

# Evaluation of CO<sub>2</sub> Emission From Rice Husk Biochar and Cowdung Manure Co-compost Preparation

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Received: June 14, 2019

Accepted: August 15, 2019

Online Published: October 15, 2019

doi:10.5539/jas.v11n17p158

URL: <https://doi.org/10.5539/jas.v11n17p158>

## Abstract

Composting of animal manure had been considered a sustainable alternative method for recycling organic waste. However the process involved had been associated with greenhouse gas emission (CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>) which play an active role in global warming. This study evaluated CO<sub>2</sub> emissions from biochar-manure co-compost production. Biochar (from rice husk) and manure were mixed in a ratio of 3:1 v/v to achieve a range of different co-compost mixtures. The treatments and controls in triplicates of 18 units were arranged in a complete randomize design. All treatments were incubated at around 28 °C and turned every two days for 2 weeks, and later five days for 39 days. CO<sub>2</sub> production in the compost bins was measured by trapping the evolved gas in 5M NaOH. Total CO<sub>2</sub> emissions varied over time with higher rates at the beginning of the composting process. Within the first 7 days, total CO<sub>2</sub> emissions (587 mg/m<sup>2</sup>) from cow dung alone was not significantly different from cow dung plus biochar (506 mg/m<sup>2</sup>). At the latter stages of the composting process, CO<sub>2</sub> emission from cowdung and biochar mixture was less than from the other treatments.

**Keywords:** rice husk biochar, CO<sub>2</sub> emission, cow dung, composting and NaOH

## 1. Introduction

The continuous decline in the fertility of tropical soils is a major challenge to sustained crop production (Henao & Baanante, 1999; Stoorvogell & Smaling, 1998). Associated impediments to food security also include high rates of organic matter decomposition, soil erosion and intensive leaching of nutrients beyond rooting zones (Barus, 2016). Though the use of inorganic fertilizers is clearly positively related to increased agricultural productivity (Cameron, Di, & Moir, 2013), their continuous use can have detrimental effects on soil quality, such as soil acidification and subsequent reductions in crop yield (Gilbert et al., 2014; Cameron, Di, & Moir, 2013; Mulvaney, Khan, & Ellswort, 2009; Fening, Ewusi-Mensah, & Safo, 2010; Ogunwole et al., 2010). Furthermore, the production of chemical fertilizers often incurs environmental consequences. Cherkasov, Ibhada, and Fitzpatrick (2015) reported that about 60% of chemical fertilizer used in agriculture, with respect to N, are produced using the Haber Bosch process which consumes large quantities of energy and produces concomitant quantities of CO<sub>2</sub>.

Plant residue and animal manure are alternatives sources of plant nutrients that can enhance soil fertility without adverse effects on the soil. Fresh animal manures are good sources of organic fertilizers that are nutrient-rich, affordable and within the reach of many small-scale farmers. However, their soil fertility enhancing effects are often short-lived, because of the high proportion of easily degradable carbon and nitrogen. One method used to improve the stability of manures and also concentrate nutrients is composting. Composting is a process that transforms organic matter into a stable product through rapid microbial transformation under aerobic conditions. Compost, if produced appropriately is stable chemically and hygienic, with a diminished pathogen load, free of viable weed seeds and have a decreased potential for production of biohazardous, phytotoxins, or other detrimental substances (Haug, 1993; Tiquia & Tam, 1998). The application of compost has been reported to significantly increase plant growth, soil and plant nutrient content and biomass production (Agegehu et al.,

2015). The major environmental challenge when composting fresh manures is the emission of greenhouse gases ( $\text{CO}_2$ ,  $\text{N}_2\text{O}$  and  $\text{CH}_4$ ) which contribute to global warming.

On the other hand, biochar, a product of pyrolysed organic residues, is known to stabilize the carbon of organic materials via increase in the proportion of aromatic recalcitrant carbon which can remain undecomposed in soils over many years (Kuhlbusch et al., 1996; Dai et al., 2005; Atkinson, Fitzgerald, & Higgs, 2010; Rostard & Rutherford, 2011). Biochars are known to have a high pH, and increased surface reactivity but low available N (Atkinson, Fitzgerald, & Higgs, 2010). Indeed, the addition of biochar to the composting process has been reported to shorten composting time; reduce the rate of greenhouse gas emissions ( $\text{CH}_4$ ,  $\text{N}_2\text{O}$  and  $\text{NH}_3$ ) and minimize manure odour production (Wang et al., 2013; Sonoki et al., 2012; Steiner et al., 2010). Conceivably the co-composting of biochar with animal manure should result in a material of enhanced plant nutritive value while offering a production method with reduced environmental impact compared with traditional composting of manure alone. It is the purpose of this study to evaluate greenhouse gas ( $\text{CO}_2$ ) emissions during the co-composting of a manure with a biochar under tropical conditions.

