

Article

Biochar–Nitrogen Composites: Synthesis, Properties, and Use as Fertilizer for Maize

Caio Pereira Mota and Carlos Alberto Silva *

Departamento de Ciência do Solo, Universidade Federal de Lavras (UFLA), Lavras 37203-202, Brazil; caio.mota2@estudante.ufla.br

* Correspondence: csilva@ufla.br

Abstract: Nitrogen (N) is highly reactive and prone to being easily lost into the air and soil water. Biochar–N composites have proven effective in nourishing and improving maize growth. The aim of this study was to synthesize and assess the properties of composites made from biochars (pyrolyzed at 300 °C) derived from chicken manure (N = 3.5%) and leguminous cake (N = 9%) and enriched with ammonium sulfate (AS), urea, and diammonium phosphate (DAP). The biochar pH was adjusted to approximately 6 using sulfuric and phosphoric acids prior to formulating the six tested composites. Maize was cultivated for 50 days under greenhouse conditions, with evaluations of the maize dry matter (DM) and N in the plant shoot. The biochar and composite properties underwent scrutiny for chemical and physicochemical attributes, as well as for soluble N in water and in an HCl solution. Throughout maize cultivation, the release of N as ammonium and nitrate from the composites and pure biochars in the Oxisol solution was successively assessed. Composites formulated with DAP and supplied at a dose of 270 mg kg⁻¹ N yielded the same maize dry matter as composites in which 400 mg kg⁻¹ N was supplied to plants. Regardless of the N source, at the end of maize cultivation, the residual N in the Oxisol was reduced and inadequate for a new cultivation, even in soils treated with urea. Notably, the biochar–N composites, particularly those formulated with DAP, were as effective as urea in nourishing and promoting robust maize growth. In contrast, the maize biomass was lower for plants fertilized with pure biochars, indicating that the N from the carbonized matrices was insufficient for optimal biomass production.

Keywords: N pools in biochar; nitrification; NH₄⁺:NO₃⁻ ratio; N volatilization; aromatic N; pyrolysis; maize



Citation: Mota, C.P.; Silva, C.A. Biochar–Nitrogen Composites: Synthesis, Properties, and Use as Fertilizer for Maize. *AppliedChem* **2024**, *4*, 157–173. <https://doi.org/10.3390/appliedchem4020011>

Academic Editor: Jason Love

Received: 20 January 2024

Revised: 19 February 2024

Accepted: 11 April 2024

Published: 17 April 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The challenge of increasing global food production is becoming progressively more daunting, given the backdrop of intensified climate change and the scarcity and expense of inputs such as nitrogen (N) synthetic fertilizers, which Brazil heavily relies on importing. Nitrogen is highly reactive and can easily escape into the air and soil water bodies, thus driving up fertilization costs and diminishing the efficiency of N use by crops. This, in turn, poses the risk of contaminating the soil, air, and water of cropland areas. Brazil stands as one of the world's major food producers and a significant importer of synthetic N fertilizers, with over 80% of the N applied in Brazilian cropland originating from other countries. On average, 50% of the N from synthetic fertilizers applied to the soil is lost, notably through ammonia volatilization, denitrification (N₂O emission), and leaching [1]. Barbosa [2] observed that N rates exceeding 150 kg ha⁻¹ N promote the leaf area index and increase corn yield. Additionally, [3] noted that yields exceeding 5.5 t ha⁻¹ of corn were achieved when plants were fertilized with N rates greater than 200 kg ha⁻¹ N, highlighting the substantial demand for N in maize fields. In addition to increasing the rate of N added to soils, it is crucial to enhance the nutrient use efficiency by crops. Therefore, understanding the characteristics of each nitrogen fertilizer is necessary, as well as exploring

novel technologies, organic residues, and wastes to develop eco-friendly synthesis routes for the production of renewable and efficient N fertilizers, thereby increasing the N use efficiency in Brazilian cropland areas.

The production of mineral N biochar-based fertilizers, hereafter named composites, is an alternative to enhance the N use efficiency by crops [4,5]. Biochar is a product obtained through the thermal degradation of renewable biomass in the absence of O₂. Apart from optimizing several N transformation processes in the soil, biochar alters the soil properties and serves as a N source for crops, although the pools, availability, and kinetics release of N by carbonized matrices are not yet fully understood. In this direction, N associated with biochar matrices is limited in the short-term to crops [6–8]. When it comes to N-doped biochars, the formulated fertilizers exhibit a characteristic of having contrasting N pools, both slow-release and N pools that are gradually supplied throughout the crop cycle, reducing N losses to the air and water, while increasing the N use efficiency by plants [4–9]. Mandal et al. [10] observed that, due to its capacity to adsorb ammonium, biochar can retain N in soil for a more extended period, preventing N losses through volatilization at soil pH levels above 6.3. The physical adsorption of nitrate N in the pores of biochar cannot be ruled out, and the physical adsorption of nitrate in carbonized matrices could be a mechanism to prevent nitrate losses through leaching in soils treated with biochar [11]. Thus, the adsorption of nitrate in biochars could be a suitable strategy to reduce N losses in the soil–plant system [12]. The use of biochar–N composites increased the nutrient use efficiency by corn in 44% over N from urea [11]. In the phase of composite formulation, the correct choice of biomass, pyrolysis conditions, mineral N sources, and reaction conditions (pH, minimal N volatilization, full interaction of N with the biochar organic matrix through weak bonds, etc.) are crucial steps. Some biochar matrices have a high capacity to sorb nutrients or are prone to strongly interact with different N chemical species; thus, they are illegible as raw materials to produce N composites. By growing maize in two contrasting soils, Banik et al. [13] verified that mixtures of biochar with urea in variable ratios and the use of slow-release biochar-based urea, urea ammonium nitrate, and S-coated urea decreased the release and loss of N from conventional urea, reduced nitrate leaching, and increased the dry matter of maize shoot (1–34%), root (0–23%) biomass, N-recovery efficiency (17–50%), and soil potential mineralizable N over pure urea and S-coated urea. Activation (H₂O₂, HNO₃, and ultrasonication) and the enrichment of biochar with N led to the formation of new surface carboxylic functional groups, which increased the interaction of the charred matrices with urea; the urea-treated biochars had 14.5% of total N soluble in water, and the N chemical species in the biochar activated with HNO₃ represented up to 60% of the total N [4]. Biochar-based fertilizers enriched with urea gradually release N for plants, acting as true slow-release fertilizers [4].

In order to maximize pyrolysis, feedstocks must be dried, and differences in the cellulose, hemicellulose, and lignin content of sources are also important in biochar synthesis [14]. It has been reported that biomass rich in lignin and poor in N can produce biochars with higher yield but lower N content over feedstocks enriched in N [15]. Pyrolysis is essentially the thermal process of converting different feedstocks into biochar [16]. Slow pyrolysis involves the use of low temperatures over a longer residence time, whereas fast pyrolysis operates at higher temperatures over a shorter residence time, ensuring less N in the final biochar [17]. Therefore, slow pyrolysis increases the biochar yield and contributes to preserving N in the final biochar [8]. In its fast version, pyrolysis is supposed to increase the production of bio-oil and gas [18], although nitrogen losses through volatilization are elevated, requiring more mineral N in composite production because the charred matrices are impoverished in recalcitrant and heterocyclic N forms [8]. However, there is still limited information regarding N pools present in charred matrices, the right synthesis conditions and biochar type to be employed in the formulation of biochar–N composites. Thus, it is necessary to add more information regarding the composite production processes, as well as on the kinetics of N release by the carbonized matrices used in the formulation of composites. The use of biochar not enriched with N in field conditions is not a suit-

able practice to fertilize crops due to the high cost of elevated biochar rates used in crop fertilization. However, the doping of biochar with mineral N fertilizers can enhance the agronomic efficiency of the novel N sources, leading to the generation of biochar-based N composites with improved capacity to supply N to crops at low rates [4,5,19]. Several feedstocks have been employed to produce nitrogen-rich biochars, including the mixture of biochar with poultry litter [20], swine manure [21], crop and post-harvest wastes, slaughterhouse wastes, and remnants of non-commercial wastes from meatpacking industrial plants. The adjustment of the pH and the chemical functionalization of biochars through acid solutions can control the pH, facilitate the interaction of N with the biochar organic matrix, and create new organic functional groups, thus elevating the agronomic efficiency of the composite as well. Functionalization of biochar with the use of inorganic acids acts to increase the cation exchange capacity (CEC), adjusting the pH of alkaline nature biochars, and enhancing nitrogen retention in more labile forms during pyrolysis, resulting in a higher availability of nitrogen in the final biochar [4,22]. Acid-treated biochar, besides exhibiting an increased yield compared to non-treated biochar, maintains the characteristics and improves the capacity of biochar to sorb nutrients and interact with mineral N. This approach has the potential to reduce or partially replace the use of conventional mineral N fertilizers, contributing to protect the environment by minimizing nutrient losses and promoting a more balanced and continuous supply of N for crops [23,24].

