Organic carbon mineralization of the biochar and organic compost of poultry litter in an Argisol

Mineralização de carbono orgânico do biocarvão e do composto orgânico de cama de aviário em um Argissolo

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Highlights

The organic compost was obtained by incubating poultry litter for 120 days.
The biochar was obtained by pyrolysis for 3 h in a muffle furnace.
The highest $C-CO_2$ mineralization was observed in the treatments with organic compost.
Biochar is efficient in reducing the soil carbon and mitigate the "greenhouse" effect.

Abstract

The dynamics of the organic residues added to the soil are closely related to its mineralization rate. Therefore, the present study aimed to evaluate the organic carbon mineralization in soil samples incubated with different doses of biochar and organic compost from poultry litter. Carbon mineralization was evaluated experimentally by measuring the $C-CO_2$ liberated by incubating 200 g of soil mixed with different doses 0, 5, 10, 15, and 20 t ha^{-1} of both biochar and organic compost for 61 days. The soil microbial activity, and consequently the carbon mineralization, increased with the application of doses of biochar and organic compost from the poultry litter. The highest $C-CO_2$ mineralization was observed in the treatments that received organic compost. The carbon mineralization process followed chemical kinetics with two simultaneous reactions. The greatest amount of released and accumulated $C-CO_2$ was observed in the soil incubated with 15 and 20 t ha^{-1} of organic compost from the poultry litter. The doses of biochar did not influence the content of mineralized carbon; this behavior was not verified with the use of this compost, whose highest content corresponded to 85.69 mg kg^{-1}, applying 20 t ha^{-1}.

Key words: Organic substrate. Microbial activity. $C-CO_2$. Chemical kinetics.

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Resumo

A dinâmica dos resíduos orgânicos adicionados ao solo está intimamente relacionada à sua taxa de mineralização. Para isso, o presente estudo teve como objetivo avaliar a mineralização do carbono orgânico em amostras de solo incubadas com diferentes doses de biocarvão e de composto orgânico da cama de aviário. A mineralização de carbono foi avaliada experimentalmente medindo-se o $C-CO_2$ liberado durante uma incubação de 200 g de solo misturado com doses de 0, 5, 10, 15 e 20 t ha^{-1} de biocarvão e de composto orgânico, durante 61 dias. A atividade microbiana do solo e consequentemente a mineralização de carbono aumentaram com a aplicação das doses de biocarvão e de composto orgânico da cama de aviário. A maior mineralização de $C-CO_2$ foi observada nos tratamentos que receberam composto orgânico. A mineralização do carbono foi um processo dividido em duas fases distintas, a primeira com mineralização intensa e meia-vida curta do carbono e a segunda com processo de mineralização lento, com tendência de redução e estabilização do fluxo de $C-CO_2$. A mineralização de carbono obtida com os substratos avaliados no presente estudo mostrou que os materiais pirolisados (biocarvão) são bastante eficientes para sequestrar o carbono do solo e mitigar o efeito "estufa".

Palavras-chave: Substrato orgânico. Atividade microbiana. $C-CO_2$. Cinética química.

Introduction

The poultry industry in Brazil annually generates more than 6.8 million cubic meters of poultry litter (Corrêa & Miele, 2011), a material containing high contents of organic carbon, nitrogen, phosphorus, potassium, and other plant nutrients, that is commonly applied to agricultural lands as a soil amendment and organic fertilizer (Guo, Tongtavee, & Labreveux, 2009). According to Santos and Grangeiro (2013), this organic fertilization constitutes a low-cost and economically viable agricultural technique. However, its repeated application results in a severe nutrients accumulation in the soil, with subsequent flow and lixiviation losses to the underwater reserves causing eutrophication and degradation of soil quality (Boesch, Brinsfield, & Magnien, 2001). To prevent nutrient wastage, poultry litter is occasionally transformed into an organic compost, comprising relatively stable humic substances that are more suitable for soil fertilization. Another efficient strategy to maintain a more constant and long-term nutrient supply to the plants and prevent rapid losses is to transform the poultry litter into biochar via pyrolysis.

Biochar reportedly has a higher carbon stability than organic carbon (Wardle, Nilsson, & Zackrisson, 2008). Kuzyakov, Bogomolova and Glaser (2014) confirmed that biochar is a carbon-rich, highly recalcitrant organic material with a long-term stability. Since biochar retains organic carbon during pyrolysis, its addition to the soil increases the total soil carbon content. (Woolf, Amonette, Street-Perrott, Lehmann, & Joseph, 2010). This causes reduction of carbon in the soil (Pokharel, Zilong, & Chang, 2020), which consequently decreases its emission to the atmosphere and reduces the greenhouse effect (Liu et al., 2016). A comparison between the in vitro carbon mineralization kinetics of several biochars and that of a wheat straw, in three different soils, revealed a higher carbon mineralization and lower half-life of the wheat straw when compared to the biochars

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(Qayyum, Steffens, Reisenauer, & Schubert, 2012).

