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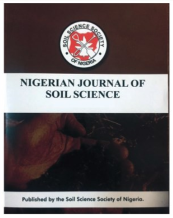

Using Urea Intercalated Biochar and Organic Fertilizer as Soil Management Option Part 1: Main Effects on Soil Properties and Carbon Implication

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ABSTRACT

The study evaluated the effect of application of some fertilizers on soil carbon dioxide evolution and unsaturated hydraulic conductivity (K_{unsat}) at daily time scale, while other soil properties were assessed at the end of the experiment. The factorial experimental design was based on completely randomized design replicated three times. 4 kg of the prepared soil was weighed into each pot and treatments consisted of control, biochar (10 tons/ha), organic fertilizer 5 ton/ha + urea 40 kg/ha, urea (40 kg/ha) intercalated with biochar (10 ton/ha) + organic fertilizer (5 ton/ha). Each was subjected to two degrees of moisture contents (50% and 70% field moisture capacity) and three levels of compaction (0 kg, 2 kg and 4 kg weights). Saturated hydraulic conductivity, K_{unsat}, $C0_2$ evolution, bulk density, total porosity, soil mean weight diameter, geometric weight diameter and organic carbon were determined using standard methods. Data collected were subjected to analysis of variance while significant means were separated using least significant difference at 5% probability level. Urea plus organic fertilizers significantly improved K_{unsat} compared to other treatments. This variation occurred on specific days starting from the second day of the experiment. Variations in the CO_2 loss were minimal indicating that the CO_2 emission arising from this soil management practice was limited. Porosity and bulk density improved the most under biochar-based treatments. Surprisingly, organic carbon was not affected by the fertilizer-related treatments. Aggregate stability was minimally affected. Thus, within a short-term frame, the treatments had minimal CO_2 loss while improving soil hydraulic properties.

1.0 Introduction

Low Nitrogen-use efficiaency has increased the rate at which urea is applied in cultivation resulting in increased N leaching, volatilization and NO_2 emissions (Gonzalez *et al*., 2015). The sole application of urea in continuous cultivation alters soil physical and chemical properties leading to soil degradation (Odunze *et al*., 2012). As a result of these problems, the use of sole urea fertilizer is not encouraged, therefore the need to provide better soil management option that will increase N-efficiency and also improve both the physical and chemical properties of the soil.

Biochar, as a by-product of pyrolysis produced from thermal decomposition of organic biomass under low or zero oxygen level (Lehmann and Joseph, 2009) has high recalcitrant aromatic carbon contents that marks the emergence of its pores and large surface area (Jung *et al*., 2019) with implication on soil properties. Biochar significantly improves physical features of soil like hydraulic conductivity, water retention and aggregate stability as well as chemical properties of soil like pH, organic carbon, cation exchange capacity (CEC), and anion exchange capacity (Liang *et al*., 2006; Asai *et al*., 2009; Peng *et al*., 2011; Xu et al., 2013). Changes in soil carbon status arising from loss of carbon dioxide following application of biochar to soil had been reported. For instance, there could be CO_2 release due to adsorption-desorption processes, as biochar has been reported to have CO_2 adsorbent capacity (Jung *et al*., 2019). Biochar can promote Gram-positive/Gram-negative bacteria ratio which triggers high CO_2 evolution (Mitchell et al. 2015). There could also be release of biochar carbon such as carbonates (Bruun and Luxhoi, 2008; Ameloot et al. 2013). Another possible source of the carbon loss few days after application of biochar is the mineralization of the indigenous soil C (Lehmann et al., 2011) or priming of native soil organic C pools due to interaction of biochar and native soil organic matter (Zimmerman et al., 2011; Ameloot et al., 2013). Studies have also reported decreased N-mineralization after biochar amendment was introduced (Riaz *et al* 2017; Wang *et al* 2017).

