

Article

What Is the Threshold Carbonization Temperature for Sustainable Preservation of the Good Nitrogen Supply Ability of Chicken Manure?

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Abstract: Chicken manure (CM) carbonization is an efficient waste control method that converts manure into an agriculturally useful amendment. However, the recommended temperature range of 300–500 °C has led to confounding results on the maintenance of the nitrogen (N) supply ability of CM after carbonization, and thus requires further investigation. The objective of this study was to identify an upper limit (threshold) temperature to guide the carbonization of CM in order to ensure that the good N supply ability of the manure after carbonization is preserved. CM was carbonized at 350, 375, 400, 425, 450, and 475 °C. Afterwards, chemical properties, surface functional groups, N speciation, N supply ability, and their relationships were investigated. The results indicated that the N supply ability of CM carbonized at 350–375 °C was comparable to the N supply ability of CM, which is possibly due to the minute alteration of the chemical properties, surface functionality, and N speciation that occurred in CM at these temperatures. At ≥ 400 °C, the N supply ability of CM was significantly reduced due to the increasing alterations of the chemical makeup as heating temperature increased. For sustainable maintenance of the good N supply ability of CM after carbonization, the manure should not be carbonized above 375 °C.

Keywords: chicken manure; carbonization; threshold temperature; N supply ability; chemical composition; surface functionality; N speciation

1. Introduction

The poultry industry is the largest and fastest growing livestock sector in the world, producing substantial amounts of meat and eggs for human consumption, but, at the same time, it produces a huge quantity of chicken manure (CM) waste [1]. Handling and storage of the manure generated from chicken rearing is problematic due to its bulky nature, high moisture content, and very offensive smell. Furthermore, application of CM to soil causes pollution to the environment (soil, water bodies, and the atmosphere), increases pest incidence, and can cause burns to plants [2]. Thus, the need for further processing of the manure to make handling and storage easier and to reduce its toxic effect before land application for crop production is necessary for sustainable use [3].

Carbonization is a popular processing method suitable for converting fresh manure into agriculturally useful amendments [4]. Carbonization of CM leads to drastic reduction in odor, weight, and volume of the manure, thereby making handling and application to soil convenient [5,6]. Other notable advantages of carbonization include that the process requires less space, is relatively

fast, eradicates potential pathogens and pharmaceutically active compounds, and reduces emissions of gases as compared to techniques like composting [7]. CM carbonization is in line with the effort to attain sustainable development through efficient use of resources and reduction of waste, while at the same time reducing the negative effects on the environment.

The decades of work on CM carbonization for the production of agriculturally useful amendment have established the importance of temperature conditions during CM carbonization [8,9]. Temperatures around 300–500 °C have been recommended as sufficient for thoroughly carbonizing the manure into value-added material that is useful as organic N fertilizer for soil fertility improvement and crop productivity [3,10]. However, confounding results have been reported with regards to the ability of CM to supply nitrogen (N) in soils after having been carbonized around these recommended temperature ranges, especially the upper limit temperature. For instance, Tagoe et al. [10] observed an increase in total N content of soybeans and a 43% increase in seed yield of the plant after application of CM that was carbonized at 500 °C. In addition, Chan et al. [3] observed a 96% increase in radish yield and a significant increase in tissue N content over that of the control for CM, which was carbonized at 450 and 550 °C. With these results, they established that carbonized CM produced around these temperatures can supply sufficient plant nutrients, including N, for sustainable plant productivity. On the contrary, Ishimori et al. [11] reported that CM carbonized at 528 °C alone cannot support the normal growth of plants after they observed that *Oryza sativa* and *Brassica rapa* komatsuna were not significantly different in their growth in plots of carbonized CM and the control. Steiner et al. [12] found lower concentrations of N in tissues of plants fertilized with CM that was carbonized at 500 °C when compared to the unfertilized control, and concluded that “N in carbonized CM is not plant available”. Despite the differential results of the N supply ability of carbonized CM, research has not been conducted to clarify this issue by elucidating the mechanism(s) governing the N supply ability of CM after being carbonized around these temperature conditions and to possibly suggest a new threshold temperature that will ensure the sustainability of the good N fertilizer value of CM after carbonization.

Thermal treatments of N-rich organic materials can increase the recalcitrance of the material to decomposition as a result of cyclization of aliphatic chains and decrease in the quantity of hydrolysable organic N due to the formation of heterocyclic N structures [8,13–15]. This drastic alteration of the materials during heat treatments significantly affects their nutrient supply ability [16,17]. Hence, thorough microscopic examination of the surface functionality and N speciation coupled with basic chemical property analysis of any N-rich organic material during carbonization for the purpose of N supply is a prerequisite.

Since the start of CM carbonization in 2008 for use as a soil amendment [3], several authors have tried to calibrate suitable temperature conditions for the production of agriculturally useful organic N fertilizer by evaluating the effects of temperature conditions on carbonized CM yield, elemental composition, pH, electrical conductivity (EC), cation exchange capacity (CEC), and other basic compositional properties [4,8,18]. However, little has been done to understand the spectroscopic transformations of the surface functional group and the speciation of the organic N in CM during carbonization and the subsequent effects of these transformations on N availability in soil. As indicated above, the temperature conditions set by the mere use of the basic physicochemical properties as a yardstick have resulted in discrepant results in the N supply ability of the carbonized product [3,10–12]. We believe that a combination of chemical and microscopic examination of the composition, surface functional group, and N speciation in CM after carbonization will provide a much clearer exposition on the underlying mechanism(s) responsible for affecting the ability of the carbonized CM to supply N in soil and how the process can be manipulated in order to ensure the preservation of the good N supply ability of the manure. This information can be used to establish a new threshold carbonization temperature, which will serve as a guide during CM carbonization for the preservation of the good N supply ability of the manure for sustainable use as organic N fertilizer.

Therefore, the objective of this study was to investigate the alteration in chemical composition, surface functional groups, and N speciation in CM carbonized at different temperatures, as well as their influence on N supply ability of the manure in order to determine a threshold carbonization temperature for preserving the N fertilizer integrity of CM for sustainable use as organic N fertilizer.

2. Materials and Methods

2.1. Sample Source and Preparation

Fresh chicken manure was collected at the poultry section of the Field Science Center, Gifu University. The fresh manure was dried at 65 °C in a conventional oven for 24 hours and then stored in air-tight plastic prior to carbonization. Fifty grams (50 g) of dried CM was placed in a ceramic crucible and carbonized in a muffle furnace. Two batches of carbonized CM were produced at the respective temperatures of 350, 375, 400, 425, 450, and 475 °C. During carbonization, the temperature was raised to the desired values at a heating rate of 5–10 °C per minute, and was thereafter kept running for a period of 1½ hours. After carbonization, the samples were allowed to cool, and the yield of the carbonized manure was recorded. The duplicate samples for each treatment were homogenized with a mortar, pestle, and sieve to pass through a 2 mm mesh. The samples were stored in air-tight plastic containers prior to the experiment. The carbonized CMs are hereafter referred to as CCM350, CCM375, CCM400, CCM425, CCM450, and CCM475 for CM carbonized at 350, 375, 400, 425, 450, and 475 °C, respectively. The un-carbonized chicken manure will still be referred to as CM.