The mineralization of organic matter, essential for soil carbon dynamics, depends on the temperature, soil water content, soil characteristics, and microbial activities, such as respiration. Few short-term incubation studies showed that the biochar in soil can be degraded by both photochemical and microbiological processes (Novak et al., 2009; Zhao, Coles, & Wu, 2015; Shrestha, Traina, & Swanston, 2010).

The microbial respiration is quantified using the soil organic matter oxidation, and CO_2 emission (Silva, Alburquerque, Santos, Oliveira, & Guedes, 2013). The microbial respiration indicates improvement and better quality of soil nutrient mineralization.

It has been observed that when biochar is applied to the soil, ~10-20% of the material mineralizes to CO_2, and aromatic and aliphatic compounds can precipitate, forming more complex molecules, thus, increasing the resistance to microbial decomposition (Jeffery, Coliins, & Bailey, 2010). Application of poultry litter biochar in two Argisols showed CO_2 mineralization of 12.5 ± 1.3 and 7.1 ± 0.7 mg CO_2 per day (Sigua et al., 2014).

Little is known about the life of biochar in soil, mainly for two reasons: 1) the recalcitrancy of biochar depends on a series of factors, including the type of biomass used in pyrolysis, production conditions, soil properties, and climate; 2) quantifying the stability of biochar requires long-term observations, which is more than the traditional periods normally considered in experiments. Labile carbon has a medium life of 1-5 years while inert organic carbon, such as biochar, may last thousands of years

(Winsley, 2007). Bruun, Jensen and Jensen (2008) reported that CO_2 evolution from plants proceeds with a lag phase, followed by a period of higher evolution, and finally, a period of very low evolution. However, CO_2 evolution from the biochar had no lag phase, but fast evolution during the first 5-8 days, followed by a period of slow evolution. The average residence time of biochar varies between 4 and 29 years, depending on the soil type and quality of biochar (Steinbeiss, Gleixner, & Antonietti, 2009). It has been reported that the biochar degradation rate depends more on the combustion temperature and duration than the source materials (Zimmerman, 2010). The particle size of biochars is an important parameter for their ability to react with soil particles (Laird, Brown, Amonette, & Lehmann, 2009), and is believed to affect their resistance to microbial mineralization (Manyà, 2012).

The objective of the present work was to study and compare the carbon mineralization of different doses of poultry litter organic compost and its biochar in an Argisol.

Materials and Methods

The study was conducted at the Irrigation and Salinity Laboratory of the Agricultural Engineering Department, Federal University of Campina Grande, Paraiba State, using an Ultisol Ustults, collected from the Paraíba State, Brazil. The Ultisol was collected from 0-20 cm depth, air-dried, and sieved using a 2.0 mm sieve. The soil, classified as a loamy sand had the following physico-chemical characteristics: 869.6 g kg^{-1} of sand; 90.4 g kg^{-1} of silt and 40.0 g kg^{-1} of clay, soil density = 1.46 g cm³; particle density = 2.69 g cm³;

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total porosity = 45.73 %; pH (H_2O) = 5.2; Ca = 2.20 $cmol_c$ kg^{-1}; Mg = 2.40 $cmol_c$ kg^{-1}; Na = 0.04 $cmol_c$ kg^{-1}; K = 0.11 $cmol_c$ kg^{-1}; H + Al = 2.38 $cmol_c$ kg^{-1}; MO = 17.9 g kg^{-1}; P = 3.8 mg kg^{-1} and CTC = 7.13 $cmol_c$ kg^{-1} (Teixeira, Donagemma, Fontana, & Teixeira, 2017).
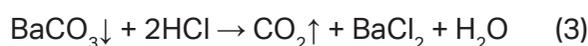
The organic compost was obtained by incubating poultry litter for 120 days, maintaining its humidity close to the field capacity of the soil, and mixing it periodically until a decomposed humic material was formed. The resultant compost was dried, sieved using a 2.0 mm sieve, and chemically characterized, according to the Manual of Official Analytical Methods for Fertilizers and Correctives (Ministério da Agricultura, Pecuária e Abastecimento [MAPA], 2017). The following characteristics were observed: Total Nitrogen = 24.00 g kg^{-1}; P_2O_5 = 5.71%; K_2O = 4.19%; Ca = 6.22%; Mg = 1.08%; pH = 9.37; organic carbon = 237.30 g kg^{-1}; C/N ratio = 9.93; and cation exchange capacity (CEC) = 82.47 cmolc kg^{-1}.

The biochar was generated through pyrolysis by putting a mixture of poultry litter bed and poultry wastes in a muffle furnace for 3 h, at a temperature of 350 °C, in the absence of oxygen, to undergo thermal decomposition. After approximately 24 h, the cooled biochar was removed from the muffle furnace. Chemical analysis of the biochar, according to the Manual of Official Analytical Methods for Fertilizers and Correctives (MAPA, 2017) developed for vegetal charcoal, presented the following results: Total Nitrogen = 30.6 g kg^{-1}; P_2O_5 = 5.76%; K_2O = 6.61(%); Ca = 5.27%; Mg = 1.08%; pH = 8.97; Organic Carbon = 400.2 g kg^{-1}; C/N Ratio = 13.08 and CEC = 58.61 $cmol_c$ kg^{-1}.