## 2. Materials and Methods

### 2.1 Biochar, Manure, and Composting Process

Rice husks were used as the biochar feedstock; a waste product from the irrigated rice fields of the University of Ghana, Soil and Irrigation Research Centre (SIREC), Kpong. Rice biochar was produced using a locally constructed kiln, following the technology of Haefele et al. (2011). The kiln comprised a perforated empty oil drum in which fuel wood was combusted. The drum was surrounded with rice husk feed stock which charred for a period of 6 h at a temperature of 350 °C. Cattle dung was obtained from SIREC cattle enclosure and co-composted with both fresh rice-husk and charred rice husks at a ratio of 3:1 v/v. Prior to co-composting the cow dung was dried, pulverized. Co-composting was implemented in 18 L bins constructed to allow the mixing of contents during production. Based on the hypothesis that increased biochar pH should reduce  $\text{NH}_3$  emission during the composting process, an additional treatment included the addition of milled dried lemon fruit peel (to acidify the mixtures). The manure-biochar treatments investigated are summarised in Table 1. All treatments were incubated at an ambient temperature of around 28 °C. The compost, within the bins, was turned every two days for the first 2 weeks, and thereafter, every five days until maturity. The treatments were watered regularly, as required.

Carbon dioxide ( $\text{CO}_2$ ) production during co-composting was measured using the alkali trapping method and back titration with 5M HCl after precipitation of the carbonate with 1 M  $\text{BaCl}_2$  following Sullivan et al. (2009). The  $\text{CO}_2$  evolution was determined every 5 h for the first seven days and taken at weekly intervals, subsequently. A beaker containing 20 ml of 5 M NaOH solution was placed in the compost bin to absorb the emitted  $\text{CO}_2$ . Ammonia gas emitted was trapped in boric acid (4%) and titrated against 0.2 M HCl using methyl red indicator. The compost temperature was measured using a non-contact infrared thermometer held close to the surface of the compost mixture. Three temperature readings were taken per treatment and average for each treatment determined. Temperature readings were taken from the same position in each compost bin and measurements were made twice a day (9:00 and 15:00). Compost maturity was determined when the temperature of the mixture had fallen to that of ambient and remained relatively constant over a period of one week.

Table 1. The treatment codes and their descriptions used to study the impacts of co-composting on  $\text{CO}_2$  emissions

Treatment code	Treatments description
CL0	Cow dung only
CL10	Cow dung + milled dried lemon at 10% (w/w)
CBL0	Cow dung + rice husk biochar only
CBL10	Cow dung + rice husk biochar + lemon (10%)
CRL0	Cow dung + rice husk only
CRL10	Cow dung + rice husk + lemon (10%)

### 2.2 Chemical Analysis of Co-compost Materials

The co-composting materials (fresh rice husk, rice husk biochar, fresh cow dung, lemon peel) were chemically analysed for pH, Total C, and N. The pH was measured on dried milled materials using an Eijkelkamp 18.21

Multi-parameter analyzer (S/N 62163), using a material: water ratio of 1:10 (Mclean, 1982). Total C and N were measured using TruMac CNS analyzer (Model 630300-200). The analyses were undertaken at the Soil Science Laboratory of the University of Ghana.

### 2.3 Experimental Design and Statistical Analysis

The data obtained was subjected to analysis using Microsoft Excel (version 2013, Microsoft Corporation) to complete raw data computations and GenStat software (GenStat version 9.2) for statistical analysis. Means were separated with the Least Significant Difference (LSD) at  $p < 0.05$ .

## 3. Results and Discussion

### 3.1 Chemical Properties of Co-composting Materials

The chemical composition of the material used for the biochar and the manure co-compost is shown in Table 2). The raw rice husk was strongly acidic, with a pH of 3, while its total carbon content was 44% and a total nitrogen of 2%, giving a C:N ratio of 22:1. When charred, the pH of the rice biochar increased to 8, while its total carbon content decreased slightly (38%). The total N content of the rice husk biochar declined to 0.8% resulting in a C:N ratio of 75, increasing the stability of the biochar. The high alkalinity of the biochar is likely due to the high ash content, which can have a liming effect when applied to acidic soils (Clarholm, 1994; DeLuca, Mackenze, & Gundale, 2009; Hua et al., 2009; Major et al., 2010a). This also corroborates the assertion of Verheijen et al. (2010) that biochar pH values are usually in the neutral to basic range.

