the CB treatments had increased tissue uptake of K, Ca, TN, TP, and Mg compared to the control. The highest P levels were found in CB treatments. The high nutrient content in CB resulted in increased bioavailability in the soil and consequently higher uptake by maize. CB increased nutrient uptake as follows: TP (63%), Ca (83%), K (48%), and Mg (38%). On the contrary, compared to the control, the uptake of nutrients from WB treatments was significantly lower ($p > 0.05$): TN (9.4%), Ca (27%), K (39%), and Mg (−5.6%). Finally, compared to the control, the soil + NPK treatment increased nutrient uptake as follows: TN (35%), TP (146%), K (256%), Ca (46%), and Mg (24.6%).

When compared to pure NPK treatments, the application of digestate-enriched biochar or biochar + NPK provided more macronutrients that subsequently resulted in relatively higher uptake of Ca, K, TP, and Mg. In particular, the digestate-enriched biochar treatments resulted in significantly higher uptake of Ca (30%–45%, $p < 0.05$) and Mg (30%–50%, $p < 0.05$) compared to NPK treatments. Likewise, when digestate-enriched biochar treatments are compared to their unenriched counter parts (biochar without fertilizer NPK/digestate), the enriched biochar treatments resulted in significantly higher ($p < 0.001$) uptake of TP, K, Ca, and Mg. On the other hand, the biochar + NPK treatment gave significantly higher ($p < 0.001$) macronutrient uptake when compared to the digestate-enriched biochar and unenriched biochar treatments (Table 4 and Supplementary Table S3). Surprisingly, even though the increase of biochar load from 10 to 20 t/ha increased macronutrients in the soil, it did not significantly increase their uptake into the plant tissues within the biochar treatments. However, significant differences were found when compared to the control (Table 4).

One plausible explanation for the increased macronutrient uptake from biochar treatments could be that biochar adds nutrients to the soil and moreover, due to high CEC and pH these nutrients are retained in the soil thus increasing their bioavailability [55]. The increased N and P uptake in digestate-enriched biochar and biochar + NPK treatments compared to the control and pure NPK fertilizer treatments implies that biochar can concentrate soil N as either NH_4^+ or NO_3^- and soil P as PO_4^{3-}. From this, the crop root systems could exploit regions of high biochar distribution and uptake more of these two nutrients from the soil.

In regard to heavy metal uptake, digestate-enriched biochar application significantly increased the content of metalloids in the soil compared to the control and pure NPK treatments (Table 4). In Table 4, it can be observed that digestate-enriched biochar significantly ($p < 0.005$) increased Fe, As, Zn, and Cu concentrations in soil compared to unenriched biochar, biochar + NPK, and the control. Interestingly, except for Fe, all biochar treatments resulted in significantly lower heavy metal tissue uptake compared with the control and pure NPK treatments. The increase in biochar load from 10 to 20 t/ha increased heavy metal immobilization with <60% reduction in Cu, Cr, As, and Zn tissue uptake.

The apparent heavy metal recovery (according to Equation (1), Section 2.5), which indicates the actual uptake as a percentage of total added ion concentration, revealed that only 20% and 25% of heavy metal content were bioavailable from WB and CB treatments, respectively. This implies that 75%–80% of the total heavy metals introduced into the soil by application of digestate-enriched biochar was immobilized. Meanwhile, >90% of the heavy metals in the unenriched biochar was immobilized. This finding provides hope that pyrolysis of agricultural wastes and the subsequent use of digestate-enriched biochar in soil could be a viable nutrient and energy recovery route for agricultural waste and manure nutrients.