2.2. Physical and Chemical Properties of the Samples

The yields of all of the carbonized CM (CCM) were expressed as the mass fraction of the original CM feedstock. Ash content was determined by dry combustion at 750 °C for 5 hours [19]. The pH and EC were measured in a deionized water suspension (1:10 w/v) after shaking at 200 rpm for 1 hour and allowed to stand for 1 hour. C, H, and N were determined by a JMA 102 auto-sampler CHN elemental analyzer (J-Science Lab co., Ltd, Kyoto, Japan). The amount of oxygen (O) was calculated by difference. The results of C, H, N, and O were used to calculate atomic H/C and O/C ratios for the preliminary evaluation of the relative degrees of aromaticity (H/C ratio) and stability (O/C ratio) and the possible type of reaction taking place during the carbonization of CM at different temperatures. The concentration of ammonium nitrogen ($\text{NH}_4^+\text{-N}$) was extracted in a 2 M KCl solution and was determined by steam distillation. The nitration of salicylic acid method [20] as reported by Logah et al. [21] was used to measure the nitrate nitrogen ($\text{NO}_3^-\text{-N}$) content after extraction of the samples with 0.5 M K_2SO_4 .

2.3. Surface Functional Group Analysis

The functional groups on the surface of CM and CCM samples were investigated by Fourier-transform infrared spectroscopy (FTIR). Potassium bromide (KBr) pellets that contained 1% (w/w) of each sample were prepared with a cylindrical piston under pressure and vacuum. FTIR analysis of all of the samples was conducted by JASCO 4100 spectrometer (JASCO Corporation, Tokyo, Japan) at wavelengths ranging from 4000 to 400 cm^{-1} and a resolution of 2 cm^{-1} . The spectrum of the pure KBr pellet was recorded before every measurement for spectra correction.

2.4. Nitrogen Forms and Speciation

The existing nitrogen structures in CM and CCM products were characterized by X-ray photoelectron spectroscopy (XPS). A Quantera SXM-GX scanning X-ray microprobe spectrometer (Ulvac-PHI, Inc., Kanagawa, Japan) was used to measure the N1s spectrum of the samples, with a monochromatic $\text{AlK}\alpha$ (1486.6 eV) X-ray source operating at 25 W with a spot size of 100 μm in diameter at an electron takeoff angle of 45°. The spectrometer was run at pass energies of 120 and 55 eV to obtain survey and high-resolution spectra, respectively. Prior to introduction in the spectrometer,

the samples were mounted on a double-sided carbon tape. All of the samples were analyzed under identical conditions. Deconvolution and quantification of the composition of each N form in the samples from their XPS spectra was done with MultiPak 8.2 software (Ulvac-PHI, Inc., Kanagawa, Japan). The binding energies (BE) of all samples were referenced to the C1s peak at 284.8 eV in order to compensate for sample charging. Spectra were fitted based on Gauss–Lorentzian line shapes with Shirley-type background subtraction. The fitted areas of peaks reflected the relative contents of different N-containing compounds.

2.5. Measurement of Nitrogen Supply Ability

The potential of CM and CCM products as N fertilizer was evaluated in a 42 day laboratory aerobic incubation study. A total of 100 g (oven dry basis) of air-dried 2 mm mesh-sieved soil was placed in a 400 mL plastic container, and deionized water was added to bring the soil to a 60% water holding capacity. The respective treatment samples were added at an equal N application rate of 120 kg N/ha, and the soil was mixed. Containers with soil but without amendments were used as controls. Three replicates were prepared for each treatment per sampling time. The initial weights of all of the samples were recorded, covered with pin hole parafilm, and incubated at 30 °C. At weekly intervals, the samples were removed from the incubator, aerated, and rewetted to their initial weight by adding deionized water.

To determine the N supply abilities of the different treatments, triplicates of each sample treatment were removed at 0, 7, 14, 21, 28, and 42 days, and their mineral N contents (NH_4^+ -N and NO_3^- -N) were assessed. Samples of 10 g each for NH_4^+ -N and NO_3^- -N for each treatment were weighed for analysis. In order to determine the moisture contents of the soils at each sampling time, 10 g samples were weighed into aluminum foil cups of known weight, dried in an oven at 105 °C for 48 hours and their weight recorded for moisture content calculations. NH_4^+ -N samples were extracted with a 2 M KCl solution, and the extracts were analyzed by steam distillation, while the NO_3^- -N samples were extracted with a 0.5 M K_2SO_4 solution and analyzed following the nitration of salicylic acid method [20] as reported in Logah et al. [21]. At each sampling time, the mineral N content of the control soil (Table A1 and Figure A1) was subtracted from each treatment at that particular date. All of the results were reported on a dry weight basis.

2.6. Statistical Data Analysis

The data obtained from the incubation studies were statistically analyzed by one-way analysis of variance (ANOVA) using Microsoft Excel 2010. Significant means were separated using Tukey's honest significant difference post hoc comparison. Regression analyses were performed between the initial properties of the different manures and their total mineral N contents released in the 42 day incubation.

3. Results

3.1. Basic Chemical Properties and Elemental Composition

Carbonization of CM at different temperatures resulted in changes in the properties of the carbonized products in comparison to the CM. As expected, the extent of variation increased with increasing temperature of carbonization. The mass yield of carbonized CM was at least 59% in CCM350, and gradually decreased to about 48% as the temperature of carbonization was increased to 475 °C (Table 1). On the other hand, the ash content in CM increased with increasing carbonization temperature. The CM contained ash content of about 30%, which increased to 43.08% when heated at 350 °C and continued to increase until it reached a quantity of about 53.18% for CCM475 (Table 1).

Accumulation of C was observed when CM was carbonized from 350 to 400 °C when compared to the un-carbonized CM. Temperatures of 425–475 °C were seen to have a negative effect on the C content of the manure. The changes of the C content during heating were interesting in that the C content was first increased from 29.60% in CM to 34.70% in CCM350. Thereafter, a decreasing trend

was observed from CCM350 up to CCM475, which consisted of a total C content of 24.31%, and was the lowest of all of the samples (Table 1). After carbonization, the N and H content in CM decreased with increasing carbonization temperatures. The N content of CM was 7.89%, which decreased step-wise as the temperature of carbonization increased to the final amount of 2.18% in CCM475. In the same vein, CM contained H content of 3.56%, which was also gradually decreased to 0.95% when the manure was carbonized at 475 °C. Although the O content decreased following carbonization of CM, the trend of the O contents in the CCM fluctuated. At first, the O content sharply decreased when the manure was heated at 350 and 375 °C from 28.88% in the CM to 13.99% and 13.95% in CCM350 and CCM375, respectively. Thereafter, O content started increasing gradually with heating temperature up to CCM425, then decreased to 13.88% for CCM450, and finally increased to 19.38% for CCM475 (Table 1). The atomic C:N ratio of the manure increased with increasing carbonization temperature from 4.38 in CM to 13.01 in CCM475. The degree of aromaticity of CM and CCM produced at different temperatures, preliminarily evaluated by their H/C atomic ratios, demonstrated a decreasing trend with increasing carbonization temperatures (Table 1). The atomic H/C ratio of CM was 1.44, which gradually decreased to 0.47 for CCM475.

