Scientific
Research
Publishing

Mitigation of Greenhouse Gas Emissions from Tropical Soils Amended with Poultry Manure and Sugar Cane Straw Biochars

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Abstract

Increases in greenhouse gases (GHG) emissions, upon changes in land use and agricultural management, lead to a search for techniques that enhance carbon residence time in soil. Pyrolysis increases the recalcitrance of organic materials and enhances their activities as physical, chemical and biological soil conditioners. Emissions of CO_2, CH_4 and N_2O quantified from a sandy soil that was treated with three rates (12.5, 25 e 50 Mg·ha^{-1}) of either non-pyrolysed poultry manure and sugarcane straw or biochars, pyrolysed at two contrasting temperatures (350°C and 650°C). Subsequently, the flux of the three gases was converted and compared in a standard unit (CO_2eq). The added biochars, significantly reduced GHG emissions, especially CO_2, relative to the non-pyrolysed materials. The greatest differences between applied rates of poultry manure, relative sugarcane straw, both to biochar and raw material, and the positive response to the increase of pyrolysis temperture, confirm the importance of raw material choice for biochar production, with recalcitrance being an important initial characteristic. Greater emissions occurred with intermediate rate of biochars (25 Mg·ha^{-1}) amendment to the soil. These intermediate rates had higher microbial biomass, provided by an intermediate C/N ratio derived from the original soil and the biochar, promoting combined levels of labile C and oxygen availability, leading to an optimal environment for microbiota.

Keywords

CO_2, CH_4, N_2O, Weathered Soil

1. Introduction

The predicted increase in greenhouse gas emissions (GHG) and the growing demand for manufactured goods [1] promote the adoption of soil management techniques that mitigate these emissions [2] and [3]. Soils can sequester and accumulate larger quantities of carbon than plant biomass and the atmosphere [4]. For the global carbon cycle, any activity that favors the decomposition and mineralization of organic material, with consequent carbon emission, should be avoided [1].

Numerous studies have investigated carbon residence time in soil, as in charcoal form ("biochar") [5] and [6]. Biochar is the product obtained from pyrolysis of various biomasses. This process occurs in the absence of oxygen (anoxic environment) or at a very low level (hypoxic environment), which produces condensable gases and vapor, as well as charcoal [7]. The pyrolysis temperature alters the proportion of fulvic and humic acids in biochar [5], concentration of nutrients, such as phosphorous and nitrogen [8], pH and porosity [9]. Aromatic and hydrophobic structures give stability, enhancing recalcitrance, and acidic groups give reactivity [4], making biochar useful to increase chemical, physical and biological qualities of soils. In regard of plant biomass, hemicellulose is the first to be lost in the pyrolysis process, since it degrades at 200˚C. From 240˚C to 350˚C, cellulose is degraded, followed by lignin at 280˚C a 500˚C [10].

There is a wide choice of raw materials that generate environmental problems upon their accumulation in the fields [11] and [12]. According to [13], agricultural soils, enteric fermentation and animal waste, are responsible for 70% of GHG emissions in AFOLU areas (Agriculture, Forestry and Other Land Use), making necessary an appropriate management of these materials. For instance, sugar cane, planted on 8.8 million hectares in Brazil, which generates, approximately, 250 million tons of straw [14], had recent laws prohibiting straw burning, which limits the management options for this residue [15]. The straw left in the field retards sprouting and tillering, reduces productivity [16], and also affects the growth and development of sockets [16]. Since two thirds of biomass produced by sugarcane is considered bagasse and straw [17], biochar production is an alternative for the management of this waste [18]. Furthermore, animal residues also have a large contribution in GHG emissions [19], and are difficult in transport and store. Increased poultry production and concerns about the waste, poses the need for an environmentally secure deposit for this residue [20].

Since biochar has higher carbon stability than the original raw material, it is relevant to GHG mitigation [6] [10] [11] and [12]. [21] concluded that pyrolysis of wheat straw would avoid the emission of 0.9 to 1.06 t CO_2eq per ton of dry weight, if the non-pyrolysed straw was allowed to decompose in the field. [22] predicted that the use of biochar could sequester 3.7 to 6.6 Pg CO_2eq by 2050, contributing 7 to 13% reduction in GHG emissions. [23] calculated a reduction of 0.7 to 1.3 t CO_2eq per ton of miscanthus, when the waste is used on biochar

production. [24] compared biochar from corn and grass straw in the USA and demonstrated a reduction of 0.885 t CO_2eq per ton of dry weight in GHG emissions. [12] considered the energy used in pyrolysis and calculated that the incorporation of biochar into the soil would reduce emissions by 2.8 to 10.2 Mt CO_2eq by 2030 and 2.9 to 10.6 Mt CO_2eq by 2050. The variation in emissions between these values is influence by the type of raw material used to produce the biochars. This author [12] observed that the highest potential for GHG emission reduction occurred with forestry residues, followed by straw from cereals and pastures; the lowest potential was biochars derived from cattle manure. [25] measured CO_2 and CH_4 emissions and did not obtain a significant difference between the untreated soil and soil amended with biochar from wheat straw; however, a significant difference in N_2O emission was observed. [26] observed an increase in CH_4 emissions of 200 $mg \cdot m^{-2}$ when applying 20 $Mg \cdot ha^{-1}$ of biochar from forestry residues on an unfertile tropical soil. However, [27] observed a reduction of 51.1% in CH_4 emission from a waterlogged paddy soil when applied biochar from bamboo fragments and, a reduction of 91.2%, when biochar from rice husks was applied, likely due to a reduction in methanogenic.