A randomized experimental design was adopted, using the two substrates, organic compost and biochar, both in the following dosages: 0 (control), 5, 10, 15, and 20 t ha^{-1}, that is, 0.00, 0.39, 0.77, 1.16, and 1.55 g, respectively, in 200 g of soil. Additionally, three repeat experiments were also set up, making 30 experimental units. The 200 g soil mixtures, with the respective doses of the two substrates, were placed in 1.3 L respirometer pots and dampened with distilled water to increase the water content of the soil by 60% of the field capacity. A 50 ml beaker, containing 20 ml of 0.5 mol L^{-1} NaOH, was placed in each pot, to adsorb the C-CO_2 released by the treatment. After this, the respirometer pots were hermetically sealed to prevent the entry of atmospheric CO_2 and the exit of experimentally produced CO_2. The pots were kept in a closed, dark chamber, at a temperature of 27 °C, for 61 days. The evolved C-CO_2 was measured each day, for the first 10 days, followed by measurement on the 14th, 19th, 27th, 37th, and 61th days, since the start of incubation. After each evaluation, the NaOH solution was replaced.

The liberated CO_2 was quantified by titrating the NaOH with standard 0.4 mol L^{-1} HCl, using 2 drops of 1% phenolphthalein after the previous precipitation of the carbonate adding 0.5 ml of 1.5 mol L^{-1} $BaCl_2$.

The chemical reactions that occurred in the quantification of CO_2 in an alkaline medium are described below by the three equations.

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad (1)$$

$$Na_2CO_3 + BaCl_2 \rightarrow BaCO_3\downarrow + 2NaCl \qquad (2)$$

$$BaCO_3\downarrow + 2HCl \rightarrow CO_2\uparrow + BaCl_2 + H_2O \qquad (3)$$

The mineralized carbon content was determined following the methodology of Hopkins (2008). The CO_2 content that reacted with the NaOH solution during the incubation was calculated as follows:

$$CO_{2\,reacted} = 0.5 \times (((V_{NaOH} \times C_{NaOH})/1000) - ((V_{HCl} \times C_{HCl})/1000)) \quad (4)$$

where V_{NaOH} and C_{NaOH} are the initial volume (ml) and the molar concentration of NaOH (mol L^{-1}), respectively, and V_{HCl} and C_{HCl} are the volume (ml) and molar concentration of HCl (mol L^{-1}) used for titration.

Once the CO_2 content was quantified, the mineralized carbon was calculated using the following equation:

$$C_{mineralized} = CO_{2\,reacted} / (\text{soil mass (g)} \times \text{incubation time (h)}), \quad (5)$$

The carbon mineralization kinetics can be explained by two models. The first model uses a first-order exponential equation (Murwira, Kirchmann, & Swift, 1990):

$$C_m = C_o (1 - e^{-k.t}) \quad (6)$$

where C_m is the cumulative mineralized organic carbon (mg C-CO_2 kg^{-1}) at time t (days), C_o is the total amount of potentially mineralizable carbon (mg kg^{-1}), and k is the constant mineralization rate.

The second model describes carbon mineralization through two simultaneous reactions (Molina, Clap, & Larson, 1980):

$$C_m = C_1 (1 - e^{-k_1.t}) + C_2 (1 - e^{-k_2.t}) \quad (7)$$

where C_1 and C_2 are the active and resistant fractions (pools) that are decomposed at mineralization rates k_1 and k_2, respectively. The sum of C_1 and C_2 has the same physical meaning as C_o in the first described model (Foo & Hameed, 2010).

The parameters of both models were calculated through linear regression, with the Microsoft Office Excel SOLVER tool, using the sum of squared errors (SSE) that represents the difference between the experimental and calculated mineralized carbon (Foo & Hameed, 2010). The determination coefficients, R^2 and SSE, were used to compare the model's adjustments.

The carbon mineralization half-life was calculated using the equation of Sposito (2008):

$$t_{1/2} = \frac{0,693}{k} \quad (8)$$

The carbon mineralization half-life denotes the time required for the mineralization of half of the potentially mineralizable carbon (C_o) during the 61 days of incubation.

The mineralization fraction (MF) was calculated at the end of the incubation period using the following equation:

$$MF = 100 C_m / C_a \quad (9)$$

The mineralization fraction corresponds to the carbon added by the biochar and the organic compost; C_m is the difference between the C-CO_2 released and accumulated in the treatment and the control (mg kg^{-1}), and C_a is the quantity of carbon added by the biochar doses and the organic compost (mg kg^{-1}).

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Results and Discussion

C-CO$_2$ evolution rate

The soil microbial activity was evaluated based on the carbon fluxes in the C-CO$_2$ form. Figures 1A and 1B show the medium C-CO$_2$ evolution rates over time during the 61 days incubation period. It was observed that the highest amount of C-CO$_2$ was liberated on the first day of incubation for both, the highest biochar doses and the organic compost, in almost equal amounts (15.7 mg kg^{-1}), corroborating the results of Shen, Zhu, Cheng, Yue and Li (2017), and Capuani, Rigon, Beltrão and Brito (2012).