The Van Krevelen plot of the H/C and O/C atomic ratios conformed to a pattern that indicated ongoing dehydration, decarboxylation, dehydrogenation, and condensation reactions during the carbonization of CM (Figure 1).

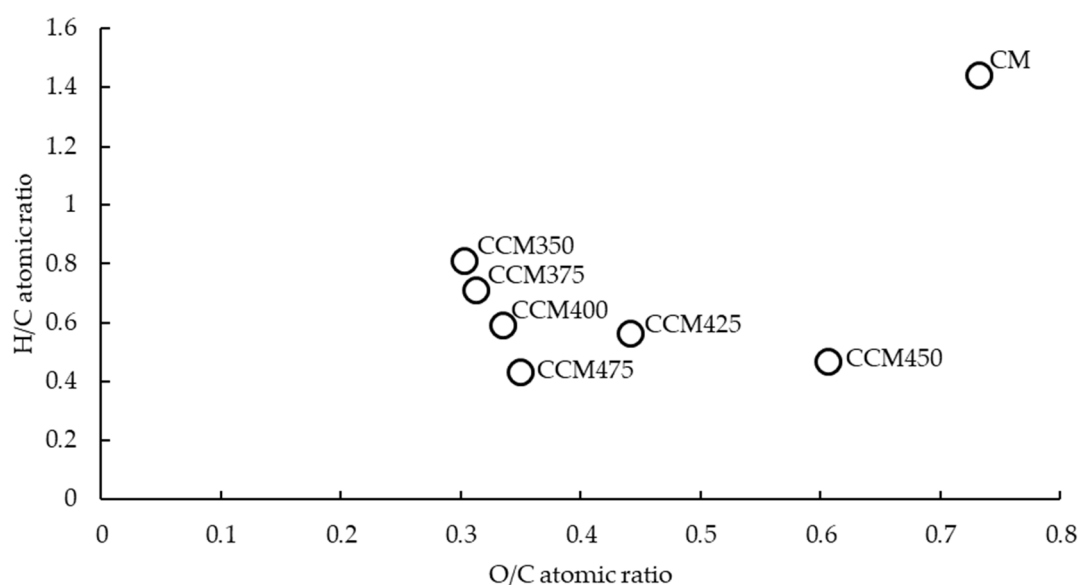


Figure 1. Van Krevelen plot of chicken manure and carbonized chicken manure produced at different temperatures. CM: chicken manure; CCM350, CCM375, CCM400, CCM425, CCM450 and CCM475 represent chicken manure carbonized at 350, 375, 400, 425, 450 and 475 °C respectively.

Table 1. Yield, ash, elemental composition, atomic ratios, and recovery for chicken manure (CM) and carbonized CM (CCM) produced at different temperatures.

Samples	Elemental Composition (%)						Atomic Ratios			Recovery with Respect to the Un-Carbonized CM			
	Yield (%)	Ash (%)	N	C	H	O ^a	C:N	H:C	O:C	N (%)	C (%)	H (%)	O (%)
CM	100.00	30.07	7.89	29.60	3.56	28.88	4.38	1.44	0.73	100.00	100.00	100.00	100.00
CCM350	59.08	43.08	5.88	34.70	2.35	13.99	6.88	0.81	0.30	44.03	69.26	39.00	28.62
CCM375	56.35	45.17	5.42	33.47	1.99	13.95	7.20	0.71	0.31	38.71	63.72	31.50	27.23
CCM400	53.48	48.03	4.15	31.97	1.58	14.27	8.99	0.59	0.33	28.13	57.76	23.73	26.42
CCM425	50.99	49.95	3.20	28.66	1.35	16.84	10.45	0.57	0.44	20.68	49.37	19.34	29.73
CCM450	49.05	52.92	2.91	29.22	1.06	13.88	11.71	0.44	0.36	18.09	48.42	14.60	23.59
CCM475	48.20	53.18	2.18	24.31	0.95	19.38	13.01	0.47	0.60	13.32	39.59	12.86	32.34

CM: Chicken manure; CCM350, CCM375, CCM400, CCM425, CCM450, and CCM475 represent chicken manure carbonized at 350, 375, 400, 425, 450, and 475 °C, respectively; ^a is calculated by difference.

The presence of mineral N content (NH_4^+ -N and NO_3^- -N) was drastically reduced in CM during carbonization (Table 2). For CCM350, the presence of mineral N was very low; however, moving from CCM350 to CCM375, the mineral N slightly increased. This increase in mineral N continues up to CCM400, which has the highest value of mineral N amongst the CCM products. Thereafter, mineral N decreased from CCM425 to CCM475, which have the lowest quantities (Table 2).

Table 2. Basic chemical properties of CM and carbonized CM produced at different temperatures.

Samples	pH	EC	NH_4^+ -N (mg/100 g)	NO_3^- -N (mg/100 g)	Total Mineral N (mg/100 g)
CM	7.9	4.5	67.5	8.4	75.9
CCM350	8.9	2.8	0.75	0.5	1.2
CCM375	10.0	4.2	1.08	0.7	1.8
CCM400	10.1	5.6	2.12	1.0	3.2
CCM425	10.3	6.0	0.85	0.6	1.5
CCM450	10.3	5.9	0.56	0.4	1.0
CCM475	10.4	6.0	0.43	0.4	0.8

CM: Chicken manure; CCM350, CCM375, CCM400, CCM425, CCM450, and CCM475 represent chicken manure carbonized at 350, 375, 400, 425, 450, and 475 °C, respectively.

Generally, CM and the CCM produced at different temperatures exhibited alkaline pH values, which increased with increasing carbonization temperatures from 350 to 475 °C, passing from a value of 8.9 to 10.4. We observed an initial reduction in the EC value of CM from 4.5 to 2.8 when carbonized at 350 °C, but it thereafter gradually increased with increasing temperature to 6.0 at 475 °C (Table 2).

3.2. Surface Functional Groups

The FTIR spectra of CM and its carbonized products are presented in Figure 2 and their proposed assignment in Table 3. Carbonization resulted in significant changes in the surface functional groups of CM, which increased with increasing carbonization temperature. The changes include:

- Decreased intensity, shifting, and subsequent loss of the broad band attributed to free amino acids mixed with O-H groups from 3500 to 2500 cm^{-1} .
- Decreased C-H band with increasing temperature of carbonization.
- Decreased C=O band on the surface of CM with increasing temperature.
- Increase in CH_2 units in biopolymer on the surface of CM with temperature increase.
- Increase in the C-O band with increasing temperature up to 450 °C.
- Increase in the aromatic C-H band with increasing carbonization temperature

Table 3. Functional groups observed in the FTIR spectra of CM and CM carbonized at different temperatures.