Under tropical soil conditions, there are a limited number of published results on biochar and its impacts on GHG emissions. Few investigations in Brazil compare different materials and rates of applied biochar. Therefore, the objective of this study was to quantify and compare GHG emissions from a tropical sandy soil, which received either different amounts of biochars from sugar cane straw and poultry manure, pyrolysed in two temperatures, or their respective non-pyrolysed materials.

2. Material and Methods

2.1. Soil Characteristics

About 30% of the Brazilian territory is occupied by sandy soils [28]. With proper management and fertilization, these soils are intensively cultivated and are highly productive [29]. Samples from the 0-20 cm layer of a Typic Quartzipsamment soil type (Table 1) were collected from the Anhembi region of São Paulo State (22°43'31.1"S e 48°01'20.2"W) under natural vegetation. The samples were dried, sieved to 2 mm size and 50 g of soil were incubated with the raw materials and the respective biochars, in different treatments.

Table 1. Characteristics of the tropical sandy soil used in the experiment.

Soil	Sand/Silt/Clay	pH	C	N	C/N
	$g \cdot kg^{-1}$	$CaCl_2$	%		
Typic Quartzipsamment	900/22/78	4.1 ± 0.1	0.9 ± 0.1	0.1 ± 0.0	14.3 ± 0.1

Source: Abruzzini, 2015 [52].

2.2. Raw Materials Selection

The raw materials were selected due to their abundant accumulation in the field, plus their contrasting attributes and characteristics of agronomic interests. Sugar cane straw was collected from a field of cane industry at Piracicaba-SP, and poultry manure was collected from a farm located at ESALQ-USP. The raw materials were dried at 45˚C, ground in a ball mill and sieved to 2 mm, forming a homogeneous material.

2.3. Biochar Production

Pyrolysis process was carried out by SPPT Company, in metallic reactors, with an N_2-saturated atmosphere. The temperature was raised by 10˚C per minute during the first 30 min followed by 20˚C per min up to the desired temperatures [30].

Two pyrolysis temperatures, 350˚C and 650˚C, were chosen based on values cited in the literature. These temperatures cover the main phases of transformation of raw materials, that results in the final characteristics of the produced biochar. Temperatures below 350˚C are considered toast rather than pyrolysis, while above 650˚C results in weight loss of the material [31].

[30] previously characterized these biochars according to their pH, electrical conductivity (EC), cation exchange capacity (CEC), elemental analysis, humidity, relative proportions, yield and biochemical composition (Table 2), as well as spectrometric analysis.

Table 2. Properties of the biochars from poultry manure (PM) and sugar cane straw (CS) pyrolyzed at 350˚C and 650˚C.

	Biochar			
Properties	PM 350˚C	PM 650˚C	CS 350˚C	CS 650˚C
pH (CaCl$_2$)	8.3	10.0	8.8	9.2
EC (µS·cm^{-1})	4256.3	4022.5	1788.7	1911.4
CEC (mmol$_c$·kg^{-1})	360.0	200.0	70.0	70.0
C (%)	60.8	68.2	36.3	32.6
N (%)	1.8	1.7	2.6	1.4
O (%)	37.5	26.8	53.4	62.3
H (%)	2.5	2.7	3.3	0.8
Moisture (%)	3.8	4.2	2.9	1.7
Volatile Material (%)	50.2	43.8	60.8	42.1
Ash (%)	24.2	13.9	32.2	48.8
C fixed (%)	21.9	36.7	0.0	7.5
Biochar yield (%)	41.5	32.8	59.6	40.2
Hemicellulose (g·kg^{-1})	53.2	78.8	211.5	291.0
Cellulose (g·kg^{-1})	56.9	72.3	82.3	75.3
Lignin (g·kg^{-1})	734.9	598.4	295.4	233.7

Source: Conz, 2015.

2.4. Treatments and Experimental Conditions

Each biochar and their respective raw material were homogenized with the soil at 60% field water holding capacity. This soil moisture content approximated the filling of the micro-pores [32], guarantying microorganisms preservation. Each soil treatment mixture was placed in 650 mL glass pots, with a septum in the top, allowing gas collection with a syringe after sealing. A small vial containing deionized water was positioned in the glass pots to maintain humidity and the water was replenished upon observation of weight loss in the experimental unit.

The experiment consisted in a factorial treatment combination [3 × (2 + (2 × 2))] + 1, with three rates (12.5; 25 and 50 Mg·ha^{-1}) of applied biochar or non-pyrolysed material, two raw materials (sugar cane straw and poultry manure), two biochars (from sugar cane straw and from poultry manure), and two pyrolysis temperatures (350˚C and 650˚C), totaling 18 treatments, with four replicates and a control with untreated soil.

The application rates, defined according to [22], correspond to the maximum viable amount of applied biochar, considered by these authors as 50 Mg·ha^{-1}. The other two rates (12.5 and 25 Mg·ha^{-1}) are fractions of this value.

The experimental units were maintained for 6 months in the Soil Organic Matter Laboratory, in Soil Science Department at ESALQ/USP, at a constant temperature of 25˚C. Starting time was when the biochar was incorporated into the soil and incubated in the glass pots.