Studies testing N fertilizer rarely involve the determination of N availability in both the soil solution and whole soil. The synthesis of composites should adhere to basic stoichiometric principles, such as maintaining the right pH to prevent N losses, adjusting carbon levels to interact effectively with N from synthetic sources, and selecting appropriate acids to acidify the feedstock. Conditions for optimizing biomass and the pyrolysis process must be observed to retain N and organic functional groups with negative charges on the surface of the final biochars. This study adhered to these fundamental principles used in the synthesis of N fertilizers, with the innovation of targeting the production of high agronomic value biochar–N composites. Globally, synthetic N fertilizers are highly soluble and rapidly released in soils. Therefore, in shaded tropical soils, N is prone to leaching and removal from the plant root zone. The use of carbon-based fertilizers (or composites) could be a suitable strategy to improve the agronomic efficiency of the imported and expensive soluble N fertilizers commonly used in Brazil. This novel category of N fertilizers encompasses different pools of N, which are released more gradually to crops in tropical soils. Nitrogen fertilizers, on a global scale, must be used more efficiently to prevent soil, water, and air pollution. As far as is known, the main principles governing the efficient use of N by crops have not yet been fully understood. The use of N composites could contribute to the development of novel fertilizer synthesis routes, waste recycling, and better-nourished crops in highly weathered tropical soils. The main goal of this study is to synthesize N composite fertilizers as effective as urea—the most commonly used N source in Brazil—for improving maize nutrition and growth. Simultaneously, N availability in the soil solution and the whole soil was monitored during different maize growth stages, as well as soil residual N after maize cultivation.

The hypotheses of this study are as follows: (i) Composites based on diammonium phosphate (DAP) and ammonium sulfate (AS) are more efficient than urea in providing N for maize; (ii) nitrogen supplied by pure biochars without N doping is insufficient to meet the maize's N requirement; (iii) the release of N from composites occurs gradually in the soil solution and is synchronized with the maize growth stages of higher N demand; (iv) Composite production represents an effective approach to increase the use efficiency of synthetic N fertilizers. Consequently, biochar–N composites have high agronomic value as N sources for maize. The aims of this study were as follows: (i) identify synthesis routes and evaluate the properties of N composites (DAP, AS, and urea) based on biochars derived from chicken manure and leguminous cake, and pyrolyzed at 300 °C; (ii) assess the efficiency of biochar–N composites in supplying N for maize, and, simultaneously, examine the release of N as ammonium and nitrate in the Oxisol solution; (iii) determine

the agronomic effectiveness of the composites in ensuring robust maize growth over plants fertilized with urea.

2. Materials and Methods

2.1. Soil and Feedstock Characterization

This study was carried out at the Laboratory of Soil Organic Matter Stud (LEMOS), Department of Soil Science, Federal University of Lavras, Lavras, Minas Gerais state (MG), Brazil. Two contrasting feedstocks were used for biochar production: chicken manure (4.38% N) and leguminous cake (9.09% N). These feedstocks were used in the synthesis of composites based on their medium and high levels of N and enormous availability in Brazil for the production of biochar. The mineral fertilizers employed in the composite formulation were ammonium sulfate (AS), diammonium phosphate (DAP), and urea (UR). The N sources chosen are those mostly used in Brazilian cropland areas. The soil utilized to grow maize was collected in Itumirim, MG, and it is classified, according to the Brazilian Soil Classification System, as a Red-Yellow Latosol (Oxisol, according to Soil Taxonomy). The main attributes of this Oxisol under native vegetation conditions are shown in Table 1. Before maize cultivation, the soil acidity was corrected with a mixture (4:1) of calcium carbonate and magnesium carbonate to achieve a pH in the soil of approximately 6.0, using analytical-grade (0.75 g kg⁻¹ carbonate) reagents to ensure the supply of Ca and Mg for optimal maize growth. The ammonium N and nitrate N content in the Oxisol were, respectively, 55 mg kg⁻¹ and 35 mg kg⁻¹, while the soil's total N content of the Oxisol was 0.15%. The Oxisol sample had 20.1 g kg⁻¹ soil organic matter (SOM), 470 g kg⁻¹ clay, 80 g kg⁻¹ silt, and 450 g kg⁻¹ sand.

Table 1. Chemical attributes of the Oxisol (under natural conditions) utilized to cultivate maize.

Soil	pH	K	P	Ca	Mg	Al	H + Al	SB *	t	
		(mg dm ⁻³)		(cmol _c dm ⁻³)						
Red-Yellow Latosol	4.7	226	0.1	0.9	0.39	0.35	2.8	1.87	2.22	
T (cmol _c dm ⁻³)	BS	m	C	P-Rem	Zn	Fe	Mn	Cu	B	S
	(%)		(mg dm ⁻³)		(mg dm ⁻³)					
4.67	40	16	1.06	36.6	0.2	36	3.5	0.1	0.1	1.2

* SB, sum of bases; BS, base saturation; m, aluminum saturation; T, CEC at pH 7; t, effective CEC at soil natural pH; m, aluminum saturation; P-Rem, remaining phosphorus, C, total carbon determined in a TOC analyzer.

2.2. Acidification of Feedstock and the Composite Synthesis

Four biochars were formulated from two feedstocks (chicken manure and leguminous cake) pyrolyzed at 300 °C. Chicken manure was collected, pre-milled in a ball mill, and subsequently ground and passed in a 25-mesh sieve. This material underwent acidification with pure per analysis sulfuric and phosphoric acids prior to pyrolysis. Before mixing with mineral N sources, the acidification procedure was performed aiming to reach a targeted biochar pH in the range between 5 and 6 (the best pH range to avoid ammonia volatilization and the predominance of ammonium over nitrate in the fertilizer to decrease N leaching). Sulfuric acid at the concentration of 0.3 mol L⁻¹ and phosphoric acid at the concentration of 0.5 mol L⁻¹ were sprayed on 100 g of chicken manure, which was in sequence dried. The sulfuric acid was used in the acidification phase to increase the S content of the DAP-biochar composites, while phosphoric acid was chosen to add more P in the AS-biochar-derived composites, considering the strong synergy of N with P and S. Both acids also act in the functionalization of the biochar matrix. The leguminous cake, naturally, had a pH (~6.0) appropriate to produce the respective biochars. Therefore, the material was mixed with mineral N sources without the acidification step. A single biochar was also made with chicken manure without acidification. The feedstocks were pyrolyzed at 300 °C with a residence time of 30 min and the use of a muffle furnace with a stainless-steel

sealed chamber. In the composite synthesis, one chicken manure biochar acidified with sulfuric acid, one chicken manure biochar acidified with phosphoric acid, one leguminous cake biochar without acidification, and three different analytical-grade mineral N sources, ammonium sulfate (21% N), diammonium phosphate (18% N), and urea (46% N), were mixed, thus resulting in the production of six contrasting biochar–N composites.

Two composites were produced with DAP through its mixture with chicken manure (CM) and leguminous cake (LC) biochars, aiming at a final total N content of 10% in the respective composites. Two composites were also created with ammonium sulfate aiming to achieve 15% of N in the final composite. In addition, two other composites were produced by mixing urea with chicken manure, and leguminous cake-derived biochars aiming at a target N level of 20% in the final composite. Therefore, the composites were formulated by mixing varying proportions of synthetic N fertilizers and biochars, based on the following equation:

$$\text{N in composite(\%)} = [(1 - a) \times (\text{N in biochar})] + [(a) \times (\text{N in synthetic fertilizer})] \quad (1)$$

where “a” represents the mass of the synthetic N fertilizer used in the synthesis of the composite.

2.3. Laboratory Analysis

The pH and electrical conductivity of the samples were determined in distilled water at a ratio of 1:10 (0.5 g of biochar composite/5 mL of water) through the shaking of the suspension at 100 rpm for 1 h in a Toledo digital pH meter (Mettler-Toledo AG, Schwerzenbach, Switzerland) [25]. After the digestion of the biochar in sulfuric acid, the total nitrogen content in the biochars and composites was determined using the Kjeldahl method [23]. The yield of the biochars was calculated by the following formula [23]:

$$\text{Biochar yield (\%)} = \left(\frac{\text{biochar mass}}{\text{feedstock mass} + \text{additive mass}} \right) \times 100 \quad (2)$$

where the additive mass corresponds to the mass of the strong acid sprayed on the feedstock used to produce the biochar.

Total carbon content was determined using an automatic analyzer (dry combustion) with the sample heating at 950 °C in an Elementar automatic analyzer, model Vario TOC Cube (Elementar, Germany). Regarding ash analysis, a routine analytical protocol was adopted [23], and samples were previously dried at 100 °C in an oven until a constant weight was achieved. After this step, the samples were burned at 650 °C for 8 h. The ratio between the mass of the residual burned material and the mass material dried at 100 °C only was then calculated to determine the biochar and composite ash content [23].