Peak Positions cm^{-1}	Proposed Assignments	References
3600–2500	Amino acid hydrohalides (N-H vibration) or OH bond in water, carboxyl and hydroxyl groups	[22,23]
2925	Aliphatic methylene band	[24]
1665–1650	Amide band I (C=O vibration)	[25]
1435–1412	CH_2 units in biopolymer	[26]
1060–1000	Polysaccharides (C-O vibration)	[27]
800 and 600	Aromatic C-H out of plane deformation	[28]

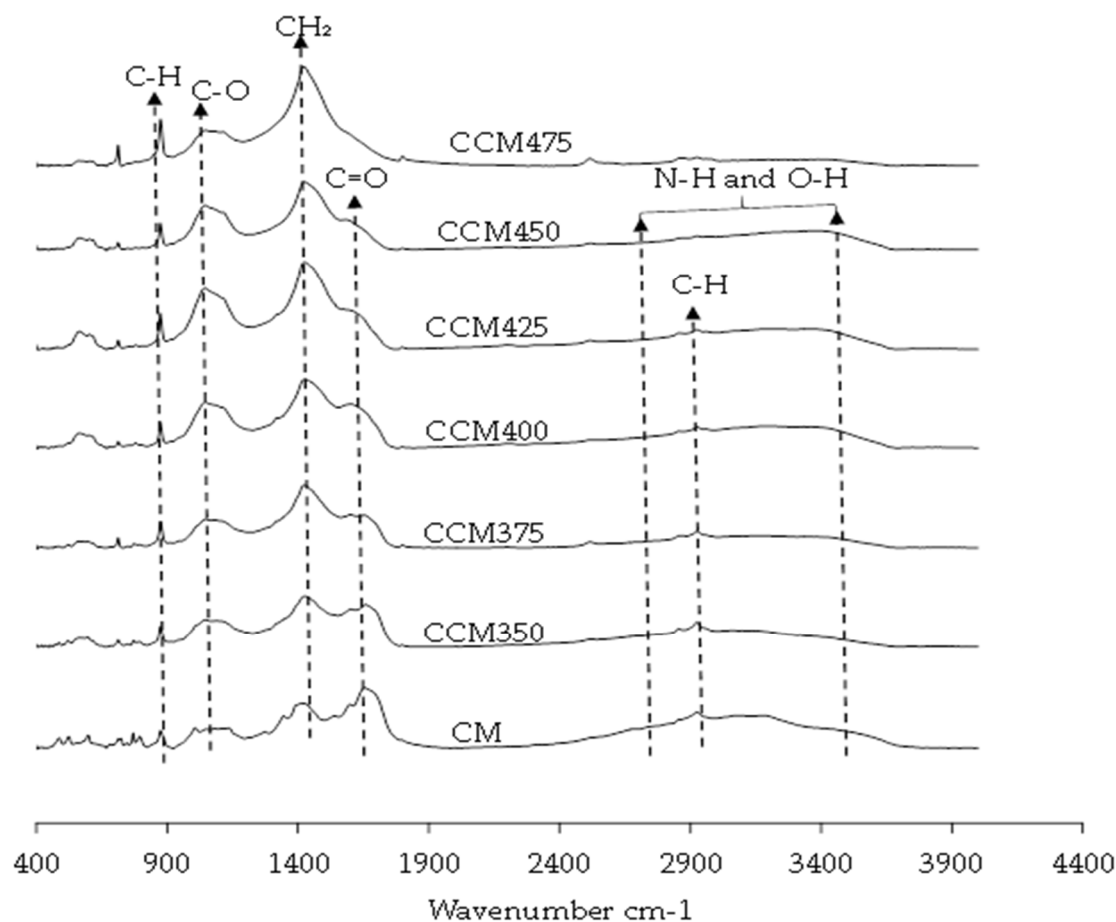


Figure 2. Fourier-transform infrared (FTIR) spectra peaks of chicken manure and carbonized chicken manure produced at different temperatures. CM: Chicken manure; CCM350, CCM375, CCM400, CCM425, CCM450, CCM475 represent chicken manure carbonized at 350, 375, 400, 425, 450, and 475 °C respectively.

3.3. Transformation of N Species in CM During Carbonization

Table 4 shows the possible assignments of peak signals and how the N forms will be referred to in this paper, Figure 3a–g shows the XPS spectra, and Table 5 shows the distribution of nitrogen functionalities of the CM and CCM products. The spectrum of CM (Figure 3a) can be fitted by a single XPS peak at 399.7 ± 0.3 eV, which corresponds to the nitrogen functionalities N-I (Table 4). With increasing carbonization temperature, the relative intensity of the N-I groups decreased, and signals of other N forms started appearing. The N-I peak shrinks with corresponding introduction of heterocyclic N forms (N-II, N-III). The N-I species completely disappeared by 450 °C, leaving only heterocyclic N forms. An important observation in these spectra is the systematic accumulation of N-II functionalities with increasing temperature of carbonization at the expense of labile N-I forms (Figure 3a–g).

Table 4. Binding energy of group N1s.

Nitrogen Forms	Symbol	Binding Energy	References
Protein-N, amino-N, amide-N, nitrile	N-I	399.7 ± 0.3	[29]
Pyridine-N	N-II	398.7 ± 0.4	[30]
Pyrrolic-N	N-III	400.3 ± 0.1	[31]