Pyrolysis has been reported to promote the elimination of H and O over C which results in a solid residue (char) with relatively higher C content. A high C:N ratio of biochars has also been reported in other studies (Jien et al., 2015; Spokas, 2010). Generally, a high C:N ratio will reduce the capacity of biochar to release inorganic N when used as a soil amendment (Prommer et al., 2014). The cow dung also had a high pH, a relatively low carbon and high N content, resulting in a C:N ratio of approximately 13.6:1, compared with the biochar. The milled lemon peel waste was acidic, a characteristic of lemon fruit, with a relatively high C and N contents giving a C:N ratio of approximately 25:1.

Table 2. Chemical properties of organic resources used in the study

Property	Fresh rice husk	Rice husk biochar	Manure (cow dung)	Lemon peel
pH (H <sub>2</sub> O)	3.2	8.6	7.8	3.4
Total C (%)	44.1	38.1	22.9	42.5
Total N (%)	1.97	0.52	1.68	1.4
C/N	22	73.5	13.6	25

### 3.2 Variation in Temperature During Co-composting of Rice Husk Biochar and Cow Dung

The variation of compost temperature with time followed the same patterns for all treatments. There was an initial rapid rise in temperature from the onset, reaching a peak on day 5, which subsequently declined gradually (Table 3). On the first day of composting, manure + lemon peel (treatment CL10) treatment had the highest temperature (35.3 °C) followed by biochar + manure + lemon peel mixture (treatment CBL10) at 33.1 °C. On day 2, raw rice husk + lemon peel (CRL10 treatment) had the highest temperature (33.5 °C) but this was not significantly different from that recorded for most of the other treatments. The highest temperature recorded on day 3 was for the CL10 (36.2 °C) treatment. Though treatment differences were not very consistent, the maximum temperatures attained by the biochar-manure co-compost treatments were generally lower than those of manure alone or raw rice husk + manure mixtures.

Table 3. The mean surface compost temperatures recorded during the composting period

Treatments	Days										
	1	2	3	5	6	7	11	15	19	25	39
CL0	29.4 c	28.1 b	30.7 c	31.5 e	31.2 cd	31.2 c	31.5 b	31.1 d	29.0 b	30.0 ab	27.7 b
CL10	35.3 a	33.3 ab	36.2 a	36.1 b	34.5 b	33.2 b	32.8 b	31.8 c	29.8 b	29.9 ab	27.8 b
CBL0	28.3 c	31.3 ab	31.0 c	33.0 d	30.8 d	30.9 c	31.5 b	32.1 c	28.5 c	30.4 a	29.1 a
CBL10	33.1 b	31.3 ab	34.5 b	34.7 c	31.7 c	32.6 b	32.0 b	31.8 c	28.6 c	30.0 ab	28.9 a
CRL0	31.5 b	33.1 ab	34.3 b	37.6 a	36.4 a	35.8 a	36.8 a	37.0 a	28.3 c	29.4 b	28.4 ab
CRL10	32.4 b	33.5 a	35.2 ab	37.7 a	35.6 a	35.5a	36.7 a	36.1 b	27.9 d	29.2 b	28.7 b
LSD	2.05	4.79	1.09	0.97	0.82	0.89	1.30	0.66	0.29	0.79	0.65

Note. CL0, Cow dung only; CL10, Cow dung and 10% milled lime; CBL0, Cow dung and rice husk biochar (1:3); CBL10, Cow dung and milled lime at 10%; CRO, Cow dung + rice husk only (1:3); CRL10, Cow dung + rice husk + 10% milled lemon.

Values with the same letter in each column are not significantly different at  $p < 0.05$ .

The observed differences in compost temperatures could be attributed to the types of substrates and the ease with which microbial decomposition took place. Except for the biochar, all the constituents (manure, raw rice husk, lemon peel) contained appreciably quantities of readily available carbon so that decomposition reactions could proceed more readily. Within the first 11 days when the decomposition process was shown to be most rapid in all treatments (Table 3), the biochar dung mixture recorded the lowest temperatures, suggesting slower decomposition. For the biochar-dung mixture, the higher portion of recalcitrant carbon in the mixture will reduce the decomposition rate (Jia et al., 2016).

The increase in compost temperature recorded with finer biochar particles was attributed to the greater surface area (increasing the microbial functional surface area) and also potentially greater water retention capacity through microbial refugia and carbon metabolites for microbial growth (Jindo et al., 2012; Zhang & Sun, 2014). This is an indication that biochar particle size also effects the temperature of the composting mixtures. This was further explained by Peachey (2016), which reported that composting mixtures using coarse (19-13 mm) biochar showed a decreased in temperature from 45 °C to < 30 °C.