In general, the treatments that received different biochar doses exhibited similar behavior after the sixth day where the liberated C-CO$_2$ decreased with time and stabilized after the 25th day (Figure 1A). This similarity in the C-CO$_2$ evolution signifies that the biochar doses did not negatively influence the microbial activity.

Till the 19th day, the soils that received the poultry litter organic compost exhibited differences among the C-CO$_2$ evolution rates for different compost doses, with the lowest gas emission in the control and the highest in the 20 t ha^{-1} compost dose (Figure 1B).

The C/N ratio of the substrate influences their decomposition during carbon mineralization. High C/N rates of the compost (9.93) and biochar (13.08), and the temperature and humidity (27 °C and 60%, respectively), probably promoted favorable conditions for microbial activity and, consequently, for carbon mineralization in the soil (Araújo, Feitosa, Primo, Taniguchi, & Souza, 2020).
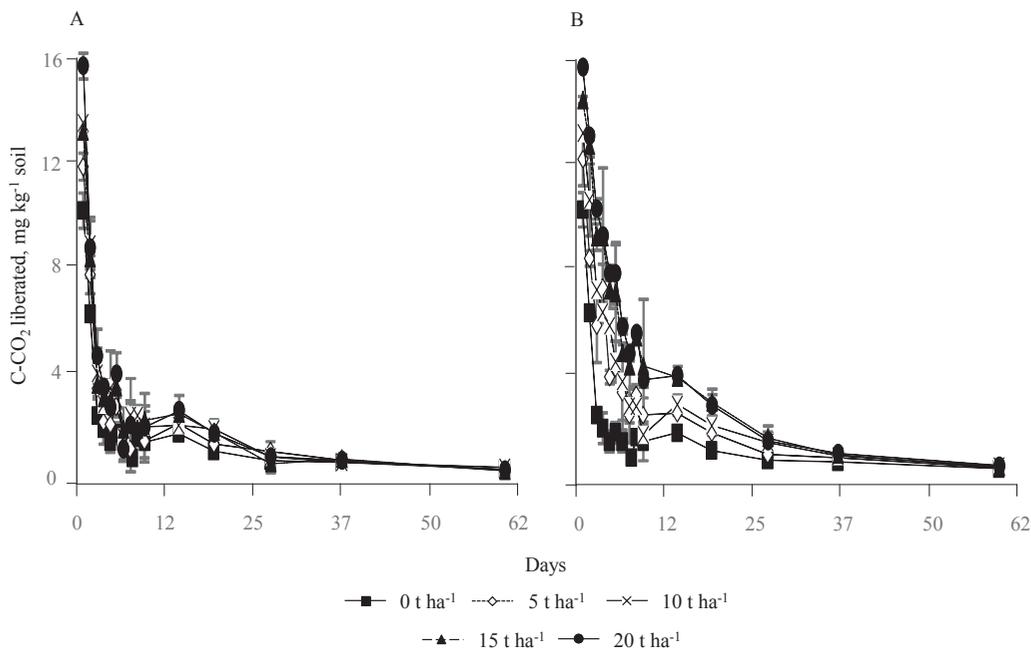

Figure 1. Carbon (C-CO$_2$) evolution rate with time during the 61 days incubation period for the biochar (Fig 1A) and organic compost (Fig IB) treatments.

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During the 61-day period, the daily $C-CO_2$ evolution, independent of the applied treatments, occurred at a rapid rate in the beginning of the incubation, followed by a lower rate, in the last evaluation period, corroborating the results of Andrade, Bibar, Coscione, Pires and Soares (2015). The rapid decrease in $C-CO_2$ evolution indicates the presence of organic fractions in the biochar and organic compost.

The biochar has a degradable organic fraction that easily exhausted at the beginning of the incubation process, and a recalcitrant fraction that remained after the degradable sources of carbon were mineralized. These results are corroborated by Cross and Sohi (2011), and Sagrilo, Jeffery, Hoffland and Kuyper (2015). The $C-CO_2$ evolution decreases in soils incubated with biochar (Shen et al., 2017; Bramble, Gouveia, & Ramnarine, 2019), suggesting a low amount of degradable substrate, and access of more recalcitrant by the microbes with time, at lower rates (Andrade, Oliveira, & Cerri, 2006).

The differences in the $C-CO_2$ evolution during the first 19 days, for different doses of the two substrates, shows that the organic compost has a larger amount of degradable carbon than the biochar.

Capuani et al. (2012) evaluated the microbial activity in different soils when applied with castor bean "pie" and corn textile residues. They verified that more CO_2 was produced at the beginning of the decomposition and decreased thereafter.