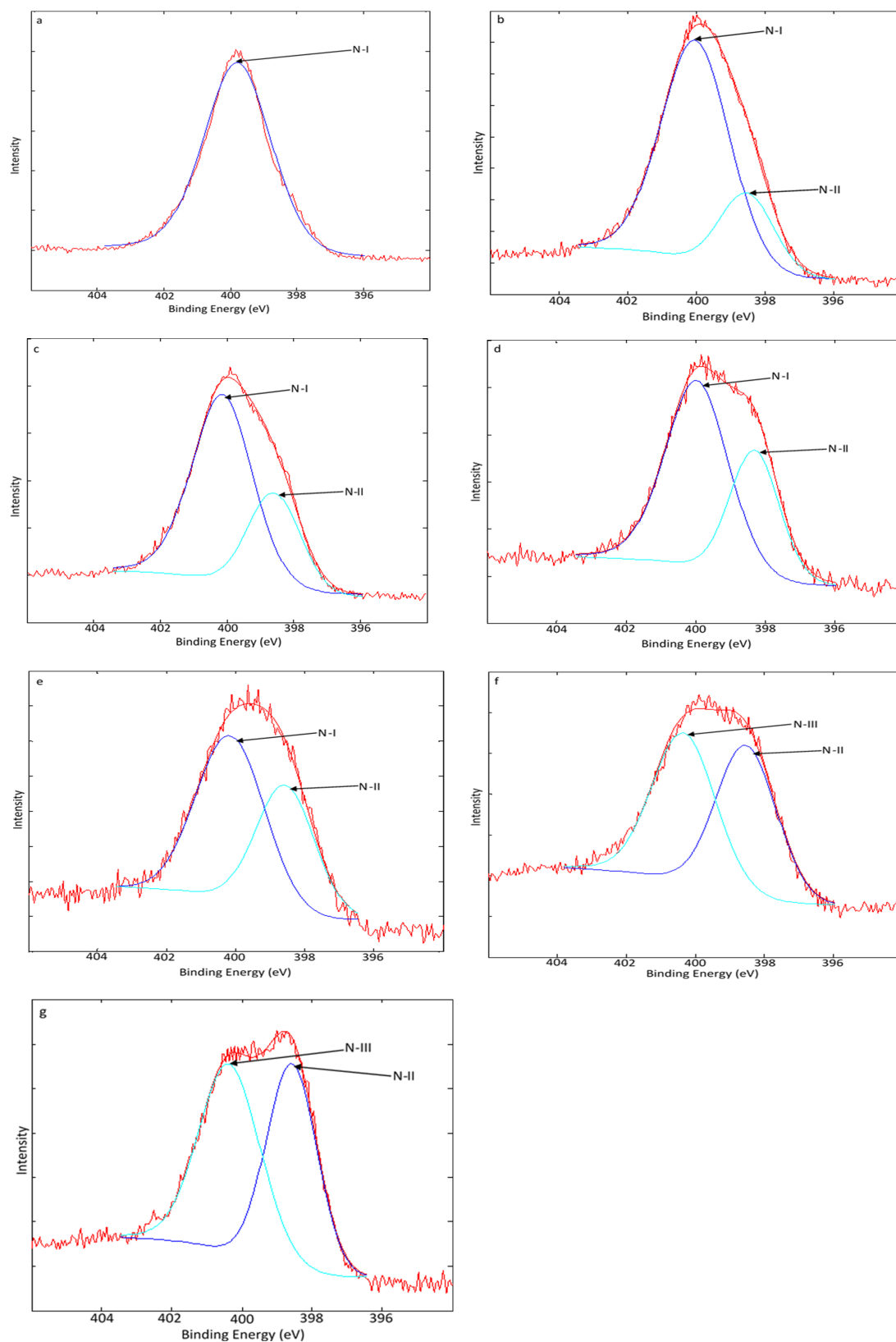


Figure 3. X-ray photoelectron N1s spectra for (a) chicken manure and carbonized chicken manure produced at (b) 350, (c) 375, (d) 400, (e) 425, (f) 450, and (g) 475 °C. Peak assignment: N-I (Protein-N, Amino-N, Amide-N, nitrile), N-II (Pyridine-N forms), NIII (Pyrrole-N forms).

Table 5. Distribution of nitrogen functionalities of CM and thermally altered CM at different temperatures.

Sample	N-I (%)	N-II (%)	N-III (%)
CM	100	0	0
CM350	77.19	22.81	0
CM375	70.36	29.64	0
CM400	64.51	35.49	0
CM425	59.75	40.25	0
CM450	0	48.38	51.62
CM475	0	46.35	53.65

CM is chicken manure; CM350, 375, 400, 425, 450, and 475 are chicken manure carbonized at 350, 375, 400, 425, 450, and 475 °C.

According to Table 5, N-I species made up all (100%) of the N forms present in CM. These, however, were reduced to 77.19% when the manure was heated at 350 °C; by 450 °C, the N-I species degraded completely. Meanwhile, the N-II species gradually accumulated from being absent in the CM to about 48.38% at 450 °C.

3.4. N Fertilizer Capacity of CM and CM Carbonized at Different Temperatures Over Time

The result of the potential abilities of CM and the different temperatures of CCM to supply N from their organic N pool are presented in Figure 4. In general, the ability of the manure to release N in soil was not significantly affected after being heated at 350–375 °C, but was significantly affected as the temperature was raised to 400 °C and higher. The nitrogen supply abilities of CM and CCM350 were not statistically different ($p > 0.05$) throughout the study period. CCM375 exhibited a similar mineral N release ability to that of CM in all of the sampling times, except at sampling day 14, in which its ability to supply mineral N was significantly lower ($p < 0.05$) than that of CM. CCM400 had a similar N release ability ($p > 0.05$) to that of CM only at day 7; thereafter, the N release ability of CCM400 was significantly lower than that of CM throughout the study period (Figure 4). Apart from CCM350, CCM375, and CCM400, the CM had a significantly higher N release ability than all of the other higher temperatures of CCM throughout the period of the incubation study. Among the CCM products, the N release from CCM350 throughout the incubation study was statistically similar to that of CCM375, but was statistically significant ($p < 0.05$) from CCM400 at days 7 and 42; CCM425 at days 7, 14, 28, and 42; CCM450 at days 7, 14, and 42; CCM475 at days 7, 14, 21, and 42. The N release from CCM375 was not significantly different from CCM400 and CCM450 throughout the incubation period but was significantly ($p < 0.05$) higher than CCM425 at day 28 and CCM475 at day 7, 21 and 42. CCM400 released statistically similar N to CCM450 throughout the incubation period, but the N released by CCM400 at day 14 was significantly ($p < 0.05$) greater than that of CCM425. In addition, a significantly ($p < 0.05$) greater N release was observed for CCM400 than for CCM475 at days 14, 21, and 42. N released from CCM425 was similar to N released from CCM450 and CCM475 throughout the study. Lastly, the N released from CCM450 was only significantly ($p < 0.05$) greater than CCM475 at day 42 (Figure 4).

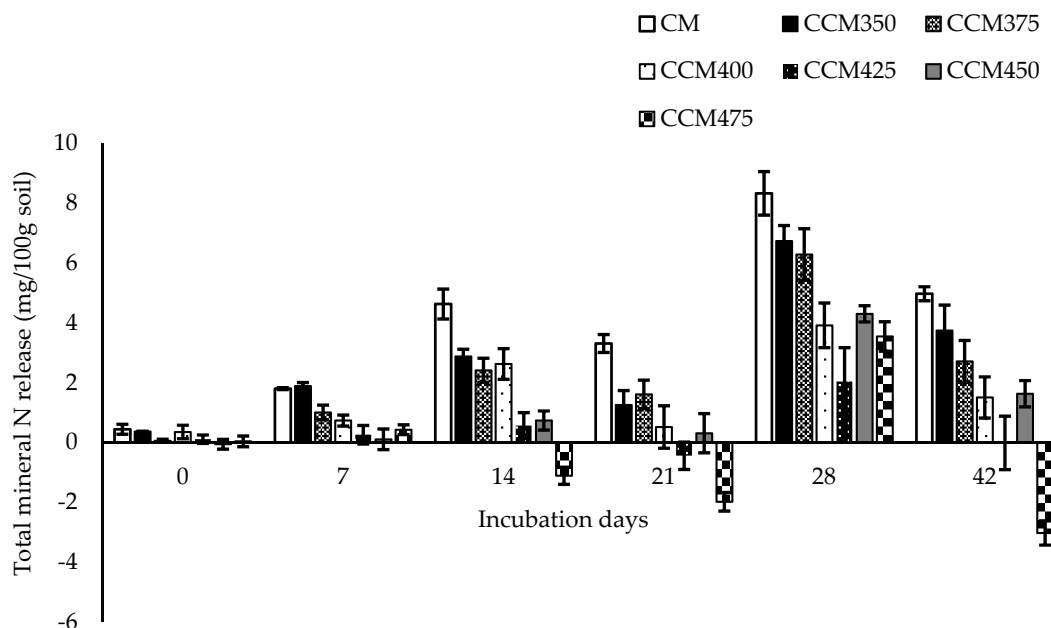


Figure 4. Mineral nitrogen release ability of CM and CCM produced at different temperatures. CM: chicken manure; CCM350, CCM375, CCM400, CCM425, CCM450, and CCM475 represent chicken manure carbonized at 350, 375, 400, 425, 450 and 475 °C respectively. Error bars represent the standard error of the means; n = 3.