2.5. Gas Sampling

Gas emissions, collected daily during the first two weeks and less frequently during the rest of the experimental period, were sampled after sealing the vials for 30 minutes, using a 25 mL syringe and needle. Five empty flasks, used as control samples, were the background established levels used to calculate the effective concentration of the gasses emitted from each treatment (Equation 1). The gas samples were immediately transferred to vials under vacuum and analyzed by gas-chromatography (SRI 8610–SRI Instruments) with a flame ionization detector (FID) and an electron capture detector ^{63}Ni (ECD), which permitted the detection of CO_2, CH_4 and N_2O in the same sample.

$$NET = AET - BEC \qquad (1)$$

where: NET is the net emission of GHG for the treatment; AET is the accumulated emission of GHG for the treatment; BEC is the background emissions in the control sample.

2.6. Post-Experiment Analysis

After the end of the experiment, carbon (C) and nitrogen (N) contents from each experimental unit were analyzed by dry combustion using a Leco TruSpec® CHN elemental analyzer, according to [33] Microbial biomass C and N (MBC and MBN) were determined by the fumigation-extraction method proposed by

[34]. The extracts from each experimental unit were analyzed using a Shimadzu Total Organic Carbon Analyzer (TOC-L) and a Total Organic Nitrogen Analyzer (TON-L).

2.7. Data Analysis and Statistics

Mean gas concentrations were used to calculate flow and accumulation and were subjected to an adjustment by a second order polynomial equation (gas concentration versus time), as proposed by [35]. The flows at zero time (empty vials) were calculated by the second order derivative equations and expressed per gram of C or N per unit area (m^2) or per unit time (h).

The conversion of the flux of the three gases into a standard unit (CO_2 equivalent), allowing a critical and ensemble view of GHG emissions, was obtained according to Equations (2) and (3).

$$CO_{2eq} = C\text{-}CH_4 \times \frac{16}{12} \times 25 \qquad (2)$$

$$CO_{2eq} = N\text{-}N_2O \times \frac{44}{28} \times 298 \qquad (3)$$

where: $C\text{-}CH_4$ and $N\text{-}N_2O$ are gases fluxes ($mg \cdot m^{-2} \cdot h^{-1}$); 16/12 is the ratio between the molecular mass of CH_4 and C; 44/28 is the rate between the molecular mass of N_2O and N; 25 is the Global Warming Potential (GWP) of CH_4 and 298 of N_2O [36].

The data from the raw materials, combined by application rate and feedstock, were subjected to a variance analysis, where a completely randomized design was adopted, in a factorial 2×3, with a control treatment and four replicates. To analyze the data from the biochars, the same experimental design was adopted, in a factorial $2 \times 3 \times 2$. The factors were combined with the raw material used in pyrolysis process, application rates and temperatures, four replicates and the control. The means, treated as separate events, were compared between treatments at a confidence interval of 95%. The treatments were considered not to be statistically different among themselves when there was an overlap of the mean intervals. Results on MBC, MBN, C and N contents and C/N ratio were statistically analyzed using a Tukey test at 5%. The statistical analyses and graphs were performed using the "plotrix" and "agricolae" packages available in the R software [37].