2.4. Nitrogen Release in Soil Solution

Throughout the maize growth cycle, the Oxisol solution was collected using solution samplers [24] inserted in all pots to assess the N as ammonium and nitrate content. An aliquot of each treatment of the soil solution was initially distilled with 0.2 g of magnesium oxide to create an alkaline condition to convert ammonium into NH₃. The distillation was followed by titration to determine the ammonium nitrogen (N-ammonium) content of each sample. Subsequently, 0.2 g of Devarda’s alloy was added to the same previously digested sample, creating an environment capable of converting NO₃[−] into NH₃. The NH₃ was collected in a boric acid solution, which was titrated with a 0.07143 mol L^{−1} HCl solution to determine the content of N as ammonium and nitrate in the soil solution [23,25].

2.5. Infrared Spectroscopy

All biochars, as well as the six composites had their spectral signatures evaluated in the middle-infrared region (ATR-FTIR). The main peaks and bands observed in the spectra were identified. To identify primary linkages, organic functional groups, and spectroscopic

signatures generated in the range of 3500 to 600 cm^{-1} , the composites' and biochars' FTIR spectra and their bands were interpreted based on the libraries available elsewhere [26–31].

2.6. Maize Cultivation Conditions

The agronomic effectiveness of the composites, pure biochars (without N doping), and the two controls (positive control with N from urea and negative control: no N supplied to plants) was assessed by growing maize for 50 days in a pot filled with 1 kg of Oxisol samples. Ten seeds were planted in each pot, and thinning was performed, leaving only two plants per pot after germination. The experiment was carried out in greenhouse conditions, using a complete randomized block design, aimed at evaluating the agronomic efficiency of the composites in supplying N to maize plants. Soil solution samplers used to extract soluble mineral N were installed on the first day of the study, with five solution sampling times performed throughout the maize cultivation cycle. In total, 10 treatments were evaluated, with 4 replicates per treatment, totaling 40 experimental units. Fertilization was performed by adding to soil 400 mg kg^{-1} N, 600 mg kg^{-1} P, and 400 mg kg^{-1} K. Regarding composites formulated with DAP, a lower N dose (270 mg kg^{-1} N, compared with 400 mg kg^{-1} N added in other treatments), was provided to maize plants. Micronutrient fertilization with Zn, Cu, Mn, and B at the concentrations of 4, 2.50, 2.65, and 1.1 mg kg^{-1} , respectively, was also performed with the use of pure per analysis sulfate salts and boric acid [27]. Fertilization was performed one day before maize planting, which took place on 28 March 2023. The N from urea was split into three applications, with the first two initial fertilizations of 150 mg kg^{-1} N each, and the last one with the addition to the soil of 100 mg kg^{-1} N as urea. On the planting day, soil sampling was carried out in each pot to quantify the content of N ammonium and N nitrate in the whole Oxisol simultaneously to maize sowing. At the end of the experiment, the maize shoot and root biomass were removed from each pot, dried, and weighed to determine the maize dry matter production. The dried biomass was ground to determine the total N and assess the N accumulated in the maize shoot. Soil samples were stored for further analysis of the soil's residual available N after maize cultivation.

2.7. Hydrolyzable N in Composites and Biochars

In order to assess the solubility of N chemical species in the composites and biochars, the hydrolyzable N was extracted in water and in an acid solution ($\text{HCl } 6 \text{ mol L}^{-1}$) [32]. To evaluate the water-soluble N, 1 g of the material was added to 20 mL of water, and this solution was shaken for two hours. Subsequently, the material was centrifuged at 4000 rpm for 15 min, filtered, and the obtained sample was analyzed according to the protocols previously described for the determination of ammonium N and nitrate N content. The fraction of soluble N in HCl was obtained by adding 0.5 g of the material to 25 mL of a 6 mol L^{-1} HCl solution, with the subsequent digestion of the suspension in a digestion block at 105 °C for 24 h. Later, the residual material was mixed with distilled water as needed to reach 15 mL and filtered for the determination of the total N content, following the protocol described in [22,32].

2.8. Statistical Analysis

All statistical procedures were performed using the SISVAR (Federal University of Lavras, Lavras, Minas Gerais state, Brazil) software [33], with the data previously submitted to analysis of variance. In sequence, means of the treatments were compared by the Tukey's test at $p < 0.05$.

3. Results and Discussion

3.1. Biochar Properties

Chemical activation of chicken manure with sulfuric and phosphoric acids contributed to reducing the pH of their derived biochars. The chicken manure-derived biochar (with no acidification) had a pH equal to 8.5. In the synthesis of the other composites, acid was

used before mixing the biochar with the synthetic N sources. In the case of the leguminous cake, acidification was not necessary, as the non-acidified biochar already had a pH within the optimal range (pH: 5–6) for the reaction and synthesis of N composites. Regarding the ash content, it is noted that leguminous cake had a lower ash content than chicken manure (Table 2). Conversely, chicken manure had a lower content of C and N over the leguminous cake, thus, the high ash and low N content demanded a greater mass of chicken manure-biochar in the synthesis of its derived N composites. During pyrolysis, a large part of the feedstock constituents is converted into gas, resulting in an enrichment of inorganic compounds in the ash, consequently causing a higher pH and ash content in the chicken manure-derived biochars [23]. The chicken manure has a lower C content than LC; thus, its biochars have a higher ash content and higher pH compared to the carbonized matrices derived from the leguminous cake (Table 2). It is important to emphasize that, concerning biochar, a high pH does not necessarily imply a high liming value of the charred matrix, as the biochar liming value depends on the properties of the feedstock pyrolyzed, ash content, chemical nature, and soil acidity neutralization equivalence of inorganic and organic constituents found in the biochar [23].

Table 2. Biochar yield, carbon (C), nitrogen (N), ash content, electrical conductivity (EC), and pH of chicken manure (CM)- and leguminous cake (LC) derived composites and biochars produced after the acidification of the feedstock with phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4).

N Source	Yield, %	C, %	N, %	Ash, %	EC, dS m ⁻¹	pH in Water
Biochar (CM) acidified— H_3PO_4						
	75	23	3.0	60	1.5	5.5
Biochar (CM)— H_2SO_4						
	66	24	3.4	51	2.6	6.1
Biochars without acidification						
BCM	73	30	4.4	35	1.2	8.5
BLC	76	50	9.1	5	2.4	6.2
Composite						
BCMAS	-	9	15	15	65	5.1
BLCAS	-	17	15	9	50.2	5.5
BCMDAP	-	8	10	50	44.9	5.5
BLCDAP	-	16	10	35	41.5	5.9
BCMUR	-	23	20	44	8.1	6.3
BLCUR	-	36	20	10	8.3	5.2

The composites refer to the following: BLCAS = biochar from leguminous cake + ammonium sulfate; BCMAS = biochar from chicken manure + ammonium sulfate; BLCDAP = biochar from leguminous cake + DAP; BCMDAP = biochar from chicken manure + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; BCM = pure chicken manure biochar; BLC = pure leguminous cake biochar.

Regarding the EC, the two composites that stand out are those produced from the mixture of biochars with urea, which had a lower EC than the other composites. Feedstock that underwent acidification showed a greater electrical conductivity than those not acidified. Composites produced with urea were not acidified, which reflects in a lower EC of its derived composites. Thus, the urea composites are less prone to provoking soil salinization or promoting seed death due to high soil EC at maize furrow. The EC of urea-composites is lower than those from the composites derived from AS and DAP. The quantity of soluble salts present in biochar is relevant for fertilizer management because significant amounts of ions in the soil can negatively affect seed germination, soil solution

EC, and plant growth [34]. "It is worth noting that biochars derived from chicken manure exhibit higher electrical conductivity (EC) levels compared to those derived from leguminous cake. The elevated EC values observed in chicken manure-derived biochars align with findings from previous studies [8,35–37], which suggest that biochars produced from more lignified feedstock with lower ash content tend to have lower EC levels.

3.2. Infrared Spectroscopy

The spectral signature of the composites and biochars was obtained through infrared spectroscopy (ATR-FTIR). In analyzing the non-acidified biochars, the main band was observed at 1600 cm^{-1} , corresponding to O–H and aromatic C stretches (Figure 1). The acidified biochars had a predominant IR band at 1300 cm^{-1} , which is assigned for carboxylic acid and ester group stretches. Regarding the composites, the bands that predominated in the biochar mixed with urea were verified in the range between 1590 cm^{-1} and 1600 cm^{-1} , and were attributed to the formation of amide or amine groups. Stretching of O–H was also observed in all composites in the range of 3200 cm^{-1} to 3500 cm^{-1} , with prevalent peaks at 3290 cm^{-1} , which indicates the presence of alcohol or phenol stretches. Aliphatic C groups in the range of 2800 cm^{-1} to 3000 cm^{-1} were mainly observed in the DAP-doped composites, although they also appeared in other composites, which is mainly explained due to C–H stretches of alkynes. Additionally, P–O groups were observed in the biochar–DAP in the region of 1000 cm^{-1} . Assignments due to O–H stretches were verified for all produced composites in the FTIR region between 1500 cm^{-1} and 1700 cm^{-1} (Figure 1).