The combination of synthetic fertilizers and organic amendments would reduce the amount of sole urea needed and the amount of N in urea will be more efficient (Vanlauwe *et al*., 2002). The use of biochar and other organic amendments (e.g. compost) increases the retention of soil organic nitrogen mineralized in soil (in particular NH_4^+) and also reduces carbon fluxes from agricultural soils (Brassard *et al*., 2018; Huang *et al*., 2018). Intercalation is the reversible inclusion or insertion of a molecule (ion) into materials with layered structures. Intercalation of fertilizer involves coating and mixing it with a specific organic material in the presence of an adhesive polymer such as starch. It is used as a process of fortification of urea with biochar to serve as a slow release fertilizer. Urea intercalated biochar fertilizer is a potential substrate that can be exploited to develop slow release N fertilizer with higher use efficiency and less environmental hazard (Manikandan and Subramanian, 2013). While there is gradually growing knowledge on how soil physical properties respond to biochar application in soils, to the best of our knowledge, studies looking at the effect of biochar on soil physical properties when impregnated with urea, as a slow release fertilizer, are scarce. In the light of challenges with global warming, it is necessary that the carbon footprint of emerging technology or product should be investigated.

Therefore, this study was carried out to determine the effects of the application of biochar intercalated with urea and organic fertilizer, on some soil properties, and associated carbon dioxide evolution at different time scales.

2.0 Materials and Methods

Soil samples used for the study were collected from Soil Fertility Unit of the Faculty of Agriculture Teaching and Research Farm, Obafemi Awolowo University, Ile – Ife, Osun State, located in Southwestern part of Nigeria between Latitudes 7° 31′ 308′′ N and 7° 33′267′′ N and Longitudes 4° 33′466′′ E and 4° 34′446′′ E with an altitude of about 244 m above mean sea level. The annual precipitation is between 1200 mm and 1500 mm. The daily temperature does not fluctuate considerably with a maximum of between 27°C and 35°C and a minimum of between 18.9°C and 23.3°C. The highly weathered soil used is an Ultisol and an Iwo series, which has been classified as Typic Isohyperthermic Paleustults (USDA system) or Chromic Lixisol (FAO/UNESCO system) (Ojetade *et al*., 2021). The soils were derived from coarse grained granite and gneiss (Okusami and Oyediran, 1985).

2.1 Screen house experiment

The composite soil sample collected from 0 – 15 cm depth was air dried, and sieved through 5 mm sieve. Approximately 4 kg of the sieved soil samples was weighed into each pot and the treatments were applied. The pots were perforated beneath to facilitate drainage of water and exchange of air. Biochar used was made from charring of hard wood and procured from local market and crushed into finer fractions. The impurities and incompletely pyrolysed biomass were removed by sieving through 5-mm sieve. Urea intercalated biochar fertilizer was produced following Manikandan and Subramanian (2013) using urea (40 kg/ha), Biochar (10 ton/ha) and organic fertilizer (5 ton/ha). The factorial experiment consisted of four (4) different rates of fertilizer-related amendments, three (3) levels of compaction and two (2) levels of moisture content giving a total of 24 treatments that were replicated three (3) times in a Completely Randomized Design. The fertilizer-related treatments consisted of control (zero fertilizer), biochar (10 tons/ha), organic fertilizer 5 ton/ha + urea 40 kg/ha, and urea (40 kg/ha) intercalated biochar (10 ton/ha) + organic fertilizer (5 ton/ha). The sets of treated soil samples were moistened with predetermined water at different moisture levels (50% and 70% field moisture capacity). The field capacity was estimated as the soil moisture content after the covered saturated soil was allowed to freely drain for 72 hours. Each was also subjected to three levels of compaction due to weights imposed (0 kg, 2 kg and 4 kg weights). The experiment lasted for about three weeks similar to duration used by Jones *et al*. (2011).

2.1.1 Determination of soil properties

The soil unsaturated hydraulic conductivity at 2 cm suction (K_{unsat}) and carbon dioxide evolution from the soil were monitored daily from the beginning of the experimentation while the soil bulk density, porosity, aggregate assessment, saturated conductivity (K_{sat}) and organic carbon were determined at the termination of the experiment.