3. Results

3.1. Raw Materials

Poultry manure (PM) provided the largest CO_2 (**Figure 1(a)**) emissions and the largest amplitude between the applied rates (**Figure 1(a)**). The greater emissions of CO_2 by the raw materials, relative to their respective biochars (**Figure 1(a)** and **Figure 1(b)**), can be observed by the magnitude of the y-axis, which are three times larger for the raw materials. Even though there was little or no statis-
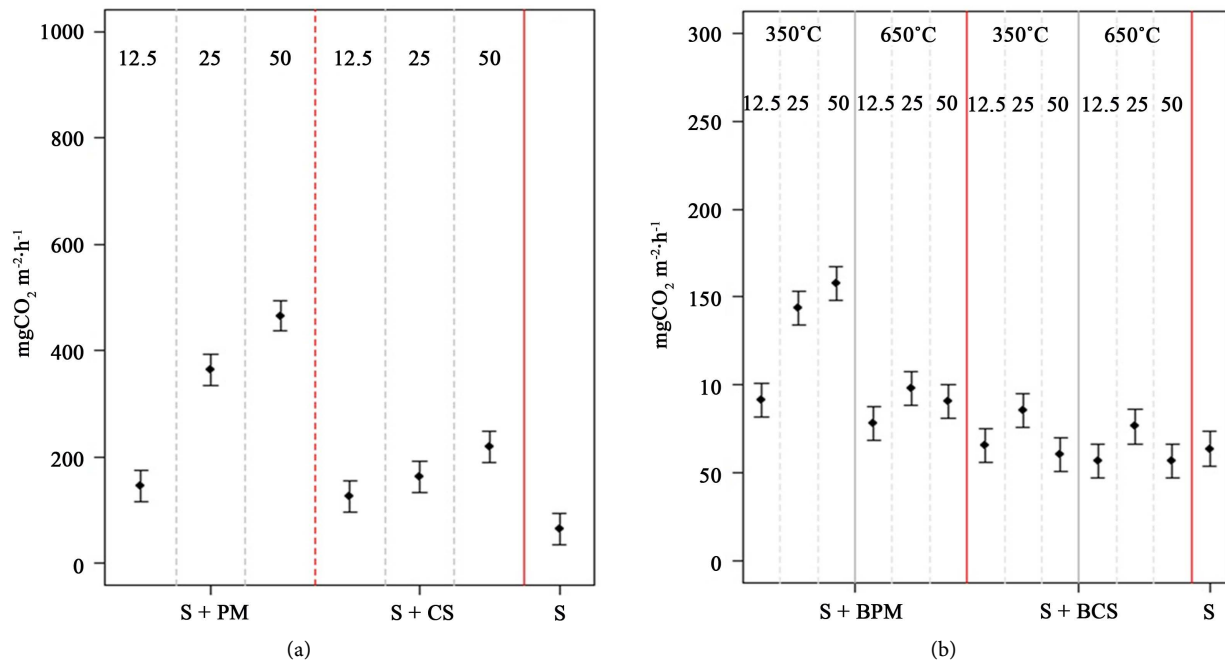
Figure 1. Emission of CO_2 from a tropical sandy soil (S) amended with (a) raw materials: poultry manure (S + PM) and sugar cane straw (S + CS); and (b) biochars: biochar poultry manure (S + BPM) and biochar of sugar cane straw (S + BCS).
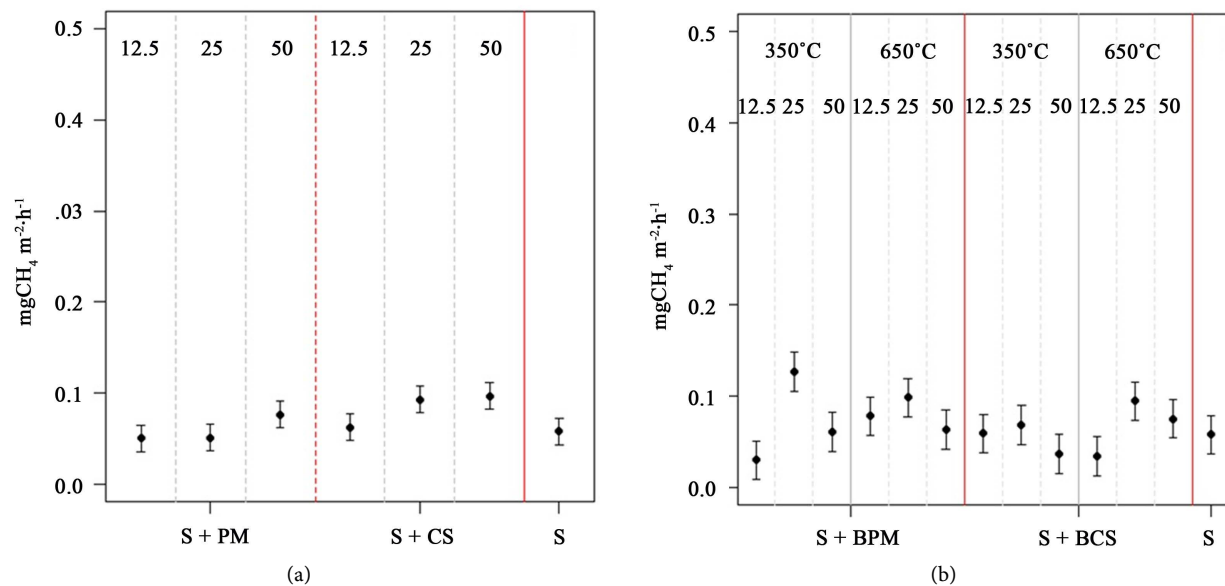

Figure 2. Emission of CH_4 from a tropical sandy soil (S) amended with a) raw materials: poultry manure (S + PM) and sugar cane straw (S + CS); and b) biochars: biochar poultry manure (S + BPM) and biochar of sugar cane straw (S + BCS).

tical difference in CH_4 emissions among rates and raw materials, the pattern of higher emission occurred for the highest application rate (**Figure 2(a)**).

3.2. Biochars

When the emissions of CO_2 from the biochars were compared (**Figure 1(b)**), the same trends between raw materials were observed. Even after pyrolysis, PM
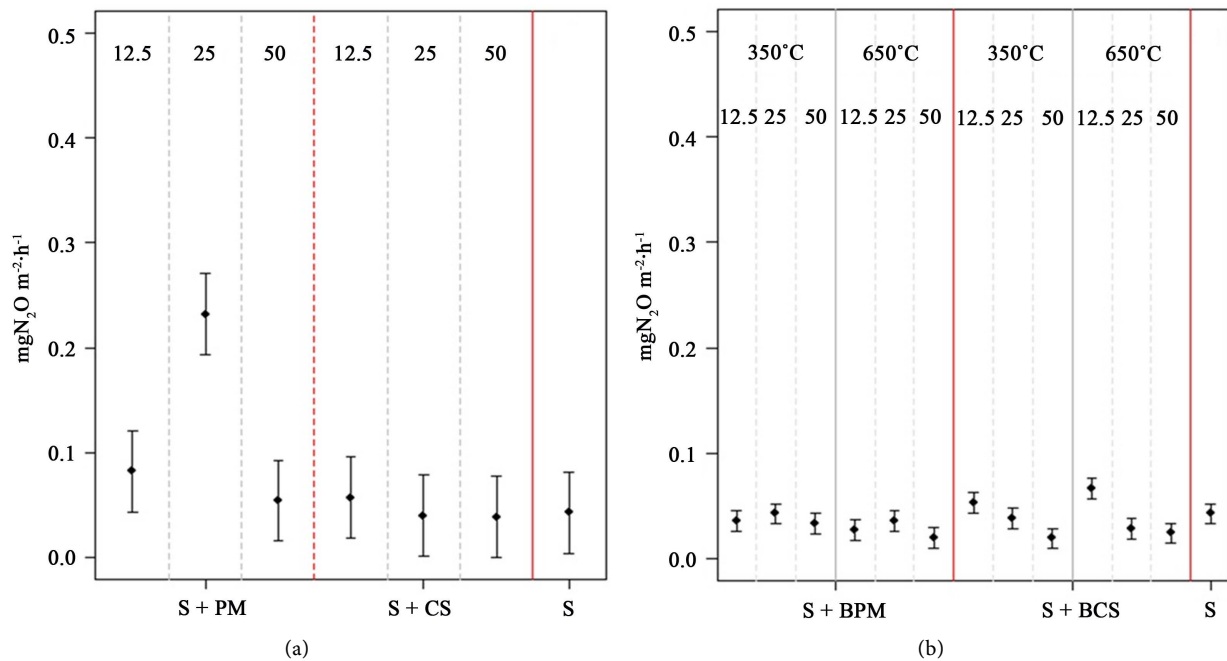
Figure 3. Emission of N_2O from a tropical sandy soil (S) amended with a) raw materials: poultry manure (S + PM) and sugar cane straw (S + CS); and b) biochars: biochar poultry manure (S + BPM) and biochar of sugar cane straw (S + BCS).