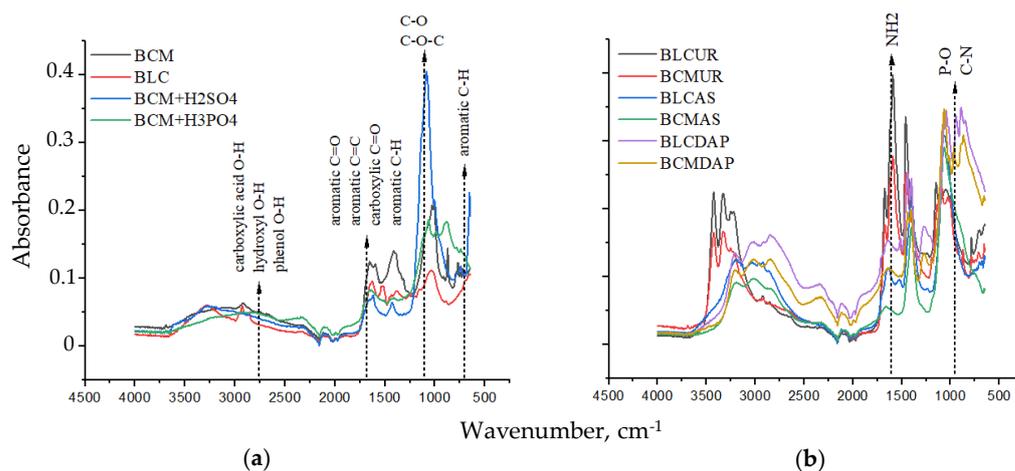


Figure 1. (a) Spectral signature of composite and biochars by the FTIR-ATR spectroscopy technique of (a) chicken manure biochar, chicken manure biochar with acidification and leguminous cake biochar; (b) composite FTIR spectra in the region between 600 cm^{-1} and 4000 cm^{-1} . The composites refer to the following: BLCAS = biochar from leguminous cake + ammonium sulfate; BCMAS = chicken manure biochar + ammonium sulfate; BLCDAP = leguminous cake biochar + DAP; BCMDAP = chicken manure biochar + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea.

3.3. Nitrogen in Oxisol solution

Regarding N in the Oxisol solution, after five samplings, it was possible to determine the dynamics of N release in the forms of NH_4^+ and NO_3^- over time in the soil liquid phase (Figure 2). The highest levels of N ammonium in the soil solution were observed in the first solution sampling (1 day after maize planting), especially for the Oxisol samples treated with composites produced with ammonium sulfate. However, N ammonium decreased during the maize growth, possibly due to being converted into N nitrate, lost to the air, or uptake by maize plants. As the cultivation time evolved, the mineral N in the soil solution reached values close to zero. This illustrates that, potentially, N ammonium could be converted into nitrate, volatilized as ammonia, or uptake by maize plants (Figure 2).

Regarding N nitrate, the levels were lower than those of N ammonium, indicating that the nitrification rate is reduced in the early days of maize cultivation, except for the composites with urea, whose N nitrate levels in the solution were slightly higher than those of the other treatments (Figure 2). Overall, almost all N in the soil solution predominated in the form of N ammonium. A high capacity to adsorb N-ammonium over N-nitrate is claimed for charred and organic matrices [38,39]. Nitrogen-doped biochars are supposed to slow down the nitrification rate, preserving N ammonium in the growth media for a much longer time than urea [19].

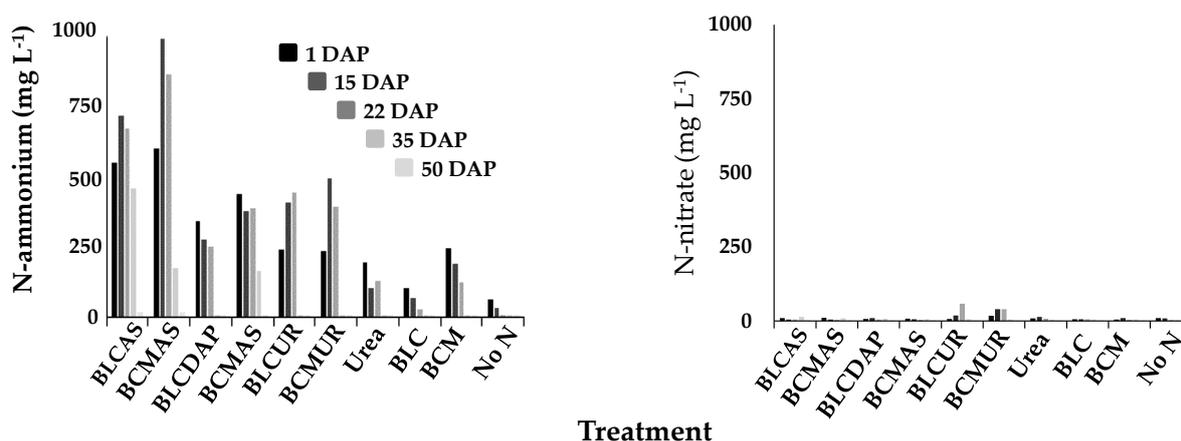


Figure 2. Mineral N as ammonium and nitrate in the Oxisol solution as affected by solution sampling time and N sources (composites and biochars) used to fertilize maize plants. DAP: days after maize planting; BLCAS = biochar from leguminous cake + ammonium sulfate; BCMAS = chicken manure biochar + ammonium sulfate; BLCDAP = leguminous cake biochar + DAP; BCMAS = chicken manure biochar + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; BLC = pure leguminous cake biochar; BCM = pure chicken manure biochar; No N = no N fertilization.

Low values of mineral N in both forms were verified for the treatment in which no N was added to the soil (negative control); thus, the soil's available N from SOM was not sufficient to meet the maize's N requirement.

3.4. Carbon in Oxisol Solution

Carbon in the Oxisol solution was determined for samples collected at 15 and 22 days after maize planting for all evaluated treatments (Table 3). Carbon levels were greater for the soil solution treated with DAP–biochar composites, urea, and treatments in which biochar was not doped with mineral N sources. This trend becomes even more evident in the second sampling time (22 DAP), with higher carbon levels in the soils fertilized with urea composites and pure biochars, thus, with a higher C content in the soil solution over other N sources. It has been observed that the use of biochar produced at a lower temperature range has a high capacity to release carbon into the soil solution [40,41]. Regarding the increase in the carbon level in the second over the first sampling time, the dynamics of N release may have contributed to increasing the water-soluble C content as the higher input of N into the soil via fertilizer contributes to an increase in C release in the soil solution [22,42,43].

Table 3. Water-soluble C content in Oxisol solution 15 and 22 days after maize planting.

Treatment	Water-Soluble Carbon (mg L ⁻¹)	
	15 DAP	22 DAP
BLCAS	806	883
BCMAS	911	768
BLCDAP	1424	1393

Table 3. Cont.

Treatment	Water-Soluble Carbon (mg L ⁻¹)	
	15 DAP	22 DAP
BCMDAP	1261	986
BLCUR	1381	1419
BCMUR	532	1681
Urea	814	960
BLC	945	1140
BCM	1397	1272
No N	809	704

The treatments refer to the following: BLCAS = biochar from leguminous cake + ammonium sulfate; BCMAS = biochar from chicken manure + ammonium sulfate; BLCDAP = biochar from leguminous cake + DAP; BCMDAP = biochar from chicken manure + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; UREA = positive control; BLC = biochar from leguminous cake; BCM = biochar from chicken manure; No N = negative control, no N added to Oxisol. DAP, days after maize planting.

3.5. Nitrogen Availability in Oxisol

Regarding the determination of N availability for maize, soil samples were taken from the pots immediately after planting, and again sampled at the end of the maize cultivation. It was observed that none of the N sources were efficient in providing enough N for a subsequent crop cultivation, considering that the levels of residual N in the Oxisol were not adequate for other crops in succession to maize (Figure 3). Thus, the supplied nitrogen was either entirely utilized by maize plants, or partially lost through volatilization. It is relevant to discuss that part of the N present in the biochars and composites could have been strongly immobilized in the organic matrix of the carbonized materials. This refers to N in heterocyclic forms and with a high aromatic character, which means that the N chemical species are less susceptible to mineralization [8]. Therefore, the residual nitrogen content in the soil is reduced after 50 days of maize cultivation (Figure 3). It is also noticeable that the biochars from chicken manure and leguminous cake caused a lower soil N availability than the composites for maize plants, resulting in a lower dry matter production over plants fertilized with composites doped with N. Wang et al. [22] also observed that the synthetic N fertilizers supply in soils nitrogen at a faster pace and in readily available forms than non-modified biochars.