Particle size distribution was determined using hydrometer method (Gee and Or, 2002). Bulk density was determined by the core method. Porosity was determined as water content at saturation (Flint and Flint, 2002). Organic Carbon was determined by chromic acid digestion method (Nelson and Sommers, 1996). Saturated hydraulic conductivity of the soil was determined using modified falling head permeameter method of Klute and Dirksen (1986). The unsaturated hydraulic conductivity was determined with the use of disc infiltrometer technique. CO_2 efflux was measured using the static chamber method. The soil sample for aggregate stability assessment were taken at the same location and brought to the laboratory in such a way that minimum structural deformation occurred. The mean weight diameter (MWD) and geometric mean diameter (GMD) were then determined according to Kemper and Rosenau (1986).

2.2 Data Analyses

All data collected were subjected to analysis of variance (ANOVA) and treatment means were compared using least significant difference at 5% level of probability using statistical analysis system.

3.0 Results and Discussion

3.1 Antecedent soil properties

The results of the antecedent soil properties assessed before treatments are presented in Table 1. The soil is sandy loam in texture and the bulk density was 1.4 g/cc. Although below the critical level (1.6 g/cc) when soil is regarded as compacted, the bulk density is above 1.2 g/cc that has been identified to have tendency to impair root elongation and soil aeration (Reynolds *et al*., 2003). The soil organic carbon (Table 1) content was high according to Adepetu and Adebusuyi, 1985; Adepetu, 1990; Adepetu *et al*., 2014.

Table 1: Antecedent Properties of the soil

Soil properties	Values
Textural class	Sandy loam
Sand (%)	70.10
Clay (%)	19.74
Silt (%)	10.10
Soil organic carbon (%)	1.52
Bulk density (g/cm^3)	1.48

3.2 Daily (high frequency) response of soil unsaturated hydraulic conductivity to fertilizer treatments

The result of the daily measurement of k_{unsat} is presented in Fig. 1, indicating a mild decline with time. Specifically, days in which the fertilizer-related treatments (both biochar-based and non-biochar-based treatments) influenced k_{unsat} significantly ($P<0.05$) started from the second day after treatment application (DAT), then 5th, 6th, 8th, 12th and 13th DATs. Except for the 8th DAT, soil amended with organic fertilizer with urea conducted water faster than any other plots, followed by soil treated with biochar and biochar intercalated with urea plus organic fertilizer. Positive improvement in hydraulic conductivity due to the combination of organic fertilizer or manure with urea has been reported (Tripathi, 2019). The early influence biochar-based amendment had on hydraulic conductivity may have been due to the potential of biochar to instantly increase soil porosity (Joseph *et al.* 2007). This implies that beyond wetting and drying cycles that may increase hydraulic conductivity over time, due to formation of new aggregates and pores in coarse soils (Villagra-Mendoza and Horn, 2018), organic amendments of coarse soils, including biochar show similar effect (Olakayode *et al*., 2019). It is likely that the decomposition at latter date (as indicated by carbon dioxide evolution) may have produced hydrophilic organic matter (OM) from less recalcitrant organic materials in the organic fertilizer resulting in the spike in K_{unsat} for the 12th and 13th DAT. Biochar is known to be porous and its porosity was reported to reduce when urea was loaded singly or in combination with bentonite and polyvinyl alcohol, hydrothermally, with attendant reduction in its water holding ratio but increase in water retention ratio (Liu, *et al*., 2019). In addition, relatively fine biochar particle can reduce the larger pore in coarse soils through in-filling causing initial drop in hydraulic conductivity (Olakayode *et al*., 2019) but with attendant increase in soil water content and hydraulic conductivity over time (Eibisch *et al*., 2015; Hartge and Horn, 2016; Ajayi and Horn, 2017; Villagra-Mendoza and Horn, 2018; Olakayode *et al*., 2019). Hydraulic conductivity drops with decrease in moisture content which explains the reason that biochar alone resulted in higher soil hydraulic conductivity than the one that was urea-intercalated. It implies that, contrary to Leonard (2013) who reported reduction in hydraulic conductivity due to biochar hydrophobicity, biochar-based amendments can actually induce increase in soil hydraulic conductivity with time compared to when no amendment is added. Biochar has been reported to have moistening effect or induced changes in soil moisture potential (Spokas *et al*. 2009; Lorenz *et al*., 2014; Hui, 2021), increase water use by crop and minimize the impact of drought stress (Faloye *et al*., 2019), thus underscoring its important in water management.