Accumulated carbon in the $C-CO_2$ form

During the 61 days of incubation, a cumulative increase of $C-CO_2$ was observed due to the application of increasing doses of biochar and organic compost (Figures 2A and 2B). The observation is in agreement with the results of Sistani, Simmons, Jn-Baptiste and Novak (2019), and Bramble et al. (2019).

Comparing the evolution of $C-CO_2$ production among the doses of 20 t ha^{-1} for both substrates, it was verified that the soil incubated with the organic compost liberated 158.84 mg $C-CO_2$ kg^{-1} of soil, an increase of 55.84% when compared with the soil incubated with biochar, which liberated only 101.92 mg $C-CO_2$ kg^{-1} of soil. Our finding supported the results of Andrade et al. (2015), who studied the carbon mineralization of the poultry litter bed and observed that the $C-CO_2$ accumulated in the biochar treatment was 30% lower than that of the organic compost treatment.
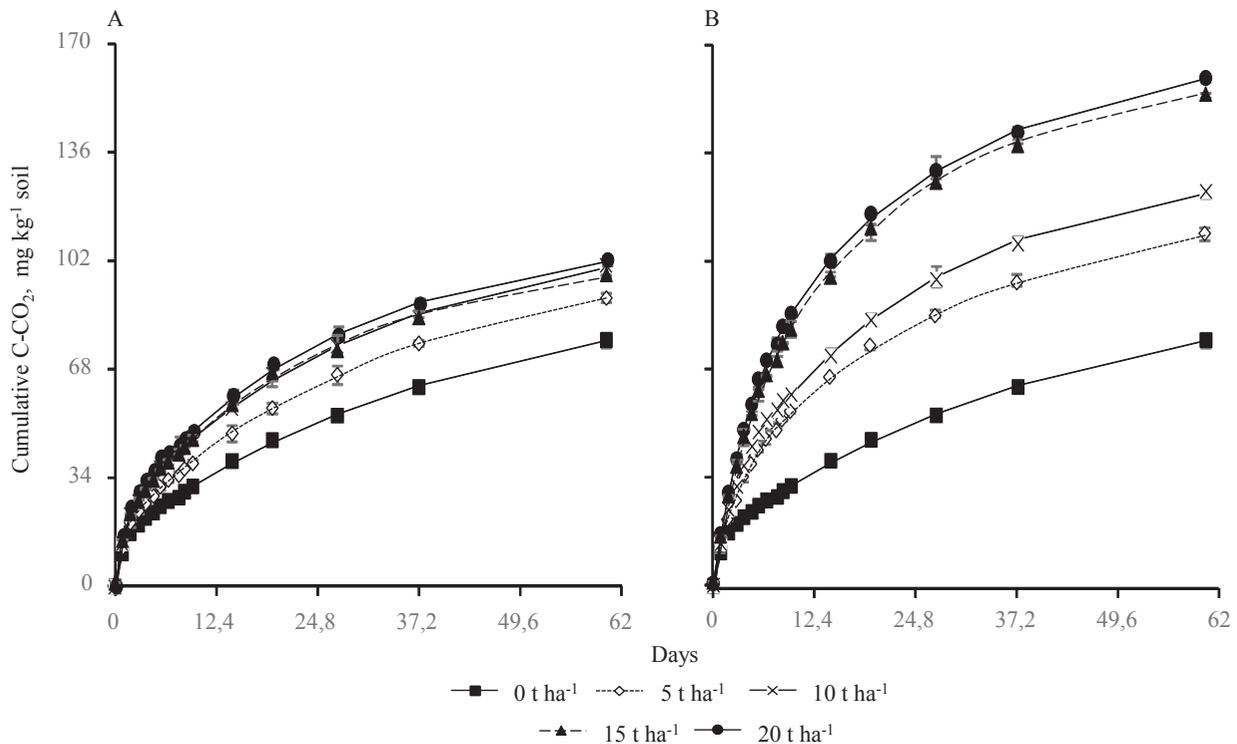
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Figure 2. Carbon (C-CO$_2$) liberated and accumulated during the 61 days incubation period for the biochar (Fig 2A) and organic compost (Fig 2B) soil mixed treatments.

As shown in Figure 2A, during the first five days of incubation, the C-CO$_2$ accumulation was similar (mean of 31.0 mg kg^{-1}) for the doses of biochar applied. After this, it was verified that the accumulation of organic carbon increased by 32.2% with the application of 20 t ha^{-1} of biochar (101.9 mg kg^{-1}) compared to the control (77.1 mg kg^{-1}).

When using the organic compost (Figure 2B), the C-CO$_2$ accumulation was similar for the doses applied only during the first three days of incubation, differing afterward, with an increase of C-CO$_2$ with the higher compost doses; higher liberation was observed at doses of 15 and 20 t ha^{-1}. An increase of 106.02% was obtained for the doses of 20 t ha^{-1} of compost (158.84 mg kg^{-1})

when compared with the control (77.1 mg kg^{-1}). These results indicate a positive contribution of the organic compost to the soil microbial activity, and is consistent with the results found by Steiner, Melear, Harris and Das (2011).

The carbon mineralization results for the doses of biochar and organic compost after 61 days of incubation are presented in Table 1.