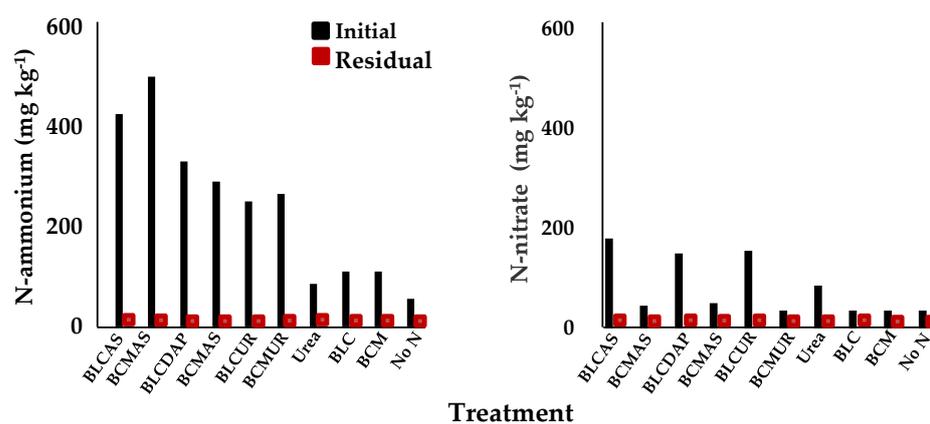


Figure 3. Availability of mineral N in the whole Oxisol in the form of N ammonium and N nitrate. Initial N refers to N available in soil after maize planting, and residual N means the available N in soil after maize cultivation.

3.6. Water- and HCl-Soluble N in Composite and Biochar

After the determination of the solubility of N in the composites and biochars, the dynamics of N release in soil was closely related to the N in maize shoot. Over other N sources, the composites formulated with ammonium sulfate and diammonium phosphate

had greater levels of hydrolyzable N, both in water and in the 6 mol L⁻¹ HCl solution, over other N sources (Table 4). It was also observed that the composites derived from chicken manure biochars have higher levels of soluble N in water and in the HCl extracts over the other N sources. This is one of the possible explanations for the fact that the composites produced from the chicken manure biochar contributed to a greater dry matter production of maize than those synthesized with the leguminous cake-derived biochar. Regarding the pure biochar without N doping, it is possible to verify that these materials contain less HCl-soluble N levels, meaning that they have N in forms less hydrolyzable or not labile N chemical species. This explains the low maize dry matter production in soils fertilized only with pure biochar (CM and LC) without N doping. Dong et al. [44] found that the difference in the fertilizer rate changed the solubility of N, even though the same N concentration was added to all treatments. The results obtained in this study are similar to those reported by [45,46], who found that the use of biochars with no mineral N doping did not provide adequate N for optimal plant growth, given that carbonized matrices have lower soluble N pools than N forms present in mineral fertilizers. Thus, when fertilizing plants exclusively with biochars, in addition to the total N content, it is necessary to observe the fraction of soluble and available N found in the charred matrix. Otherwise, the maize growth will be limited by the supply of readily available N by the pure biochar.

Table 4. Concentration of water-soluble and HCl-soluble N forms in biochars and their composites.

N Source	N Soluble in Water (%)	N Soluble in HCl (%)
BLCAS *	6.72	10.4
BCMAS	8.57	14
BLCDAP	4.80	8.66
BCMDAP	6.07	9
BLCUR	0.19	4.55
BCMUR	0.22	7.57
UREA	0.43	-
BLC	0.01	0.65
BCM	0.01	1.24
Biochar + H ₃ PO ₄	0.09	0.69
Biochar + H ₂ SO ₄	0.18	0.37

* BLCAS = leguminous cake biochar + ammonium sulfate; BCMAS = chicken manure biochar + ammonium sulfate; BLCDAP = leguminous cake biochar + DAP; BCMDAP = chicken manure biochar + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; Urea = positive control; BLC = leguminous cake biochar; BCM = chicken manure biochar.

3.7. Composite Agronomic Effectiveness

The treatment means of the maize shoot and root were compared using the Tukey test ($p < 0.05$). Therefore, the agronomic effectiveness of the composites in nourishing plants was evaluated (Figure 4). It was observed that all the composites did not differ regarding the dry matter production. Considering the maize growth, the biochar-N composites did not differ from the urea-N-treated plants, despite the DAP-biochar composite added to Oxisol only at the dose of 270 mg kg⁻¹ N. The composites have an advantage over the exclusive use of urea to fertilize maize as they do not require splitting fertilization, unlike urea, which was divided into planting fertilization and two additional topdressing fertilizations. Regarding the DAP-biochar composites, the use of 270 mg kg⁻¹ N was enough to meet the maize's N nutritional requirement. Thus, at this dose, a similar dry matter was obtained, compared to the other N sources, eliminating the need for higher concentrations of 400 mg kg⁻¹ supplied by the other N composites. Similar results were verified by [47,48] as an increase in the dose of N fertilizer augmented the N leaching, while reducing the N use efficiency by plants. According to [11], the N use efficiency by crops fertilized with biochar + N fertilizer was higher over the exclusive use of urea to fertilize maize plants. All biochar-N composites and the positive control (plants fertilized with urea) statistically differed from the treatments in which pure biochars without N doping were used to nourish maize plants. This implies that the pure biochar provided almost

no readily soluble N to maize plants, meaning that the N chemical species in CM and LC derived biochars are not available in the short-term for maize plants, contrasting with the soluble mineral N sources mixed with the same biochars. The exclusive use of biochar as a N source surpasses the maize dry matter production observed for the treatment where no N (negative control) was added to Oxisol. The results reported in this study are in line with those reported by [49], which found that the use of N-enriched biochars, even at a lower dose, resulted in a greater maize dry matter over plants treated with biochar without the N enrichment (Figure 4).

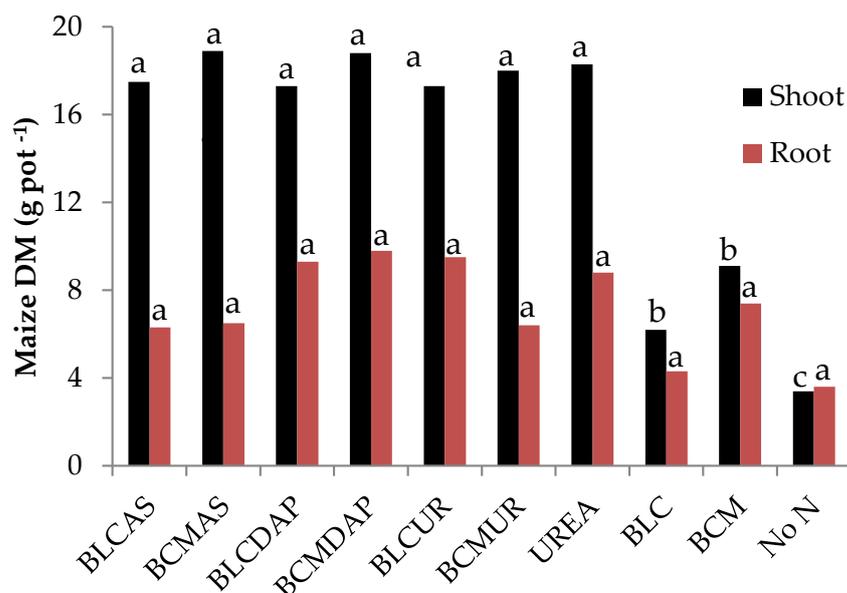


Figure 4. Maize dry matter (DM) production (shoot and root) as affected by pure biochar, urea, and composites as N sources to plants. Treatment means followed by the same letter did not differ statistically regarding the dry matter (shoot or root) production based on Tukey's test ($p < 0.05$). BLCAS = biochar from leguminous cake + ammonium sulfate; BCMAS = chicken manure biochar + ammonium sulfate; BLCDAP = leguminous cake biochar + DAP; BCMDAP = chicken manure biochar + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; BLC = pure leguminous cake biochar; BCM = pure chicken manure biochar; No N = no N fertilization.