3.5. Regression Analysis Between Total Mineral N Released over the 42 Days and Compositional Makeup of the CM and CCM Produced at Different Temperatures

The relative importance of basic chemical properties and nitrogen species in influencing N mineralization of CM and CCM produced at different temperatures was evaluated with linear regression analysis (Figure 5a–f). The quantity of total mineral N released during the 42 day incubation was positively influenced by the initial total N content of the manure ($R^2 = 0.82$; $p = 0.005$), the presence of labile organic N content in the manure ($R^2 = 0.64$; $p = 0.03$), and the atomic H:C ratio of the manure ($R^2 = 0.73$; $p = 0.01$) (Figure 5a–c, respectively). On the other hand, the amount of total mineral N released during the 42 day incubation was negatively influenced by the atomic C:N ratio ($R^2 = 0.92$; $P = 0.001$) of the manure, the presence of pyridine-N content ($R^2 = 0.82$; $P = 0.005$), and the initial pH of the manure ($R^2 = 0.77$; $P = 0.01$) (Figure 5d–f). Pyrrole-N forms had a negative influence on the total mineral N released, but the relationship was not statistically significant (data not shown).

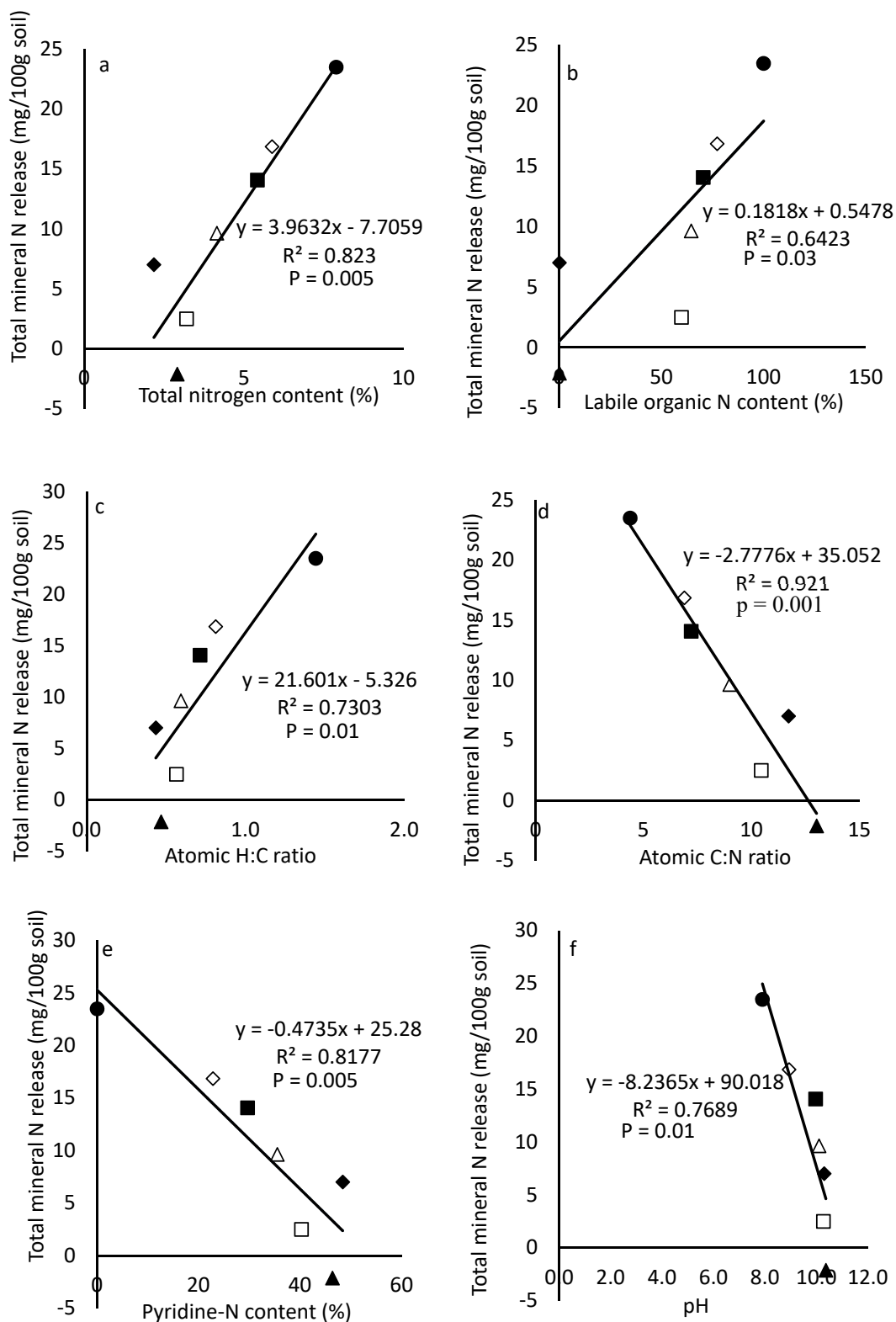


Figure 5. Relationships between total mineral N released from chicken manure and carbonized chicken manure produced at different temperatures in 42 days of incubation and (a) total N content, (b) labile organic nitrogen content, (c) atomic H:C ratio, (d) atomic C:N ratio, (e) pyridine-N content, and (f) pH, respectively. The symbols $\bullet$ $\diamond$ $\blacksquare$ $\triangle$ $\square$ $\blacktriangle$ represent chicken manure and chicken manure carbonized at 350, 375, 400, 425, 450, and 475 °C, respectively.

4. Discussion

4.1. Alteration of the Chemical Properties of CM After Carbonization at Different Temperatures

Research on CM carbonization in the last decades focused widely on the changes of physicochemical properties in response to different temperature conditions [4,8,18]. The results of our physicochemical properties presented in Tables 1 and 2 corroborated with earlier reports stating that with increased carbonization temperature, changes are instituted in the physical and chemical properties of the manure [4,8,18]. Therefore, only properties related to N supply ability and aromaticity of CM after carbonization will be discussed.

In the present study, vast variation was observed in the chemical composition of the CM after carbonization at different temperature conditions (Tables 1 and 2). Nitrogen and its mineral components in CM were gradually degraded with increased carbonization temperatures, leading to a drastic reduction in the amount of total N of the manure (Tables 1 and 2). Following N degradation, C content was concentrated in the manure, which automatically resulted in an increased C/N ratio as carbonization temperature increased (Table 1). In addition to N reduction, the H and O contents also decreased with increasing temperature (Table 1), which is as a result of ongoing dehydration, dehydrogenation, decarboxylation, and condensation reactions during carbonization [32]. The reduction in the N, H, and O during carbonization of the CM could be mainly due to their transformation into volatile gases, bio-oil, and/or incondensable exhaust [33].