The application of 5 t ha^{-1} of biochar showed the highest mineralization fraction, MF (1.69%), decreasing with the biochar doses (Table 1). The low MF values obtained with higher doses reinforces the assumption that there are recalcitrant compounds in its structure, that is, of difficult biological degradation in the soil. (Sagrilo et al., 2015;

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Andrade et al., 2006). Sigua et al. (2014) found a higher MF of 4.3% when poultry litter biochar was mixed with soil (5.110 mg kg 1 of C) and incubated for 50 days.

The MFs were higher in the organic compost than biochar, for all doses, with an average 7.21% total added carbon in 5 t ha^{-1} of compost. This rate was inferior to the one obtained by Andrade et al. (2015) that had a value of 49.7%. The low carbon mineralization of the organic compost found in the present study may be associated with the

utilized biomass, containing chicken excreta, sugarcane residues, and other rations given to the poultry. The poultry ration was formulated using corn, soybean, calcareous, calcic phosphate and a supplement of amino acids, vitamins, minerals, and antibiotics such as salinomycin, a growth promoter (Dalólio, Silva, Baêta, Tinôco, & Carneiro, 2017). According to Chee-Sanford et al. (2009), salinomycin is not completely absorbed by animals and ~75% is probably released into the environment.

Table 1
Added, liberated and mineralized carbon (mg kg^{-1}), and Mineralization Fraction (MF, %) of the biochar and organic compost for the different doses applied, after 61 days of incubation

Dose	Added C (Ca)	Liberated C[1]	Mineralized C (Cm)	MF[2]
t ha^{-1}	----------------------------mg kg^{-1}-----------------------			
Biochar				
0	-	77.29 (±3.06)	-	-
5	780.39	90.50 (±5.22)	13.22	1.69 (±0.1)
10	1540.77	100.77 (±1.86)	23.48	1.52 (±0.15)
15	2321.16	96.54 (±1.06)	19.25	0.83 (±0.17)
20	3101.55	102.32 (±5.77)	25.03	0.81 (±0.15)
Organic Compost				
0	-	77.29 (±3.06)	-	-
5	462.74	110.66 (±4.13)	33.37	7.21 (±1.55)
10	913.61	124.00 (±6.22)	46.71	5.11 (±0.89)
15	1376.34	153.35 (±5.11)	76.06	5.53 (±0.44)
20	1839.08	159.12 (±0.81)	81.83	4.45 (±0.21)

[1] Mean ± standard error; [2]MF (%) = 100 Cm/Ca ; Cm = mineralized carbon calculated by the difference among the liberated and accumulated C-CO_2 in the treatment and in the control; Ca = carbon added to the soil.

Although the amount of accumulated C-CO_2 increased with the substrate doses (Figure 2A and 2B), the MF decreased (Table 1), similar to the results of Andrade et al. 2006). The metabolic needs of the microorganisms were

overcome due to the carbon-rich substrate added, thus, incapacitating the degradation of the excess organic carbon. Furthermore, the respiration of microorganisms generate a great demand for oxygen, resulting in low

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aeration in the substrate, prejudicing the remaining carbon consumption (Khalil et al., 2002).

Mineralized Carbon

The cumulative mineralizable carbon (C_m) of the substrates were evaluated by calculating the difference between the liberated and accumulated $C-CO_2$ in the treatments (Table 1).

At the lowest dose, the C_m of the incubated poultry bed was 64.27% more than that of the biochar, and this difference increased with the substrate dose (Figure 3). Carbon mineralization increased significantly ($p < 0.01$), at a rate of 3.496 mg kg^{-1} per t ha^{-1}, reaching maximum (85.70 mg kg^{-1}) in the highest dose (20 t ha^{-1}). However, this value was lower than that of Andrade et al. (2015), that had a mineralizable carbon of 1535.47 and 1529.39 mg kg^{-1} after incubation of soil and plain sand, respectively, with 3101.55 mg kg^{-1} of organic compost.
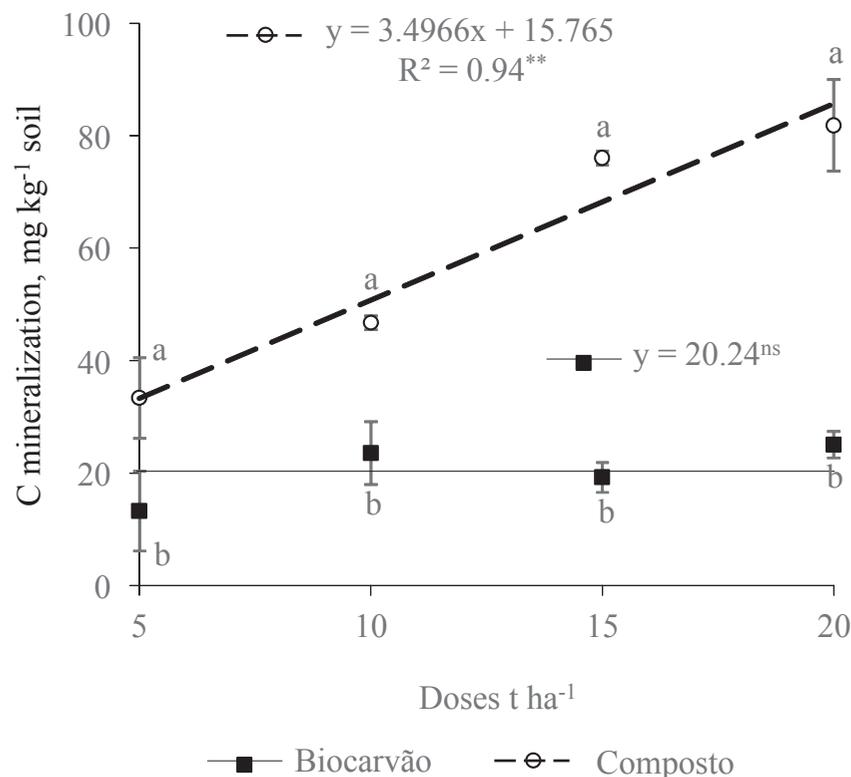