emitted higher levels of CO_2, and showed a greater variation among rates, despite no statistical difference between the poultry manure biochar (BPM) rates of 25 and 50 Mg·ha^{-1}, regardless pyrolysis temperature. The BPM also presented a statistical difference between the two pyrolysis temperatures. The sugar cane straw biochar (BCS) had a small amplitude of gas emissions between treatments, with little or no significative response.

3.3. Application Rate

The lowest rate (12.5 Mg·ha^{-1}) of both raw materials showed higher emissions of CO_2 than the control (**Figure 1(a)**). As expected, there was an increase in CO_2 and CH_4 emissions (**Figure 1(a)** and **Figure 2(a)**) with increased application rate, such that the highest rate of both raw materials (50 Mg·ha^{-1}) provided the greatest emission of these gases. For CH_4 emissions (**Figure 2(a)**), only the application of 25 and 50 Mg·ha^{-1} of SC resulted in higher emissions than the control. For N_2O (**Figure 3(a)**), only the application of 25 Mg·ha^{-1} of PM resulted in a superior emission compared to the control.

The intermediate rate of applied BCS had higher CO_2 emissions than the other rates, at both pyrolysis temperatures (**Figure 1(b)**). This pattern, also observed for CH_4 emissions (**Figure 2(b)**), had the largest emission values observed with the 25 Mg·ha^{-1} rate, regardless biochar raw material source or pyrolysis temperature. Both observations are in agreement with the higher MBN values found for this rate (**Table 3**).

The application of BCS at the lowest rate resulted in a higher emission than the control treatment, regardless of the pyrolysis temperature (**Figure 3(b)**).

Table 3. Effects of raw materials, biochar application rates and pyrolisis temperature on C and N in a tropical sandy soil.

Treatment	Dose	MBC[1]		MBN[2]		C[3]		N[3]		C/N		Cmic: Ctot[4]	
	Mg·ha⁻¹	mg L⁻¹										%	
		Raw Materials											
S + PM	12.50	38.78	Cb	6.73	Ab	0.75	Bb	0.06	Ba	12.64	Aa	0.19	Ca
	25.00	72.69	Ba	20.30	Ab	0.90	Abb	0.08	Aba	11.73	Ab	0.80	Ba
	50.00	170.25	Aa	25.67	Aa	1.12	Ab	0.11	Aa	10.41	Ab	1.53	Aa
S + CS	12.50	73.71	Aa	29.84	Ba	0.95	Ca	0.06	Aa	17.27	Ba	0.82	Aa
	25.00	36.32	Cb	41.49	Aa	1.19	Ba	0.05	Ab	26.63	Aa	0.31	Aa
	50.00	54.98	Bb	15.62	Ba	1.91	Aa	0.07	Ab	27.96	Aa	0.29	Ab
		Biochar											
S + BPM 350°C	12.50	170.49	Ca	93.19	Ba	0.93	Ba	0.06	Aa	15.12	Aa	1.85	Aa
	25.00	204.04	Ba	124.95	Aa	1.22	Ba	0.08	Aa	16.94	Aa	1.68	Aa
	50.00	223.96	Aa	39.95	Cb	1.79	Aa	0.12	Aa	16.45	Aa	1.29	Aa
S + BPM 650°C	12.50	190.16	Ba	101.16	Bb	0.95	Ca	0.06	Aa	16.67	Ba	2.00	Aa
	25.00	116.51	Ca	112.13	Aa	1.16	Ba	0.07	Aa	17.54	Ba	1.03	Ba
	50.00	213.99	Aa	94.46	Ba	1.70	Aa	0.09	Aa	21.15	Aa	1.27	Aba
S + BCS 350°C	12.50	127.93	Aa	72.24	Aa	1.25	Ca	0.08	Aa	16.16	Ba	1.04	Aa
	25.00	106.28	Ba	76.91	Aa	1.92	Ba	0.12	Aa	16.76	Ba	0.58	Ba
	50.00	126.04	Aa	63.09	Aa	2.80	Aa	0.11	Aa	26.59	Aa	0.41	Ba
S + BCS 650°C	12.50	103.41	Ab	49.87	Ba	1.34	Ba	0.07	Aa	22.55	Ba	0.77	Aa
	25.00	85.58	Ba	63.24	Aa	1.78	Ba	0.07	Aa	28.70	Ba	0.50	ABa
	50.00	111.84	Aa	59.65	Aba	3.18	Aa	0.09	Aa	37.31	Aa	0.36	Ba