Regarding the root dry matter production, it was observed that the N sources did not statistically differ from each other concerning the use of composites, biochars and the absence of N addition to Oxisol. The root/shoot dry matter ratio increased as the N supply to maize decreased, i.e., mainly in the treatments with pure biochars and in soil not treated with N (negative control) (Figure 5). The treatment mean differences related to low levels of N available throughout the experiment were observed. Treatments with a lower root/shoot ratio were those that caused a higher maize dry matter production, while the treatments that increased this ratio had, proportionally, a lower maize shoot biomass (pure biochars and cultivation without N addition to Oxisol). In soil with reduced N availability, root proliferation prevails at the expense of shoot growth to increase the acquisition by plants of less available N in the growing medium. Thus, a high proliferation of roots did not assure a greater plant growth and yield (Figure 5). These results align with those reported by [50], who reported an increased root proliferation of plants fertilized with biochar in response to the reduced N availability in the growing medium.

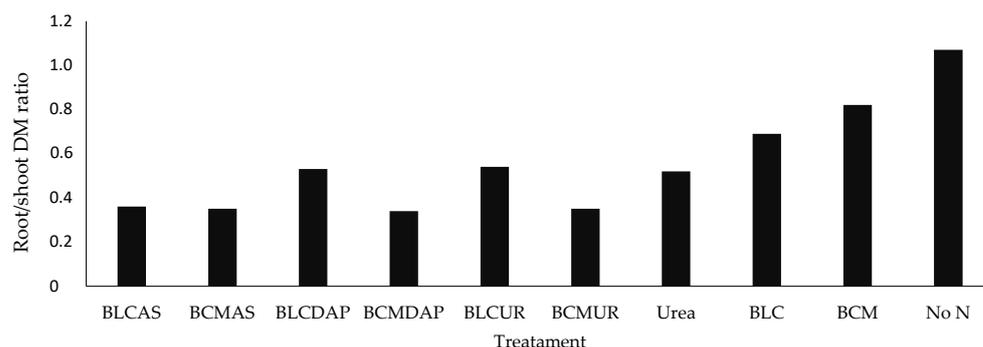


Figure 5. Root/shoot dry matter ratio as a function of the use of urea, pure biochar, and composite as N sources for maize plants. BLCAS = leguminous cake biochar + ammonium sulfate; BCMAS = chicken manure biochar + ammonium sulfate; BLCDAP = leguminous cake biochar + DAP; BCMDAP = chicken manure biochar + DAP; BLCUR = leguminous cake biochar + urea; BCMUR = chicken manure biochar + urea; UREA = positive control with N; BLC = leguminous cake biochar; BCM = chicken manure biochar; No N = negative control, maize cultivated without N.

3.8. N in Maize Shoot

Regarding the accumulation of N in the maize shoot, it was observed that all composites had values between 0.17 and 0.25 g pot⁻¹, indicating that even in more concentrated fertilizations, the plants could not uptake the excess of N in the growth media (Table 5). The lowest accumulation of N in the maize shoot was noted for plants fertilized with pure biochars (without N doping), mainly in pots with plants nourished with N from the leguminous cake-derived biochar (Table 5).

Table 5. Nitrogen in maize shoot as affected by composite and pure biochar utilized to fertilize maize plants.

Treatment	N in Maize Shoot (g pot ⁻¹)
BLCAS *	0.25
BCMAS	0.24
BLCDAP	0.17
BCMDAP	0.23
BLCUR	0.21
BCMUR	0.23
UREA	0.18
BLC	0.03
BCM	0.08
No N fertilization	0.01

* BLCAS = biochar from leguminous cake + ammonium sulfate; BCMAS = biochar from chicken manure + ammonium sulfate; BLCDAP = biochar from leguminous cake + diammonium phosphate, DAP; BCMDAP = biochar from chicken manure + DAP; BLCUR = biochar from leguminous cake + urea; BCMUR = biochar from chicken manure + urea; UREA = positive control, N from the synthetic urea; BLC = pure biochar from leguminous cake; BCM = pure biochar from chicken manure; No N fertilization = negative control, plants cultivated without N addition to Oxisol.

3.9. Agronomic and Environmental Implications

The long-term use of synthetic N fertilizers can alter the biodiversity and structural composition of the soil microbiome. Reductions in soil biological activity and challenges faced by microorganisms in heavily N-fertilized soils may decrease the populations of soil microbes, which could require greater N rates to maintain consistent crop yields over time. Furthermore, this practice leads to soil and water (eutrophication with soluble N) pollution in several crop fields. Under appropriate pyrolysis conditions, biochar exhibits a high specific surface area, pores of varying sizes, and organic functional groups capable of adsorbing and mitigating organic and inorganic metal pollutants found in soils [23,51,52]. Depending on the type, rate, and successive load charges added to soils, biochar modifies the composition, diversity, and structure of the soil microbiome by providing nutrients,

altering the soil pH, and offering sites and substrates for microbial colonization and biodiversity [53]. The influence exerted by biochar on the soil properties and pH, along with its interaction with microorganisms in the rhizosphere, aids in remediating polluted soils and altering the population, diversity, and community structure of the soil microbiome [52].

Future studies should investigate the role played by N combined with biochar (composites) in altering the soil nitrogen-fixing bacteria population, as well as the N use efficiency by crops in field conditions. Additionally, the influence of N composites on the soil microbiome, soil enzymes, and the supply of N from soil organic matter should be examined under field trials. The use of biochar-inoculant (N-fixing bacteria) consortia should also be tested in field conditions. Therefore, it is imperative to recognize how the addition of biochar–N composites affects not only the chemical and physicochemical properties of the soil but also its biological life, rendering the soil a more resilient and complex system for crop cultivation, growth, and development. Many microbes support soil life and contribute to the production of biostimulants, enhancing plant growth and nutrient acquisition. Biochar protects soil microbes and can increase the availability of P in soils [54], and nitrogen fixed from the air as well [53,55,56]. While N is crucial for food production globally, synthetic N fertilizers continue to be inefficiently utilized in many cropland areas. Biochar–N composites represent a promising strategy for optimizing crop N use efficiency, particularly considering that the primary synthetic fertilizers are majorly derived from non-renewable resources.

In summary, we comprehensively assessed the main properties and N content and pools found in biochar–N composites obtained from contrasting N feedstocks mostly available in Brazil. Biochar was pyrolyzed at 300 °C, and mixed with the main synthetic N fertilizers (urea, ammonium sulfate, and diammonium phosphate, DAP) used in Brazilian cropland areas. This study has revealed that the choice of feedstock and, notably, the source of synthetic N play pivotal roles in determining the maize biomass production. Readily available N is released from composites gradually in the Oxisol solution, predominantly in the ammonium form. Pure biochar without N doping is not as effective as urea and composites in nourishing and promoting the full growth of maize plants. The hydrolysis of N in a HCl solution is a suitable index to predict the N present in the maize shoot. Among the biochar–N composites, employing DAP in synthesizing the novel N sources reduced the amount of N necessary for maize fertilization. Biochar–N composites are as effective as urea in promoting plentiful maize growth. Regardless of the N source (composite, biochar, or urea) used to fertilize maize plants, the residual available N in Oxisol is not sufficient to nourish subsequent crops. As far as we know, it is the first time that biochar–N composites have been synthesized with high N content feedstocks available in Brazil, using the main synthetic N sources available in our country. This study is innovative because N composites were generated based on the best reaction conditions and stoichiometric principles used to formulate fertilizers with high agronomic value, as was demonstrated in this research trial.

4. Conclusions

The main objective of this study was to synthesize biochar–N composites that could be as effective as urea in supplying nitrogen to maize plants. Maize dry matter was reduced (with biomass 18–39% lower compared to those produced by urea) in plants fertilized with pure biochars without N doping, indicating that the availability of nitrogen from the carbonized matrices was insufficient to meet the required N needs of maize plants within the specified timeframe. Composites formulated with diammonium phosphate and supplied at a dose of 270 mg kg⁻¹ N yielded the same maize dry matter as other composites (ammonium sulfate and urea) in which 400 mg kg⁻¹ N was supplied to plants. The maize biomass produced with the use of the biochar–N composites is statistically similar to that of the plants fertilized with urea. Regardless of the nitrogen source, at the end of the maize cultivation, the residual nitrogen in the whole Oxisol diminished and was inadequate for a new cultivation, even in soils treated with urea. Throughout the sampling period, nitrogen as ammonium prevailed over N-nitrate in the Oxisol solution.

The concentration of nitrogen from HCl hydrolysis serves as a suitable index for predicting the capacity of composites to provide nitrogen to maize plants. Further investigation is necessary to understand the influence of biochars and composites on maize nutrition and growth, as well as on the amounts of carbon and N released in the Oxisol solution. Overall, the role played by biochar–N composites on the nitrogen use efficiency, soil organic matter dynamics, and nutrition and growth of maize plants should be tested in field trials.

Author Contributions: Conceptualization, C.A.S.; methodology C.A.S. and C.P.M.; validation, C.A.S.; formal analysis, C.P.M.; investigation, C.P.M.; resources, C.A.S. data curation, C.A.S. and C.P.M.; writing—C.P.M. and C.A.S.; writing—review and editing, C.A.S.; visualization, C.A.S.; supervision, C.A.S.; project administration, C.A.S.; funding acquisition, C.A.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the CNPq (grants #307447/2019-7 and 311212/2023-9) and CAPES-MEC Brazil (grant Proex/AUXPE 593/2018).