Figure 3. Mineralized and accumulated Carbon in 61 incubation days for the different added doses of organic compost and biochar.
**, ns significant to the 1% probability and not significant, respectively, Vertical bars correspond to the standard error intervals. Means followed by the same values are not different among them.

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After incubation of poultry litter with soil and plain sand, Andrade et al. (2015) observed a significant increase in carbon mineralization with the applied doses of poultry litter that corroborates the results obtained in the present study. Similar behavior, independent of the applied dose, was not observed when poultry litter biochar was used. Although the biochar had a carbon (C) content of 400.00 g kg^{-1}, higher than the organic compost (237.30 g kg^{-1}), the mineralization rate of biochar was low. This can be explained by the pyrolysis process, where volatile losses (methanol, acetic acid, CO, H_2, CO_2, low mass molecules, fatty acids, oils, and resins) occur, in addition to hemicellulose decomposition and water liberation (Zhao, Cao, Mašek, & Zimmerman, 2013). Thus, the biochar has a higher stability, due to the variable losses of H, O, C, and N, which preserves relatively more carbon, reducing the H/C, O/C, and (O+N)/C ratios (Novak et al., 2009).

The carbon mineralization evaluated in the present study partially corroborates the results of Lehmann, Gaunt and Rondon (2006) that pyrolyzed materials are more efficient in reducing soil carbon and mitigating the greenhouse effect. Bruun and EL-Zehery (2012) evaluating whether the addition of biochar to the soil affects the degradation of litter and of soil organic matter (SOM) found that the biochar mineralization occurred more slowly when compared to litter and soil organic matter, confirming its high stability.

Kinetic study

The C-CO_2 mineralization obtained in the present study adjusted satisfactorily to the two kinetic models (first-order and two simultaneous reaction) (Table 2).

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Table 2

Chemical kinematic and half-life mineralization ($t_{1/2}$) obtained throughout the adjustment of the liberated carbon to kinematic equations of first order and with two simultaneous reactions

Dose t ha⁻¹	First order model					Two simultaneous reactions model									
	C_0 mg kg⁻¹	K day⁻¹	$t_{(1/2)}$ day	R^2	SSE	C_1 mg kg⁻¹	k_1 day⁻¹	$t_{(1/2)1}$ day	C_2 mg kg⁻¹	k_2 day⁻¹	$t_{(1/2)2}$ day	R^2	SSE	C_1/C_2 (%)	K_1/K_2
---Biochar---															
0	70.78	0.0664	10	0.96	377.8	14.84	1.017	1	81.12	0.024	29	0.99	3.26	18.3	42.4
5	83.31	0.0714	10	0.96	456.7	17.23	0.976	1	87.57	0.030	23	0.99	2.79	19.7	32.5
10	90.93	0.0822	8	0.96	516.4	21.45	0.762	1	90.15	0.034	20	0.99	11.42	23.8	22.4
15	88.41	0.0820	8	0.97	418.5	18.36	0.916	1	85.40	0.039	18	0.99	12.21	21.5	23.5
20	92.38	0.0889	8	0.96	608.7	22.45	0.925	1	88.80	0.037	18	0.99	8.12	25.3	25.0
---Organic Compost---															
0	70.78	0.0664	10	0.96	377.8	14.84	1.017	1	81.12	0.024	29	0.99	3.26	18.3	42.4
5	100.74	0.0868	8	0.98	389.4	31.56	0.347	2	91.95	0.032	21	0.99	8.70	34.3	10.8
10	113.06	0.0865	8	0.97	546.1	33.22	0.397	2	104.89	0.033	21	0.99	6.44	31.7	12.0
15	144.36	0.0871	8	0.99	361.8	38.34	0.308	2	122.45	0.046	15	0.99	13.56	31.3	6.7
20	148.10	0.0927	7	0.99	421.9	54.65	0.248	3	115.37	0.039	18	0.99	11.57	47.4	6.4

SSE = Sum of squared errors; C_0, C_1, C_2 = Potentially mineralizable carbon in 61 days, during the first phase and the second phase of the degradation, respectively; k, k_1, k_2 = Velocity of the carbon degradation reaction during the first 61 days, first and second phase of the degradation reaction, respectively, and $t_{(1/2)}$, $t_{(1/2)1}$, $t_{(1/2)2}$ = carbon half-life during the first 61 days, first and second phase of the degradation, respectively.