S + PM: Soil + Poltry Manure; S + CS: Soil + Case Straw; S + BPM 350°C: Soil + Biochar of Poultry Manure pyrolysed at 350°C; S + BPM 650°C: Soil + Biochar of Poultry Manure pyrolysed at 650°C; S + BCS 350°C: Soil + Biochar of Case Straw pyrolysed at 350°C; S + BCS 650°C: Soil + Biochar of Case Straw pyrolysed at 650°C; [1]Microbial Biomass Carbon; [2]Microbial Biomass Nitrogen; [3]Total C and N of the treatments; [4]Ratio of Microbial Biomass C/Total C. Averages followed by the same capital letter refer to the comparison among doses of the same treatment; Averages followed by the same lowercase letters refer to the comparison of the same dose among treatments.
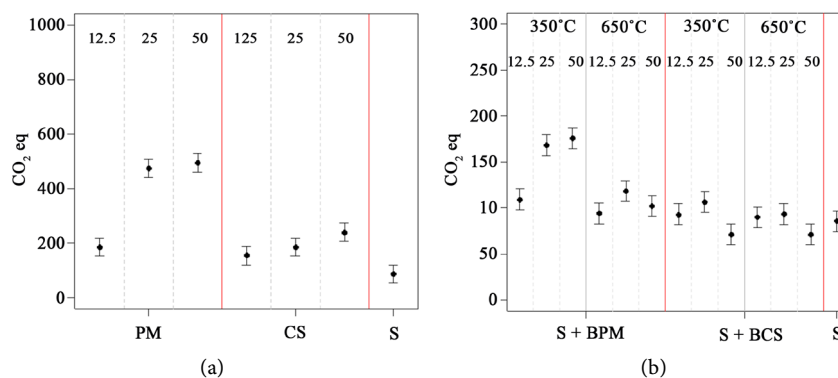
Figure 4. Emissions in CO_2 equivalent from a tropical sandy soil (S) amended with (a) raw materials: poultry manure (S + PM) and sugar cane straw (S + CS); and (b) biochars: biochar poultry manure (S + BPM) and biochar of sugar cane straw (S + BCS).

Emission values for N_2O decreased with the increasing application rates above 12.5 Mg·ha^{-1}. No statistical differences were detected for N_2O emissions by BPM, regardless the applied rate or pyrolysis temperature (**Figure 3(b)**).

3.4. Pyrolysis Temperatures

When the pyrolysis temperatures were compared for BPM (**Figure 1(b)**), the higher GHG emission levels at 350˚C were to be expected. For BCS the pyrolysis temperature did not affect CO_2 emission (**Figure 1(b)**), since no significant differences were observed between temperatures, comparing the same rate.

The CO_2 emissions for the soil without the addition of residue (control) did not significantly differ from the emissions obtained from the soil after the BCS addition, regardless of the applied rate or pyrolysis temperature (**Figure 1(b)**). When the addition of SC (**Figure 1(a)**) is compared to its respective biochar, produced at 350˚C (**Figure 1(b)**), the emissions were 1.89, 1.90 and 3.60 times higher for non-pyrolyzed material at the rates 12.5, 25 and 50 Mg·ha^{-1}, respectively. When compared to the biochar produced at 650˚C the non-pyrolyzed material produced emissions 2.19, 2.13 and 3.82 times higher, at the same rates. For BPM the same pattern was observed. Although the emissions were slightly higher than the control, when compared to the raw material, the non-pyrolyzed form showed emissions 1.36, 2.58 and 3.03 times higher than the biochar produced at 350˚C, for the rates 12.5, 25 and 50 Mg·ha^{-1}, respectively. Using a pyrolysis temperature of 650˚C, the emissions from the raw materials were 1.67, 3.95 and 5.78 times higher, at the same rates.

3.5. CO_2 Equivalent

The same pattern obtained in CO_2 emissions (**Figure 1**) was observed for SC and biochars (BPM and BCS) at the standard unit (**Figure 4**), regardless the different treatments. For poultry manure as a raw material, the highest rates (25 and 50 Mg·ha^{-1}) were not statistically different, which does not occur for CO_2 emission (**Figure 1(a)**).

4. Discussion

The largest emission of GHG, observed during the first 15 days, was slowly reduced. From day 36, treatments were no longer statistically different from the control, confirming that the gas emissions had already stabilized and no longer needed to be collected (**Figure 5**). The gas sampling continued for more 103 days, in order to confirm that the microbiota had already stabilized and would not have a new peak of emission, as sometimes reported by few authors [38]; [39] and [40].