Data Availability Statement: The data presented in this study are available in the article.

Acknowledgments: The authors would like to thank the Department of Soil Science at the Federal University of Lavras (UFLA) and the National Council for Scientific and Technological Development (CNPq, grants #307447/2019-7 and 311212/2023-9) for the financial support and scholarship provided.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study, in the collection, analyses, or interpretation of data, in the writing of the manuscript or in the decision to publish the results.

References

1. Beig, B.; Niazi, M.B.K.; Jahan, Z.; Hussain, A.; Zia, M.H.; Mehran, M.T. Coating materials for slow release of nitrogen from urea fertilizer: A review. *J. Plant Nutr.* **2010**, *43*, 1510–1533. [[CrossRef](#)]
2. Barbosa, W.S.S. Milho Cultivado Sob Diferentes Lâminas de Irrigação e Adubação Nitrogenada. Master's Thesis, Universidade Federal de Alagoas, Delmiro Gouveia, Brazil, 2017.
3. Lyra, G.B.; Rocha, A.E.Q.; Lyra, G.B.; Souza, J.L.; Teodoro, I. Crescimento e produtividade do milho, submetido a doses de nitrogênio nos Tabuleiros Costeiros de Alagoas. *Rev. Ceres* **2014**, *61*, 578–586. [[CrossRef](#)]
4. Pino, R.C.; Cayuela, M.L.; García, M.S.; Monedero, M.A.S. Nitrogen availability in biochar-based fertilizers depending on activation treatment and nitrogen source. *Waste Manag.* **2023**, *158*, 76–83. [[CrossRef](#)]
5. Puga, A.P.; Grutzmacher, P.; Cerri, C.E.P.; Ribeirinho, V.S.; Andrade, C.A. Biochar-based nitrogen fertilizers: Greenhouse gas emissions, use efficiency, and maize yield in tropical soils. *Sci. Total Environ.* **2020**, *704*, 135375. [[CrossRef](#)]
6. 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.; et al. How biochar works, and when it doesn't: A review of mechanisms controlling soil and plant responses to biochar. *GCB Bioenergy* **2021**, *13*, 1731–1764. [[CrossRef](#)]
7. Melo, L.C.A.; Lehmann, J.; da Silva Carneiro, J.S.; Camps-Arbestain, M. Biochar-based fertilizer effects on crop productivity: A meta-analysis. *Plant Soil* **2022**, *472*, 45–58. [[CrossRef](#)]
8. Paiva, I.O.; Morais, E.; Jindo, K.; Silva, C.A. Biochar N Content, Pools and Aromaticity as Affected by Feedstock and Pyrolysis Temperature. *Waste Biomass Valorization* **2024**. [[CrossRef](#)]
9. Jia, Y.; Hu, Z.; Ba, Y.; Qi, W. Application of biochar-coated urea controlled loss of fertilizer nitrogen and increased nitrogen use efficiency. *Chem. Biol. Technol. Agric.* **2021**, *8*, 3. [[CrossRef](#)]
10. Mandal, S.; Donner, E.; Vasileiadis, S.; Skinner, W.; Smith, E.; Lombi, E. The effect of biochar feedstock, pyrolysis temperature, and application rate on the reduction of ammonia volatilization from biochar-amended soil. *Sci. Total Environ.* **2018**, *627*, 942–950. [[CrossRef](#)]
11. Zheng, J.; Han, J.; Liu, Z.; Xia, W.; Zhang, X.; Li, L.; Liu, X.; Bian, R.; Cheng, K.; Zheng, J.; et al. Biochar compound fertilizer increases nitrogen productivity and economic benefits but decreases carbon emission of maize production. *Agric. Ecosyst. Environ.* **2017**, *241*, 70–78. [[CrossRef](#)]
12. He, Z.; Wang, C.; Cao, H.; Liang, J.; Pei, S.; Li, Z. Nitrate Absorption and Desorption by Biochar. *Agronomy* **2023**, *13*, 2440. [[CrossRef](#)]
13. Banik, C.; Bakshi, S.; Laird, D.A.; Smith, R.G.; Brown, R.C. Impact of biochar-based slow-release N-fertilizers on maize growth and nitrogen recovery efficiency. *J. Environ. Qual.* **2023**, *52*, 630–640. [[CrossRef](#)]
14. El-Gamal, E.; Saleh, M.; Elsokkary, I.; Rashad, M.; Abd El-Latif, M.M. Comparison between properties of biochar produced by traditional and controlled pyrolysis. *ASEJ* **2017**, *38*, 413–424.
15. Novotny, E.H.; de Freitas Maia, C.M.B.; de Melo Carvalho, M.T.; Madari, B.E. Biochar: Pyrogenic Carbon for Agricultural Use—A Critical Review. *Rev. Bras. Ciênc. Solo* **2015**, *39*, 321–344. [[CrossRef](#)]