### 3.3 Variation in pH During Co-composting of Rice Husk Biochar and Cow Dung

Soil pH is a major factor that affects the activities of the microorganism during the composting process. For a conventionally compost processes the pH increases from the onset and gradually declines towards the end of the process (Chen et al., 2017). Here the variation of pH with time was generally minimal with no clear differences in treatment trends. The pH of the compost mixture increased over the first 3 days with the CRL10 treatment having the highest pH (8). Subsequently, the pH declined in all the mixtures over the 39 days of the experiment (Table 4). There were no significant differences in pH between the treatments on days: 1, 2, 6, 19 and 25. However, treatment CRL10 recorded the lowest pH at 5.3 and 5 on days 15 and 39 respectively. Other studies have shown an increase in pH during the composting process and attributed this to the decomposition of organic matter which enhances the release of CO<sub>2</sub> and NH<sub>3</sub> (Beck-Frii et al., 2003). Agyarko-Mintah et al. (2017) reported an increase in pH during the incubation period of a poultry manure and biochar mixture, but this was at higher pHs around 8.

The addition of lemon peel did not significantly reduce treatment pH. The non-significant fall in the pH of treatments CL10 and CBL10 on day 1 was only evident on day one. Also, though the raw rice husk had a significantly lower pH than the biochar (Table 2), its effect on reducing the overall pH of the mixtures was not significant.

Table 4. The mean compost pH measurements during composting period

Treatments	Days										
	1	2	3	5	6	7	11	15	19	25	39
CL0	6.8 a	6.7 ab	6.7 b	7.0 a	7.0 a	7.0 a	7.0 ab	6.7 a	7.0 a	6.8 a	6.8 a
CL10	6.0 a	6.7 ab	7.2 b	7.0 a	7.0 a	7.0 a	7.0 ab	6.8a	7.0 a	6.7 a	7.0 a
CBL0	7.0 a	6.2 b	6.7 b	5.8 b	6.5 a	6.5 b	6.5 bc	6.3 ab	6.8 a	6.5 a	6.2 ab
CBL10	6.2 a	7.0 ab	7.2 b	6.0 b	6.7 a	6.6 ab	6.3 c	5.8 ab	7.0 a	6.2a	6.7 a
CRL0	6.8 a	7.2 ab	7.2 b	6.8 a	7.2 a	7.0 a	7.0 ab	6.0 ab	7.2 a	7.0 a	5.7 bc
CRL10	6.5 a	7.5 a	8.0 a	6.5 ab	7.2 a	7.0 a	7.2 a	5.3 b	7.0 a	7.0 a	5.0 c
LSD	0.73	0.66	0.59	0.47	0.52	0.21	0.47	0.78	0.59	0.89	0.55

Note. CL0, Cow dung only; CL10, Cow dung and 10% milled lime; CBL0, Cow dung and rice husk biochar (1:3); CBL10, Cow dung and milled lime at 10%; CRO, Cow dung + rice husk only (1:3); CRL10, Cow dung + rice husk + 10% milled lemon.

Values with the same letter in each column are not significantly different at  $p < 0.05$ .

### 3.4 CO<sub>2</sub> Emission During Biochar-Manure Co-composting

CO<sub>2</sub> emissions were initially high for all treatments but declined over time (Tables 5a and 5b). By day 7, the emission of CO<sub>2</sub> from the cow dung only (CL0) and biochar-cow dung mixture (CBL0) had diminished considerably. The evolution pattern and total amount of CO<sub>2</sub> at the end of 7 days for the CL0 and CBL0 treatments was not significantly different, suggesting that despite the higher total carbon of the CBL0, the CO<sub>2</sub> evolution was largely from the dung component. The combination of CL0 with CRL0 produced the highest CO<sub>2</sub> emissions, almost twice the values of the CL0 alone or the CBL0. Though the CBL0 and CRL0 treatments have similar carbon contents, the CRL0 contained fresh and readily degradable carbon, which can explain the observed higher CRL0 CO<sub>2</sub> emissions. This available carbon can function as a source of energy for soil microorganism and induce higher evolution of CO<sub>2</sub> (Chowdhury, Neergaar, & Jensen, 2014).