The higher emissions by both raw materials, relative to the control, demonstrates that even small quantities of applied feedstocks increase CO_2 emissions (**Figure 1(a)**). The higher values of CO_2 emissions by the addition of PM, non-
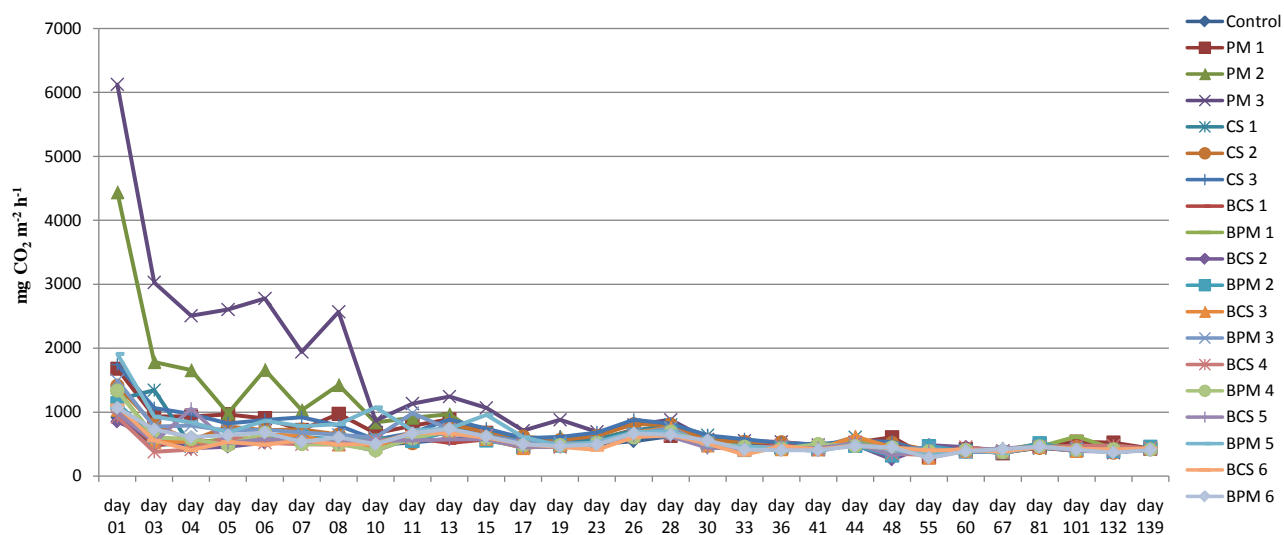
Figure 5. Flow of CO_2 measured in the chamber during 139 days. Control = Only soil; PM 1 = poultry manure dose 12.5 Mg·ha^{-1}; PM 2 = poultry manure dose 25 Mg·ha^{-1}; PM 3 = poultry manure dose 50 Mg·ha^{-1}; CS 1 = Cane Straw dose 12.5 Mg·ha^{-1}; CS 2 = Cane Straw dose 25 Mg·ha^{-1}; CS 3 = Cane Straw dose 50 Mg·ha^{-1}; BCS 1 = Biochar Cane Straw dose 12.5 Mg·ha^{-1} Temperature of pyrolysis 350˚C; BPM 1 = Biochar poultry manure dose 12.5 Mg·ha^{-1} Temperature of pyrolysis 350˚C; BCS 2 = Biochar Cane Straw dose 12.5 Mg·ha^{-1} Temperature of pyrolysis 650˚C; BPM 2 = Biochar poultry manure dose 12.5 Mg·ha^{-1} Temperature of pyrolysis 650˚C; BCS 3 = Biochar Cane Straw dose 25 Mg·ha^{-1} Temperature of pyrolysis 350˚C; BPM 3 = Biochar poultry manure dose 25 Mg·ha^{-1} Temperature of pyrolysis 350˚C; BCS 4 = Biochar Cane Straw dose 25 Mg·ha^{-1} Temperature of pyrolysis 650˚C; BPM 4 = Biochar poultry manure dose 25 Mg·ha^{-1} Temperature of pyrolysis 650˚C; BCS 5 = Biochar Cane Straw dose 50 Mg·ha^{-1} Temperature of pyrolysis 350˚C; BPM 5 = Biochar poultry manure dose 50 Mg·ha^{-1} Temperature of pyrolysis 350˚C; BCS 6 = Biochar Cane Straw dose 50 Mg·ha^{-1} Temperature of pyrolysis 650˚C; BPM 6 = Biochar poultry manure dose 50 Mg·ha^{-1} Temperature of pyrolysis 650˚C.

pyrolysed or pyrolysed, than with applied SC (**Figure 1(a)** and **Figure 1(b)**), suggests greater stability of cane straw and a less drastic effect on the environment, from GHG emissions point of view.

For the raw materials, the CO_2 and CH_4 emissions (**Figure 1(a)** and **Figure 2(a)**) increased with increasing application rates. According to [41], the waste management is one of the principle causes of GHG emissions in the agricultural environment, which corroborates the loss of C and N after the application of these residues to soil. The higher emission of N_2O (**Figure 3(a)**) for the 25 Mg·ha^{-1} rate of applied PM (the only one that differs statistically from the control) was attributed to a combination of oxygen and C availability. The hypothesis, based on a perfect environment, which combines oxygen availability and labile C for the microbiota, was found on the intermediate rate. However, this assumption was not confirmed by the values found in the microbial biomass (**Table 3**), perhaps because these data were obtained only at the end of the experiment, when the GHG emissions were already stable.

We could imply that the absence of statistical difference between the BPM rates of 25 and 50 Mg·ha^{-1}, for both pyrolysis temperatures, is due to a "maximum point", above which there is no effect on CO_2 emission. According to [27], the flow of CO_2 presents higher relative reductions with application of raters

lower than 20 Mg·ha^{-1} of biochar, while the total organic carbon increases at applied rates from 20 to 40 Mg·ha^{-1}. This is due to an increase in microbial biomass of 50% in rates lower than 20 Mg·ha^{-1}, in contrast to an increase of only 8% in 20 to 40 Mg·ha^{-1} rates. The negative effect of applying high rates of biochar to the soil microbiota is justified by the high C/N ratio of the applied material, inducing N immobilization and reducing microbial activity (Table 3).