16. Tomczyk, A.; Sokołowska, Z.; Boguta, P. Biochar physicochemical properties: Pyrolysis temperature and feedstock kind effects. *Rev. Environ. Sci. Bio/Technol.* **2020**, *19*, 191–215. [[CrossRef](#)]
17. Sohi, S.; Lopez-Capel, E.; Krull, E.; Bol, R. Biochar, climate change and soil: A review to guide future research. *CSIRO Land. Water Sci. Rep.* **2009**, *5*, 17–31.
18. Chatterjee, R.; Sajjadi, B.; Chen, W.Y.; Mattern, D.L.; Hammer, N.; Raman, V.; Dorris, A. Effect of pyrolysis temperature on physicochemical properties and acoustic-based amination of biochar for efficient CO₂ adsorption. *Front. Energ. Res.* **2020**, *8*, 85. [[CrossRef](#)]
19. Shi, W.; Ju, Y.; Bian, R.; Li, L.; Joseph, S.; Mitchell, D.R.G.; Munroe, P.; Taherymoosavi, S.; Pan, G. Biochar bound urea boosts plant growth and reduces nitrogen leaching. *Sci. Total Environ.* **2020**, *701*, 134424. [[CrossRef](#)]
20. Steiner, C.; Das, K.C.; Melear, N.; Lakly, D. Reducing nitrogen loss during poultry litter composting using biochar. *J. Environ. Qual.* **2010**, *39*, 1236. [[CrossRef](#)]
21. Zhou, J.; Qu, T.; Li, Y.; Zwieten, L.; Wang, H.; Chen, J.; Song, X.; Lin, Z.; Zhang, X.; Luo, Y.; et al. Biochar-based fertilizer decreased while chemical fertilizer increased soil N₂O emissions in a subtropical Moso bamboo plantation. *CATENA* **2021**, *202*, 105257. [[CrossRef](#)]
22. Wang, L.; Ok, Y.S.; Tsang, D.C.W.; Alessi, D.S.; Rinklebe, J.; Wang, H.; Hou, D. New trends in biochar pyrolysis and modification strategies: Feedstock, pyrolysis conditions, sustainability concerns and implications for soil amendment. *Soil Use Manag.* **2020**, *36*, 358–386. [[CrossRef](#)]
23. Domingues, R.R.; Trugilho, P.F.; Silva, C.A.; De Melo, I.C.N.A.; Melo, L.C.A.; Magriotis, Z.M.; Sánchez-Monedero, M.A. Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits. *PLoS ONE* **2017**, *12*, e0176884. [[CrossRef](#)]
24. Carmo, D.L.; Silva, C.A.; Lima, J.M.; Pinheiro, G.L. Electrical Conductivity and Chemical Composition of Soil Solution: Comparison of Solut ion Samplers in Tropical Soils. *Rev. Bras. Ciênc. Solo* **2016**, *40*, e0140795. [[CrossRef](#)]
25. Singh, B.; Camps-Arbestain, M.; Lehmann, J. *Biochar: A Guide to Analytical Methods*; CSIRO Publishing: Clayton, Australia, 2017; ISBN 1486305105.
26. Maluf, H.J.G.M.; Silva, C.A.; Morais, E.G.D.; Paula, L.H.D.D. Is Composting a Route to Solubilize Low-Grade Phosphate Rocks and Improve MAP-Based Composts? *Rev. Bras. Ciênc. Solo* **2018**, *42*, e0170079. [[CrossRef](#)]
27. Morais, E.G.; Silva, C.A.; Maluf, H.J.G.M.; Guilherme, L.R.G. Slow-Release Humic Acid-Based Zinc Fertilizers Improve Growth and Nutrition of Maize and Brachiaria Grass Successively Grown in Oxisols. *ACS Agric. Sci. Technol.* **2022**, *3*, 17–32. [[CrossRef](#)]
28. Boguta, P.; Sokołowska, Z. Interactions of Zn (II) Ions with Humic Acids Isolated from Various Type of Soils. *Effect of pH, Zn Concentrations and Humic Acids Chemical Properties.* *PLoS ONE* **2016**, *11*, e0153626.
29. Lin-Vien, D.; Colthup, N.B.; Fateley, W.G.; Grasselli, J.G. *The 1233 Handbook of Infrared and Raman Characteristic Frequencies of Organic 1234 Molecules*; Elsevier: Oxford, UK, 1991.
30. Gautam, R.; Vanga, S.; Ariese, F.; Umopathy, S. Review of Multidimensional Data Processing Approaches for Raman and Infrared Spectroscopy. *EPJ Tech. Instrum.* **2015**, *2*, 1–38. [[CrossRef](#)]
31. Parikh, S.J.; Goyne, K.W.; Margenot, A.J.; Mukome FN, D.; Calderon, F.J. Soil Chemical Insights Provided through Vibrational Spectroscopy. *Adv. Agron.* **2014**, *126*, 1–148.
32. Wang, T.; Camps Arbostain, M.; Hedley, M.; Bishop, P. Chemical and bioassay characterization of nitrogen availability in biochar produced from dairy manure and biosolids. *Org. Geochem.* **2012**, *51*, 45–54. [[CrossRef](#)]
33. Ferreira, D.F. Sisvar: A computer statistical analysis system. *Ciência E Agrotecnologia* **2011**, *35*, 1039–1042. [[CrossRef](#)]
34. Joseph, S.; Peacocke, C.; Lehmann, J.; Munroe, P. Developing a biochar classification and test methods. *Biochar Environ. Manag. Sci. Technol.* **2009**, *1*, 107–126.
35. Cantrell, K.B.; Hunt, P.G.; Uchimiya, M.; Novak, J.M.; Ro, K.S. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresour. Technol.* **2012**, *107*, 419–428. [[CrossRef](#)]
36. Claoston, N.; Samsuri, A.; Ahmad Husni, M.; Mohd Amran, M. Effects of pyrolysis temperature on the physicochemical properties of empty fruit bunch and rice husk biochars. *Waste Manag. Res.* **2014**, *32*, 331–339. [[CrossRef](#)]
37. Rehrh, D.; Reddy, M.R.; Novak, J.M.; Bansode, R.R.; Schimmel, K.A.; Yu, J.; Watts, D.W.; Ahmedna, M. Production and characterization of biochars from agricultural by-products for use in soil quality enhancement. *J. Anal. Appl. Pyrolysis* **2014**, *108*, 301–309. [[CrossRef](#)]
38. Borchard, N.; Schirrmann, M.; Cayuela, M.L.; Kammann, C.; Wrage-M^onnig, N.; Estavillo, J.M.; Novak, J. Biochar, soil and land-use interactions that reduce nitrate leaching and N₂O emissions: A meta-analysis. *Sci. Total Environ.* **2019**, *651*, 2354–2364. [[CrossRef](#)]
39. Wang, Y.; Villamil, M.B.; Davidson, P.C.; Akdeniz, N. A quantitative understanding of the role of co-composted biochar in plant growth using metaanalysis. *Sci. Total Environ.* **2019**, *685*, 741–752. [[CrossRef](#)]
40. Saha, A.; Basak, B.B.; Gajbhiye, N.A.; Kalariya, K.A.; Manivel, P. Sustainable fertilization through co-application of biochar and chemical fertilizers improves yield, quality of *Andrographis paniculate* and soil health. *Ind. Crop. Prod.* **2019**, *140*, 111607. [[CrossRef](#)]
41. Han, L.F.; Sun, K.; Yang, Y.; Xia, X.H.; Li, F.B.; Yang, Z.F.; Xing, B.S. Biochar's stability and effect on the content, composition and turnover of soil organic carbon. *Geoderma* **2020**, *364*, 114184. [[CrossRef](#)]

42. Xu, A.X.; Li, L.L.; Xie, J.H.; Wang, X.Z.; Coulter, J.; Liu, C.; Wang, L.L. Effect of long-term nitrogen addition on wheat yield, nitrogen use efficiency, and residual soil nitrate in a semiarid area of the Loess Plateau of China. *Sustainability* **2020**, *12*, 1735. [[CrossRef](#)]
43. Gao, Y.; Shao, G.C.; Yang, Z.; Zhang, K.; Lu, J.; Wang, Z.Y.; Wu, S.Q.; Xu, D. Influences of soil and biochar properties and amount of biochar and fertilizer on the performance of biochar in improving plant photosynthetic rate: A meta-analysis. *Eur. J. Agron.* **2021**, *130*, 126345. [[CrossRef](#)]
44. Dong, L.; Yang, X.; Shi, L.; Shen, Y.; Wang, L.; Wang, J.; Li, C.; Zhang, H. Biochar and nitrogen fertilizer co-application changed SOC content and fraction composition in Huang-Huai-Hai plain, China. *Chemosphere* **2022**, *291*, 132925. [[CrossRef](#)]
45. Zhang, J.N.; Zhou, S.; Sun, H.F.; Lü, F.; He, P.J. The soluble fraction from straw-derived biochar supplies nutrients and affects carbon storage of coastal mudflat soil in rice paddy. *Environ. Sci. Pollut. Res.* **2020**, *27*, 18079–18088. [[CrossRef](#)] [[PubMed](#)]
46. Lin, Q.Y.; Zhang, L.; Riaz, M.; Zhang, M.Y.; Xia, H.; Lv, B.; Jiang, C.C. Assessing the potential of biochar and aged biochar to alleviate aluminum toxicity in an acid soil for achieving cabbage productivity. *Ecotoxicol. Environ. Saf.* **2018**, *161*, 290–295. [[CrossRef](#)] [[PubMed](#)]
47. Laird, D.; Fleming, P.; Wang, B.Q.; Horton, R.; Karlen, D.L. Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma* **2010**, *158*, 436–442. [[CrossRef](#)]
48. Liao, P.; Huang, S.; van Gestel, N.C.; Zeng, Y.J.; Wu, Z.M.; van Groenigen, K.J. Liming and straw retention interact to increase nitrogen uptake and grain yield in a double rice-cropping system. *Field Crop. Res.* **2018**, *216*, 217–224. [[CrossRef](#)]
49. Feng, W.; Yang, F.; Cen, R.; Liu, J.; Qu, Z.; Miao, Q.; Chen, H. Effects of straw biochar application on soil temperature, available nitrogen and growth of corn. *J. Environ. Manag.* **2021**, *277*, 111331. [[CrossRef](#)]
50. Chimento, C.; Amaducci, S. Characterization of fine root system and potential contribution to soil organic carbon of six perennial bioenergy crops. *Biomass Bioenergy* **2015**, *83*, 116–122. [[CrossRef](#)]
51. Somenahally, A.; Mclawrence, J.; DuPont, J.I.; Brady, J.; Sarkar, R.; Rouquette, M., Jr. Root-mycorrhizae interactions contributed to organic carbon density in the sandy soil profiles of adapted grazing lands. *Appl. Soil Ecol.* **2020**, *154*, 103656. [[CrossRef](#)]
52. Fan, C.; Cui, Y.; Zhang, Q.; Yin, N.; Cai, X.; Yuan, X.; Senadheera, S.; Cho, Y. A critical review of the interactions between rhizosphere and biochar during the remediation of metal (loid) contaminated soils. *Biochar* **2023**, *5*, 1–33. [[CrossRef](#)]
53. Xu, W.; Xu, H.; Delgado-Baquerizo, M.; Gundale, M.J.; Zou, X.; Ruan, H. Global meta-analysis reveals positive effects of biochar on soil microbial diversity. *Geoderma* **2023**, *436*, 116528. [[CrossRef](#)]
54. Glaser, B.; Lehr, V.I. Biochar effects on phosphorus availability in agricultural soils: A meta-analysis. *Sci. Rep.* **2019**, *9*, 9338. [[CrossRef](#)] [[PubMed](#)]
55. Gou, Z.; Zheng, H.; He, Z.; Su, Y.; Chen, S.; Chen, H.; Chen, G.; Ma, N.L.; Sun, Y. The combined action of biochar and nitrogen-fixing bacteria on microbial and enzymatic activities of soil N cycling. *Environ. Pollut.* **2023**, *317*, 120790. [[CrossRef](#)] [[PubMed](#)]
56. Phares, C.A.; Atiah, K.; Frimpong, K.A.; Danquah, A.; Asare, A.T.; Aggor-Woananu, S. Application of biochar and inorganic phosphorus fertilizer influenced rhizosphere soil characteristics, nodule formation and phytoconstituents of cowpea grown on tropical soil. *Heliyon* **2020**, *6*, e05255. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.