3.3 Daily (high frequency) carbon dioxide emissions in response to fertilizers treatment

The daily evolution of carbon dioxide is presented in Fig. 2. On the implication of the fertilizer treatments alone on carbon dioxide evolution, a greenhouse gas, it is interesting to note that the effect was minimal relative to the control. The urea intercalated biochar plus organic fertilizer and urea plus organic fertilizer were only significantly higher ($P<0.05$) than the control in the release of carbon dioxide on 12th DATs representing 5% of the time of the short-term experiment whereas addition of biochar alone did not bring significant change in the volume of CO_2 released relative to the control for the duration of the experiment. Among the amendments, urea plus organic fertilizer was significantly higher in carbon dioxide loss to the atmosphere than urea intercalated biochar plus organic fertilizer and others on the 4th and 10th DATs, and biochar alone on the 4th and 19th DATs. Contrastingly, urea intercalated biochar plus organic fertilizer was only higher than urea plus organic fertilizer on the 20th DAT which was late into the experiment whereas biochar was higher in loss of the gas than urea plus organic fertilizer on 11th and 13th DATs. The two biochar-based amendments were not different from each other. Although very minimal the loss of carbon dioxide from plots treated with biochar-based amendment corroborated earlier works that reported that biochar application can cause carbon dioxide release within a short time (Spokas *et al*., 2009; Jones *et al*., 2011) and biochar tends to physically degrade with time (Brodowski *et al*., 2007 and Spokas *et al*., 2014; Naisse *et al*., 2015). Apart from biotic use and microbial decomposition (Cross et al., 2011; Zimmerman et al., 2011), it is also possible that the CO_2 released might occur due to direct addition of labile carbon of biochar (Cross et al., 2011) among other processes. Abiotic factor such as soil moisture content through application of water to maintain the soil at a known value of moisture content relative to field capacity as done in this study, may be responsible for variation in carbon dioxide release under each treatment over time. Dissolve organic carbon in biochar, as a labile source of carbon from biochar (Huang and Hall, 2017), had been observed to get washed out from biochar in soil when water is added (Jones et al. 2011) and can subsequently be lost to the atmosphere as carbon dioxide through microbial activity.