The Van Krevelen diagram (Figure 1) validated the pattern of change observed when the H/C and O/C ratios were plotted. In fact, the H/C atomic ratio can be used as an indicator to assess the degree of aromaticity. Progressive decrease was observed in the atomic H/C ratio with increasing carbonization temperature, indicating the formation of structures containing unsaturated carbons, such as aromatic rings. This is consistent with the aromatization of CM observed with increasing extent of thermal alteration caused by increased carbonization temperatures [34]. The pattern of change observed in the chemical composition with carbonization temperatures in the present study is in line with previously reported studies [8,35].

4.2. Changes on the Surface Functional Group of CM After Carbonization at Different Temperatures

Heating at increasing temperatures has a transformational and degrading effect on the surface functional groups of CM [36]. In the present study, several alterations were noted in the surface functionalities of CM as the carbonization temperatures increased from 350 to 475 °C.

The decreased weak broad band of amino acid-N and OH groups ($3600\text{--}2500\text{ cm}^{-1}$) with increasing temperature indicates thermal degradation and loss of compounds containing N, H, and O. This is consistent with the decrease observed in the elemental composition with increased carbonization temperature, as shown in Table 1. The degradation of the OH group with increasing temperatures can also be attributed to continuous dehydration process during carbonization, causing the carboxylic acid to possibly dissolve and hydrolyze [34].

The aliphatic C–H methylene band at 2925 cm^{-1} was reduced with increasing carbonization temperature, and finally disappeared when the manure was carbonized at 450 °C. Hadroug et al. [34] also reported a decrease in the aliphatic C–H methylene band during pyrolysis of CM as the temperature increased due to hydrolysis of the aliphatic chain and dissolution.

The heat also had a reducing effect on the C=O vibration of amide band I, which presented a clear decrease in the intensity of the band as carbonization temperature increased. The decrease in amide band I with increasing temperature also indicates the loss of N in CM through carbonization. This result is similar to that of Hadroug et al. [34], and is probably due to the decomposition of the C=O bond, leading to the formation of carbon monoxide and carbon dioxide [37]. This can result in substantial change in the N functional groups during heat treatment [38,39]. The observed CH_2 deformation peak at around $1435\text{--}1412\text{ cm}^{-1}$ increased gradually with increasing carbonization temperature, which is in line with Hadroug et al. [34].

Compared to the CM, the C–O band at around $1060\text{--}1000\text{ cm}^{-1}$ exhibited stronger peak intensities for the CCM products (Figure 2). However, reduction of the peak started at $450\text{ }^{\circ}\text{C}$, thus suggesting the degradation of cellulose and hemicelluloses, as is expected at higher temperatures [4,40]. The increase in the C–O bands associated with the aromatic ring system supports the increased aromaticity associated with increasing temperature proposed earlier by the H/C atomic ratios (Table 1).

In addition, the peaks between $600\text{ and }800\text{ cm}^{-1}$ are associated with aromatic C–H out-of-plane deformation. This peak increased with carbonization temperature, thus showing the gradual development of aromatic structures during the carbonization process of CM. The changes observed in the surface functional group of CM with increasing carbonization temperatures may affect nutrient dynamic properties and N fertilizer potential.

4.3. N Speciation Pattern During Carbonization of CM at Different Temperatures

In line with previous reports on the effects of thermal treatments on N speciation in organic materials [14,23], the XPS results of this study showed a systematic transformation of the N species within the CM when heated at increasing carbonization temperatures.

The dominant easily mineralizable N-I forms in CM, which are responsible for the high quality and good N fertilizer value of the manure, started decreasing from the lowest carbonization temperature. The reduction in the N-I during carbonization can be partly accounted for by volatile losses of N (Table 1) and also by transformation of the aliphatic N species into aromatic N compounds (Figure 3). Indeed, the reduction of the labile N-I forms in CM is accompanied by the accumulation of N-II forms (a highly stable heterocyclic aromatic N form). The accumulation of the N-II forms continued at the expense of the N-I forms such that, at $450\text{ }^{\circ}\text{C}$, the N-I groups were totally expelled from CM, leaving only heterocyclic N forms and the development of a new aromatic structure, which is in the region proposed to be the N-III form. The N-III further increased when heated to $475\text{ }^{\circ}\text{C}$ at the expense of the N-II functionalities.

Generally, heating of N-rich organic materials like CM considerably affects the molecular composition and functionalities of the resulting heated product, which occurs due to the thermal cracking and polymerization of aliphatic protein–N to heterocyclic N forms [41]. The slight decrease observed in N-II forms at $475\text{ }^{\circ}\text{C}$ and an increase in the N-III could be attributed to bond disruption during thermal treatment at this high temperature, which might have caused depolymerization, leading to the cleavage of some thermally stable bonds [42].

4.4. Relationship Between Total Mineral N Release During the 42 Day Incubation Study and Compositional Makeup of CM and Carbonized CM Produced at Different Temperatures

The regression analysis showed a clear significant influence of the compositional makeup of CM and CCM products on the total mineral N released during the 42 day incubation study (Figure 5). The influence of the basic chemical properties (elemental composition) on N supply ability of CM have been documented, but the influence of the N species present after carbonization of the manure on the subsequent N supply ability of CM is limited. Mubarak et al. [43] reported that the higher the N content of the manure, the higher its N supply ability; the C/N ratio plays a crucial role in the decomposition of the manure, which, when high, can increase the biochemical recalcitrance of the manure to decomposition, and thus limit the N supply ability of the manure.

The H/C atomic ratio can show the possible extent of aromaticity within the material, in which the quantity of aromatic compounds will increase as the H/C atomic ratio decreases [44]. In the present study, the 73% variation of the N supply ability of the manure in soil can be explained by the H/C atomic ratio, and the trend observed was that a decrease in H/C atomic ratio simultaneously decreased the N supply ability of the manure (Figure 5c). This existing relationship between the H/C atomic ratio and the N supply ability of CM in the present study has also been reported for sewage sludge [16].

In addition, the influence of the state of N species present on the ability of the manure to release N during the incubation study showed that N species strongly influence the N supply ability of the

manure. The presence of labile N-I forms had a positive influence on N supply ability of CM and its carbonized products, which was responsible for about 64% of the changes in N released from the manure. The increase in N-II forms, on the other hand, had a negative influence on N supply ability, which accounted for about 82% of the variation. This observation is possible due to the fact that the N-I nitrogen forms consisted of the hydrolysable easily decomposable aliphatic N fractions, such as amino acid-N, amino sugar-N, uric acids, amines, amides, and nitriles, which are mainly responsible for contributing to immediate N mineralization [45]. The N-II forms, on the other hand, are large heterocyclic aromatic N structures that cannot be easily hydrolyzed and decomposed in soil, and could hence limit N supply ability [24].