The higher emissions of CO_2 and CH_4 (Figure 1(b) and Figure 2(b)) from the intermediate rate (25 Mg·ha^{-1}) of the BCS, are in agreement with the higher MBN values for these treatments (Table 3) and was attributed to a more beneficial environment at this application rate. [42] and [43] also found a similar pattern in their studies, with application of three different rates of biochar. These authors assumed that the higher gas emission values for the intermediate rate could be due to a combined C/N ratio, coming from the original soil and the biochar. Considering that the soil's C/N ratio will prevail in the lowest applied rate whereas the biochar's C/N ratio will prevail at the highest rate, it is plausible to assume that on the intermediate rate there will be an intermediate C/N ratio providing an optimal environment for microbiological growth. Although we did not find a statistical difference for all treatments, we can observe this pattern occurring among treatments, where the C/N ratio of the intermediate application rate approaches the average of the extreme rates (Table 3).

The higher emissions of GHG for BPM pyrolysed at 350°C was due to the maintenance of the original characteristics of the material. With pyrolysis temperature at 650°C, aliphatic chains, aromatic rings and elemental composition of C, N and O are reduced, making the biochar more recalcitrant [44]. Many characteristics, such as ash content, CEC and C/N ratio, vary according to the raw material [45] and [46], which justifies similar CO_2 emission values for the BCS, whether pyrolyzed at 350°C or 650°C. The BCS material is already highly recalcitrant, producing a biochar with lower ash content, lower nutrient diversity and greater surface area [47]. We can also infer that BPM pyrolysed at 650°C is more efficient in GHGs mitigation, since this procedure will increase surface area, ash content and stability of the biochar [48] and [49], reducing, CO_2 emissions, mostly at higher applied rates. In a study with biochar from sugar cane straw, [50] observed an 80% loss of N from the material, using a pyrolysis temperature of 750°C. These authors reached a C/N ratio of 47 after using pyrolysis at 450°C, whereas the C/N ratio was 280 when pyrolyzed at 750°C. They also observed a reduction in the H/C and O/C ratios and an increase in the ash content with the increase in the pyrolysis temperature. This suggests an increase in aromatic structures and degree of carbonization, when compared to the raw material. The similarity in CO_2 emissions between the pyrolysis temperatures of BCS (Figure 1(b)) can be attributed to the nature of the raw material, allowing the inference that there is no advantage in GHG mitigation when pyrolyzing material such as straws at temperatures above 350°C.

The lower CO_2 emission values of biochars relative to the raw materials, in the

same applied rate and pyrolysis temperature (for the biochars), allowed the conclusion that the production of biochars from these raw materials is a viable solution for adding these residues to soil, without an increase in GHG emissions. [51] observed a decomposition of 56% of the C added as wheat straw after 84 days, while over the same period, only 2.8% of the C from its respective biochar had decomposed.

However, regardless the higher N_2O emission for the lower rate of BCS application at either pyrolysis temperature (**Figure 3(b)**), relative to the control, is probably due to the formation of aerobiotic sites in the extremely porous biochar. This observation leads us to think that increases in this biochar application would increase the availability of oxygen, reducing the anaerobic environment and N_2O emissions. No statistical difference was observed for N_2O emissions from BPM, regardless the applied rate or pyrolysis temperature (**Figure 3(b)**). We assume that this material reduces the chance of anaerobiosis through a higher amount of micropores than the BCS, and its lower C/N ratio (**Table 3**) limits the amount of soluble C available for microbiota performance.

The CO_2 equivalent graph (**Figure 4**) indicates there are few differences between the combined emission of the three gases and CO_2 emissions alone. In soils that are not flooded or for any reason have hypoxic/anoxic condition, there are no expressive emissions of CH_4 and N_2O. Even though we found statistical differences among some treatments of these two gases, the emission were small. The lack of differences between the highest rates of PM (**Figure 4(a)**), differently from CO_2 emissions alone (**Figure 1(a)**), is due to the high emission of N_2O in the intermediate rate (25 Mg·ha^{-1}) that raised the value close to the rate of 50 Mg·ha^{-1} when added into the standard unit. Even though the initial value of N_2O emission in 25 Mg·ha^{-1} rate is low (0.23 mg N_2O m^{-2}·h^{-1}), its GWP is high (298); when calculated for CO_{2eq} (Equation (3)) this contribution is amplified.

Agricultural production, since 1970, has grown 118% and livestock production 102%, with an increase in emissions of 65 and 119%, per harvest and per head, respectively [19]. This implies that a secure environmental destination has to be found, for plant and animal residues.

5. Conclusion

The biochar from poultry manure causes higher GHG emissions than the biochar produced from sugar cane straw, but both cause a significant reduction in the CO_{2eq} emission and represent an environmentally secure way of depositing residual material in the field. For the poultry manure biochar, higher pyrolysis temperatures have a significant effect in reducing GHG emissions, however this was not observed for the biochar produced from sugar cane straw thus it is much more recalcitrant and is not affected by different managements. There is a greater emission of the three gases when applying the intermediate rate, demonstrated by a greater microbial biomass in this treatment, nevertheless, the cause is still not well known and deserves to be furthered studied.

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