3.4 Response of other selected soil properties to the

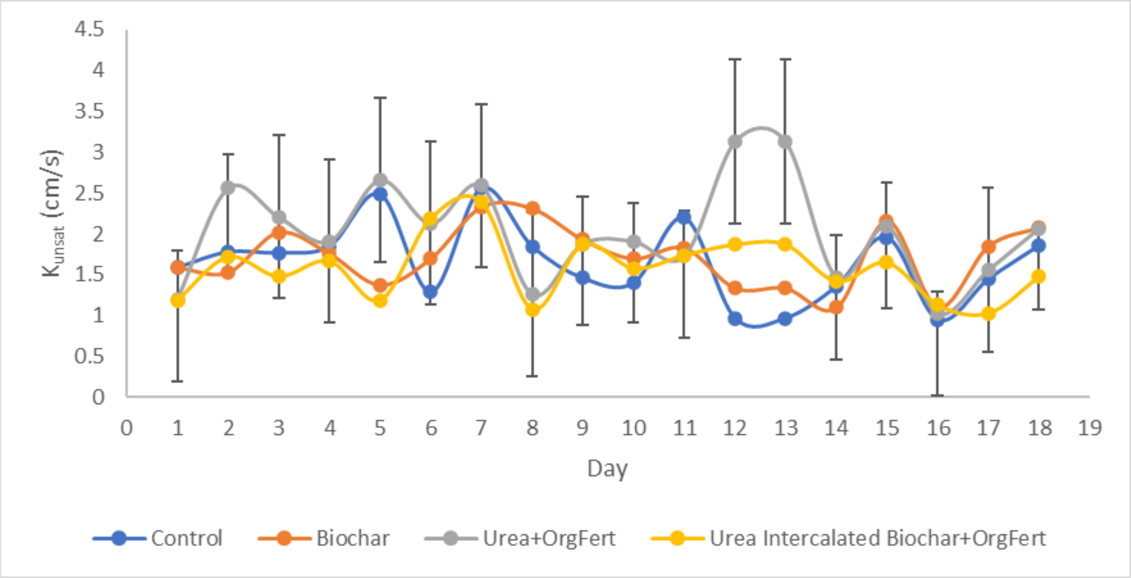

Figure 1: Effects of fertilizer-related treatments on K_{unsat} (cm/s)

Urea + Orgfert – urea plus organic fertilizer; Urea intercalated biochar + Orgfert - urea intercalated biochar plus organic fertilizer

K_{unsat} is the soil unsaturated hydraulic conductivity at 2 cm suction

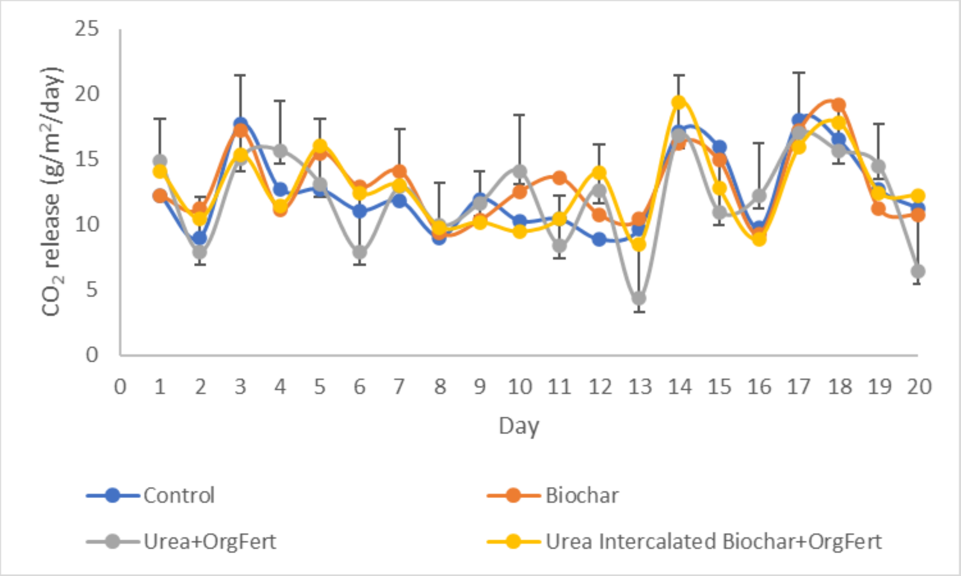

Figure 2: Carbon dioxide evolution (g/m^2/day) in response to fertilizer treatments

Urea + Orgfert – urea plus organic fertilizer; Urea intercalated biochar + Orgfert - urea intercalated biochar plus organic fertilizer

amendments

For other parameters assessed at the end of the experiment (Table 2), it is somewhat surprising that the organic amendments, including the biochar that was applied at 10 tons/ha, did not significantly ($P<0.05$) increase the OC content in the soil relative to the control. It is possible that the biochar added was not sufficient to significantly raise the moderately high level of organic carbon met in the soil. Guo (2020) in their extensive review advocated for minimum of 20 Mg/ha (20 tons/ha or 1 mass% soil) and 40 Mg/ha of biochar addition to soil for a sustainable impact on soil for manure-based- and wood or crop residue-based biochar, respectively.