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The determination coefficient (R^2) and the SSE show the efficiency of adjustment between the model estimates and the experimental data. The second model, using two simultaneous reactions, was the most efficient, describing 99% of the mineralization, carbon variation with time, and incubation conditions. This model also showed lower SSE values, independent of the substrate and doses utilized.

The two simultaneous reactions model suggests that the carbon mineralization is a biphasic process: the first stage (C_1) is characterized by an initial increase of the microbial activity, when the labile organic carbon is easily degraded and exhausted, and the second stage (C_2), when the microorganisms start to use the most recalcitrant carbon, and the mineralization becomes relatively stabilized (Figure 2). This inference is supported by the studies of Ribeiro et al. (2010) and Rivas, Tabatabai, Olk and Thompson (2014).

According to Dodor, Amanor, Asamoah-Bediako, Maccarthy and Dovie (2019), the proportion of labile organic and recalcitrant carbon determines its mineralization rate and potential CO_2 emission when applied to the soil. The low C_1/C_2 proportion of the biochar suggests that it contains more recalcitrant compost as compared to labile carbon. The low labile carbon, degraded in the first stage (C_1), consisted of small, volatile aliphatic composts, low carbon content in its structure, and the presence of oxygenated groups, which induced a mineralization greater than in the second stage (C_2). In the second stage, the presence of more stable carbon, nonvolatile aromatic composts, and low concentration of oxygen in its structure caused low carbon

mineralization. These data corroborate the findings of Zimmerman, Gao and Ahn (2011).

The soil incubated with biochar presented a lesser amount of potentially mineralizable carbon, in both phases C_1 and C_2, independent of the applied doses, than the one verified for the soil incubated with organic compost. The highest C_1/C_2 ratio for biochar was 25.3% at 20t ha^{-1}. The organic compost-incubated soil presented a C_1/C_2 ratio of 47.4% at 20t ha^{-1} (Table 2). The high C_1/C_2 obtained for the organic compost is justified by the high labile carbon content of this substrate. Increase in the carbon mineralization observed with the dose application for the organic compost was due to the increase in the readily mineralizable carbon (Cross & Sohi, 2011; Fernández et al., 2014).

In general, independent of the substrate used and the applied dose, the first phase of the organic material degradation was characterized by an elevated velocity (K_1), which was higher to the velocity of the second phase (K_2) (Table 2). The higher K_1 velocities of the biochar-incubated soil were due to the lower concentration of labile carbon in the substrate during the first phase. In the second phase, although the organic compost had a high content of mineralizable carbon, its mineralization velocity (K_2) was similar to that of the biochar, independent of the applied dose. The difference between the carbon degradation velocity in the first and second phases of the process can be observed from the K_1/K_2 ratio (Table 2), which is an indication of how high the degradation velocity of the first phase is when compared with the second phase. As expected, and already discussed, the higher K_1/K_2 values observed for the biochar indicate higher organic material

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degradation velocity of the first phase when compared with the second phase (Zhao, et al., 2015; Zimmerman et al., 2011).

The half-life values ($t_{1/2}$) (time required for half of the carbon be mineralized) of the biochar-incubated treatments (Table 2), independently of the applied dose, indicate that during the first phase of the carbon degradation, half of the carbon degraded on the first day of incubation. For the treatments with organic compost, the half-life increased with the applied dose, obtaining the highest $t_{1/2}$ after 3 days, at 20 t ha^{-1}. During the second phase, due to the presence of recalcitrant materials in both substrates, the values of $t_{1/2}$ were high, indicating that more time is required for mineralization.

Although the kinetics study confirms that the biochar has a more stable carbon fraction than the organic compost, the amount of carbon materials readily degradable by soil microbes over time is still small.

Due to rapid initial mineralization, the biochar was able to release nutrients for the plants on the first day of incubation, corroborating the results of Fernandes, Chaves, Mendes, Chaves and Tito (2018), who verified significant improvements in soil fertility when it was incubated with poultry litter biochar.

Conclusion

1. The soil microbial activity and carbon mineralization increased with the application of substrate doses of biochar and organic compost made from poultry litter bed.

2. The highest C-CO$_2$ mineralization was observed in the treatments that received organic compost.

3. The carbon mineralization process was divided into two different phases, the first with an intense mineralization and a short half-life, and the second with a slow mineralization process, with a tendency to reduce and stabilize the C-CO$_2$ flux.

4. The carbon mineralization obtained with the substrates evaluated in the present study showed that the pyrolyzed materials (biochar) are efficient in reducing the soil carbon and mitigating the "greenhouse" effect.

Acknowledgements

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