The observed heavy metal immobilization in the soil could be directly linked to the biochar surface chemistry. In particular the studied biochar had a high CEC, large surface area, and a wide variety of surface functional groups (OH^-, C–H, O–C=O, and C=C) (see FT-IR results in Supplementary Material) all of which could facilitate the chemisorption and complexation of metalloids making them less bioavailable for plant uptake [70,71]. The complexation of the heavy metals with biochar may have occurred via physical adsorption or surface functional group interactions involving metalloid exchange with biochar alkali and alkaline earth cations [71]. Secondly, CB in particular had a relatively high mineral content (Table 3). In this case, higher metalloid immobilization could have occurred via co-precipitation with carbonates, silicates, and phosphate in biochar matrix forming precipitates of metal hydroxide, carbonate, or phosphate that plants cannot uptake [49,55].

4. Conclusions

This study evaluated the potential of recycling nutrients from liquid digestate via biochar adsorption and its application as a media for soil amendment and fertilizing maize growth. The results demonstrated the possibility of using biochar for concentrating digestate nutrients and their efficient recycling.

The digestate-enriched biochar treatments significantly improved soil quality as it provided higher soil organic matter (232%–514%) and macronutrients (110%–230%) as opposed to the unenriched biochar and control treatments. Consequently, application of digestate-enriched biochar achieved higher total biomass yield, which was 75%–85% of what was achieved using NPK fertilizer.

Biochar could immobilize >70% of added heavy metals in the soil as well as enabling a slow release of macronutrients in the soil. This was demonstrated by the high content of nutrients and heavy metals in biochar amended soils in post-harvest soil sample analyses. Based on the observed slow release of macronutrients and heavy metal immobilization, the use of nutrient enriched biochar instead of liquid digestate could be a better alternative to increase nutrient utilization efficiency as well as reducing on heavy metal pollution in soils.

In summary, this study established that the use biochar to concentrate nutrients from the liquid phase of the digestate and their recycling into the soil gives positive effects on soil micro and macro nutrients, organic matter, heavy metal immobilization, and biomass yield. In this context, for the impoverished farmers, digestate enriched biochar could partly replace the demand for chemical fertilizer and promote organic farming. Meanwhile, the added value of liquid digestates and biochar could be improved and thus a zero waste agricultural production system could be achieved on farms in the context of a circular economy.

Supplementary Materials: The following are available online at http://www.mdpi.com/2071-1050/11/11/3211/s1, Table S1: Summary of anaerobic digestate slurry characteristics used in the study. Table S2: Percentage increase in soil nutrients and heavy metals over the control as influenced by different biochar treatments at 10 ton and 20 ton per ha application rates. Table S3: Percentage increase over the control treatment (only soil) of nutrients uptake (mg.kg-1 dry matter) and heavy metal uptake (mg.g-1 dry matter) in plant tissues as influenced by different treatments. Figure S1: FTIR diagram showing the peaks for corncobs biochar (CB) and Wood biochar (WB). Figure S2: Scanning Electronic Microscopy (SEM) and Energy-Dispersion X-ray Spectroscopy (EDS) images of biochar before and after Sorption (a) Wood biochar (WB) before sorption (b) Corn Cobs biochar (CB) before sorption, (A) Wood biochar (WB) after digestate nutrients enrichment (B) Corncobs (CB) after digestate nutrients enrichment.

Author Contributions: S.W. participated in conceptualization, design of experimental methodology, research supervision and writing, S.K. participated in the conceptualization, actual data collection (experimentation) and original drafting of the manuscript, and H.L. and J.L. participated in the experimental setup, direct data collection and analysis, H.B. participated in the manuscript review process and statistical analysis and R.D. was the principal investigator and research project administrator.

Funding: This research was funded by the project of "Research Fund for International Young Scientist (51650110489). We also would like to give thanks to the AIAS-COFUND Fellowship Programme, which is funded by the European Union's Seventh Framework Programme for Research, Technological Development and Demonstration under grant agreement no. 609033. We likewise greatly appreciate the critical and constructive comments from the anonymous reviewers, which have helped improve this manuscript.

Conflicts of Interest: The authors declare absolutely no conflict of interest in the preparation and submission of this manuscript.

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