The fertilizer treatments did not significantly ($P<0.05$) affect the soil saturated hydraulic conductivity (K_{sat}) (Table 2). This agrees with the work of Ouyang *et al*., (2013) who did not observe any significant change in K_{sat} in silty clay and sandy loam soils amended with biochar. This was likely due to biochar type and rate. Zebarth *et al.* (1999) also attributed the unchanged K_{sat} despite organic amendments to coarse-textured soil used. Another work indicated that at the initial stage, there was no change in K_{sat} after addition of manure until after two to five wet and dry cycles when the manure significantly affected it (Hafez, 1974; Eusufuzai and Fujii, 2012). Therefore, looking at the coarse data collected ranging between 20 – 40 days interval in Ouyang *et al*. case and a number of wet and drying cylces before K_{sat} was affected as reported by the other authors, and compared with the assessment of K_{sat} at the end of the study in our case, it is likely that essential period of significance in the hydraulic response of the soil may have been missed as it is the case with our experience with K_{unsat} as reported in Section 3.2. Significant changes in K_{unsat} was not steady with measurement taken at daily time scale. This requires further investigation and raises a question on the appropriateness of sampling time for K in soil experiment and may provide a hint on why study on effects of biochar on Ksat contradicts (e.g. Laird *et al*., 2010 and Major *et al*., 2010, Ovie *et al*. 2013). Another reason is the rate of amendment applied. It may not have been high enough to significantly increase K_{sat} in a coarse soil used for the study based on recommendation by Guo (Guo, 2020). Wang *et al*. (2009) reported reduced wettability of sandy soil and negative relationship between K_{sat} and soil organic matter (SOM) under grass in a Semi-arid region of Nebraska at very low range of SOM (particularly sensitive at SOM≤0.1%). This is capable of counteracting the tendency of SOM to induce soil aggregation with subsequent increase in K_{sat}. Contrastingly, the effect of the fertilizer treatments on the bulk density and porosity was significant ($P<0.05$) (Table 2). The bulk density was significantly highest in control (1.48 g/cm^3) followed by urea plus organic fertilizer which in turn was higher than urea intercalated biochar plus organic fertilizer while biochar plot was the least (1.40 g/cm^3). All these values are still within the safe threshold (1.6 g/cm^3) and there was improvement due to the two biochar-based amendments, albeit in a range within moderate limitation according to the critical level suggested by Lal (1994). Porosity was only significantly highest in biochar plots compared to other treatments. By significantly depressing the soil bulk density and increasing the porosity, improvement of bulk density by biochar-based fertilizer treatments translated to enhancement of soil porosity (from 43.37 to 47.36%). Improvement in porosity and bulk density agrees with previous work that used organic amendments (Ekebafe et al., 2013; Ovie *et al*., 2013, Cercioglu *et al*., 2014; Ajayi *et al*., 2016; Faloye *et al*., 2019). The geometric mean diameter (GMD) of the soil aggregates were unaffected by the amendments. Except for the reduction in the mean weight diameter (MWD) in biochar-treated plot relative to control, soil aggregate was not affected by the amendments and the values across all treatments were without any agronomic limitation (Lal, 1994). This agrees with Nweke *et al.* (2015) whose soil MWD was not affected when treated with sole or combination of urea and cow dung. This was attributed to the low quantity of organic materials applied and type of organic manure applied and on duration of the cropping season.