The cumulative CO<sub>2</sub> evolution, at the end of the first 7 days, was shown to be similar for the dung alone (CL0) and biochar-dung mixture without the addition of lemon peel (CBL0) (Table 5a). A significant increases in CO<sub>2</sub> evolution could be observed when lemon peel was added to these treatments. Hence, without any further additional readily degradable carbon source (*e.g.*, lemon peel), the evolution of CO<sub>2</sub> in the biochar-dung mixture could be solely attributable to the dung. The raw rice husk generally produced higher amounts of CO<sub>2</sub> irrespective of addition of lemon peel (Table 5a, *i.e.*, CRL0, CRL10).

From day 11 to 39, the additional CO<sub>2</sub> evolved by the biochar-dung with no lemon peel (CBL0) exceeded that by the dung alone without lemon peel (CL0), suggesting that the biochar was becoming decomposed (Table 5b). This confirmed the findings of Czekala et al. (2015) who reported that the amendment of compost with biochar triggered an increase in the cumulative CO<sub>2</sub> emissions. In effect, the initial CO<sub>2</sub> emissions could be attributed to the dung component of the mixture while the later emissions are from the biochar component. The addition of lemon peel to these treatments further enhance the CO<sub>2</sub> emissions (CL10; CBL10). Other non-microbial causes have been used to explain the increase in CO<sub>2</sub> emissions during the composting of mixtures amended with biochar. One of such is the abiotic oxidation of biochar (Dias et al., 2010).

Table 5. Carbon dioxide emissions (CO<sub>2</sub> mg m<sup>-2</sup> 24 h<sup>-1</sup>) measured over time during the study (a) the first 7 days and (b) from 11 to 39 days

(a) Treatments	Day 1	Day 2	Day 3	Day 5	Day 6	Day 7	Accumulative total
CL0	259.7 b	77.8 b	125.28	48.0 c	67.2 abc	9.07	587
CL10	401.7 ab	373.3 a	193.9 abc	181.9 b	44.6 bc	250.6	1,446
CBL0	241.9 b	62.9 b	116.6	50.9 c	18.2 c	116.2	506
CBL10	590.4 a	287.5 a	229.9 ab	146.4 b	71.0 abc	65.7	1,390
CRL0	372.9 ab	271.7 a	215.0 ab	195.4 ab	71.0 abc	107.4	1,233
CRL10	417.6 ab	304.3 a	253.9 a	155.0 b	44.6 bc	53.7	1,229
LSD	215	101	73	75	74	131	669

(b) Treatments	Day 11	Day 15	Day 19	Day 25	Day 39	Accumulative total
CL0	42.2 b	1.4 b	256.3 c	110.9 b	134.4 d	542
CL10	68.6 ab	44.6 ab	296.6 abc	235.2 a	182.9 d	828
CBL0	46.1 b	69.6 a	289.9 bc	212.6 a	215.0 c	833
CBL10	52.3 b	82.1 a	304.8 abc	237.6 a	253.9 ab	930
CRL0	39.4 b	83.5 a	293.3 bc	258.7 a	282.2 a	957
CRL10	41.3 b	60.9 a	354.2 b	272.2 a	276.0 ab	1,004
LSD	41.3	49.4	51.84	59.52	32.16	234.2

Note. CL0, Cow dung only; CL10, Cow dung and 10% milled lime; CBL0, Cow dung and rice husk biochar (1:3); CBL10, Cow dung and milled lime at 10%; CRO, Cow dung + rice husk only (1:3); CRL10, Cow dung + rice husk + 10% milled lemon.

Values with the same letter in each column are not significantly different at  $p < 0.05$ .

Generally, treatments that received milled lemon peel had the highest CO<sub>2</sub> emissions. This is attribute here to the addition of the readily degraded carbon source from the lemon, rather than a pH effect, given that the peel did not change the pH of the mixture significantly, and because NH<sub>3</sub> emissions were negligible.

#### 4. Conclusions

This study investigated the effect of organic resource mixtures, during co-composting, on CO<sub>2</sub> emissions in a tropical environment. Compost temperatures increased rapidly initially peaking on day 5 and thereafter decreased gradually to ambient temperatures. The biochar-dung mixtures had lower temperatures than the rice husk, dung or milled lemon peel mixtures alone. The pH of the mixtures increased initially during the composting process and subsequently declined, but treatment differences were largely not significant. The CO<sub>2</sub> emissions varied with the composition of the mixtures. The addition of rice husks biochar to cow dung, reduced the CO<sub>2</sub> emission during the composting process. However, the addition of lemon peel to the mixtures increased the CO<sub>2</sub>. The study has shown that biochar-dung co-composting was an effective method of producing an enriched organic soil amendment with lower greenhouse gas emissions than traditional composting of the organic residues.

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