It is worth noting that the parameters that affected N supply ability negatively have the possibility to influence it more greatly than the parameters that have positive influence on the N supply ability of the manure. For instance, the atomic C:N ratio had 92% influence on the N supply ability, while the total N content had 82% influence. In addition, the presence of N-II species had 82% influence on N supply ability of the manure, but the N-I species had 64%. Overall, this indicated that CM carbonization should be done with care in order to prevent huge accumulations of highly stable heterocyclic aromatic N compounds, which will in turn greatly negatively affect the sustainable supply of N from this high-quality organic fertilizer.

4.5. Connection Between the Chemical Alteration and N Supply Ability of CM During Carbonization at Different Temperatures

In response to the increased alterations in the properties of CM during carbonization, the N fertilizer capacity of the manure also decreased, which is more evident at temperatures ≥ 400 °C. According to the N availability results (Figure 4), despite the chemical composition, surface functional group alterations and N transformation that occurred during CM carbonization at 350 and 375 °C, CCM350 and CCM375 still exhibited statistically similar N supply ability to those of CM throughout the incubation study, except at day 14 for CCM375. This indicated that the alterations at these temperatures were minute to have been capable to cause significant reduction in the N supply ability of the manure. On the other hand, the alterations in chemical composition, surface functional groups, and speciation of labile N species to heterocyclic aromatic N compounds that occurred to CM during carbonization at temperatures ≥ 400 °C are huge (see Figures 2 and 3). Therefore, the N supply abilities of the manure carbonized at these temperatures were highly compromised, which led to significant reduction in mineral N released compared to the CM throughout the 42 day incubation study. For comparison, Song and Guo [8], in a sequential extraction with HCl or deionized water, found that pyrolysis at increasing temperature conditions significantly decreased the potential N availability of CM, especially at temperatures ≥ 400 °C. Similarly, Zheng et al. [46] performed a sequential extraction of biochar produced from giant reed at different temperatures using water, HCL, and KCL; their results showed a decrease in the availability of N at higher carbonization temperatures, and concluded that low temperatures (below 400 °C) may be optimal for producing biochar from giant reed in order to improve nutrient availability. Our results therefore suggested that carbonization of CM at temperatures ≥ 400 °C, as previously practiced and recommended [3,10,33], will lead to alterations of the composition and surface functional groups and accumulation of highly stable heterocyclic aromatic N structures that are substantial and can negatively affect the N supply ability of the manure. This has serious negative implications for the use of carbonized CM for sustainable production of crops. Indeed, Steiner et al. [12] already observed negative effects on the quality of ryegrass due to the decreased N supply ability of CM carbonized at 500 °C. The results of Ishimori et al. [11] on plant growth and yield indicated that carbonized CM at 528 °C cannot supply sufficient N to independently support plant productivity.

Altogether, the basic chemical properties play an important role in determining the ability of the manure to supply N after carbonization, and thus can be used as preliminary forms for assessing the N release capacity of the manure after carbonization. Nonetheless, the chemical state of the N species within the solid matrices of the manure seems to be the most prominent factor influencing

the N fertilizer capacity of the manure. This is so because, despite the fact that equal quantities of N were applied to soil for all of the manure forms used in this study, the N supply ability of the manure still decreased with carbonized manure that contained huge quantities of heterocyclic N compounds, indicating that the differences in the chemical state of N within the manure indeed might have greatly affected their decomposition and subsequent supply of N in the soil system. Studying the major characteristics that might influence the release of P and K from CM after carbonization, Hadroug et al. [34] reported that the pyrolysis process converts P into more stable magnesium phosphate and/or calcium phosphate complexes, which, overall, is the main influence for the reduced P availability after CM pyrolysis. To date, in-depth systematic microscopic N alteration studies on carbonized CM and how such compositional alterations affect the potential N availability are lacking, but this topic has been well documented for other N-rich organic materials, and they indicated that heat can cause thermal degradation of the chemical composition of volatile compounds, alteration of the structural functionalities, and development of heterocyclic aromatic compounds, which in turn will affect the bioavailability of nutrients in soil [13,16,17,47].

5. Conclusions

The compositional alteration that took place during carbonization of CM at 300–375 °C were minute; thus, N supply abilities of CCM350 and CCM375 were comparable to the N supply ability of the CM. When the manure was carbonized at 400 °C or higher, large compositional variations occurred. Hence, the N supply ability of the manure started decreasing significantly for the majority of the sampling days at 400 °C and continued with increasing carbonization temperatures. In order to utilize the carbonization process for converting the manure into environmentally safe organic material while preserving the good N fertilizer value of the manure for sustainable use in agriculture, CM should not be carbonized above 375 °C. Hence, we recommend that 375 °C instead of 500 °C should be considered as the new threshold carbonization temperature for CM in order to sustainably maintain the good N fertilizer value of the manure.

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Appendix A

Table A1. Basic chemical properties of the experimental soil.

Parameters	Amount of Nutrient
Total N (%)	0.1
Total C (%)	1.1
C/N ratio	9.4
NH ₄ ⁺ -N (mg/100 g)	0.82
NO ₃ -N (mg/100 g)	1.84
Organic N (%)	0.11
pH	6.7

Appendix B

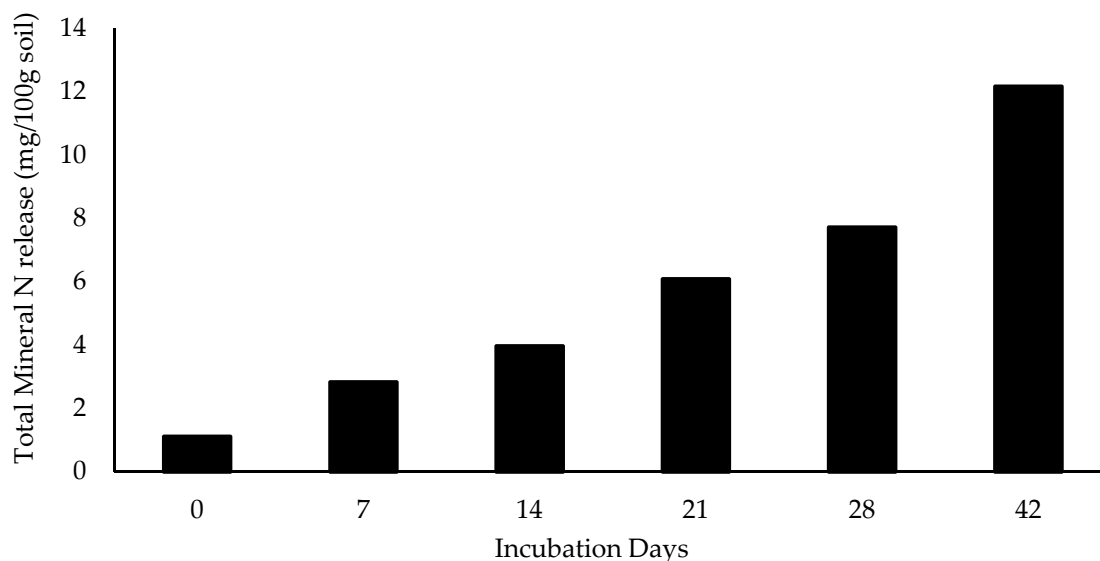


Figure A1. Mineral nitrogen release ability of the control soil.

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