Table 2: Effects of fertilizer types on selected soil properties

FERTILIZERS	Organic C (%)	MWD (mm)	GMD (mm)	K_{SAT} x 10^{-3} (cm/s)	Porosity (%)	Db (g/cm^3)
A	1.12	4.38	1.02	1.88	43.37	1.48
B	1.24	3.66	1.01	1.56	47.36	1.40
C	0.93	4.00	1.02	1.82	42.54	1.44
D	1.15	4.13	1.03	1.43	44.04	1.40
LSD	NS	0.70	NS	NS	2.20	0.04

A-control; B-Biochar only; C-organic fertilizer with urea; D-Biochar intercalated with urea plus organic fertilizer

3.5 Carbon dioxide emission from the soil over time

Although Fig. 3 reveals that when pooled together, more carbon was lost from biochar-amended plot than others with the plot treated with urea intercalated biochar plus organic fertilizer being the least; the difference was not distinct. The minimal difference may be down to the limitation to gas transport posed by the blockade of soil pores by the particles of these amendments. In fact, Kuncoro *et al*. (2014a, b) observed higher gas transport properties in unamended plots than those organically amended, due to blocking or bottle neck effect caused by the organic amendment. Therefore, the use of the three amendments (urea plus organic fertilizer, urea intercalated with biochar plus organic fertilizer and biochar) in the sandy loam soil, within a short-term, does not pose any additional threat to the environment.

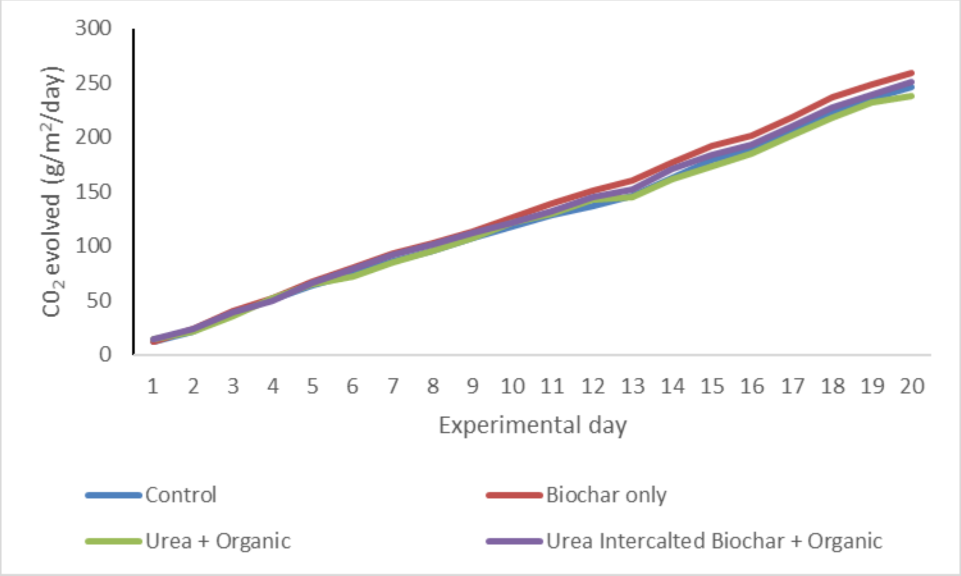

Figure 3: Cumulative CO_2 emission in response to fertilizer application

4.0 Conclusion

The study considered changes in soil properties and associated carbon dioxide released into the atmosphere following soil amendment with biochar-based and non-biochar-based fertilizers. Porosity and bulk density were improved by the fertilizer-related treatment imposed. The soil aggregate was minimally affected. The fertilizer-related treatments were unsteady in the improvement of soil unsaturated hydraulic properties for a porous sandy loam with time, raising consideration for appropriate timing of its assessment. The carbon released based on this fertilizer treatment was minimal relative to unamended soil. Thus, within a short-term frame, the urea intercalated with biochar (a slow release fertilizer) and organic fertilizer when used as soil management option posed limited threat on associated CO_2 loss to the environment while it improved the soil hydraulic properties. Thus, the use of the slow release fertilizer for improvement of physical properties of a sandy loam soil is desirable.

Declaration of interest: none

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