Article

Carbon, Nitrogen Dynamics and CO_2 efflux in the Calcareous Sandy Loam Soil Treated with Chemically Modified Organic Amendments

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Abstract: In Saudi Arabia, more than 335,000 tons of cow manure is produced every year from dairy farming. However, the produced cow manure is usually added to the agricultural soils as raw or composted manure; the recovery of ammonia from cow manure is a promising technique for producing concentrated nitrogen fertilizer and reducing nitrogen losses from raw manure. The byproduct effluents from the recovery process are characterized by different chemical properties from the raw manure. The effect of using the recovery effluents as soil amendments on the soil carbon and nitrogen dynamics is not apparent. Therefore, A 90-day incubation experiment was conducted to study the impact of these effluents on CO_2 efflux, organic C, microbial biomass C, available NH_4^+, and NO_3^- when added to agricultural soil. In addition to the two types of effluents (produced at pH 9 and pH 12), cow manure CM, cow manure compost CMC, cow manure biochar CMB, and control were used for comparison. The application of CM resulted in a considerable increase in soil available nitrogen, CO_2 efflux compared to other treatments. Cow manure biochar showed the lowest CO_2 efflux. Cumulative CO_2 effluxes of cow manure effluents were lower than CM; this possibly due to the relatively high C: N ratio of manure effluent. The content of P, Fe, Cu, Zn, and Mn decreased as incubation time increased. Soil microbial biomass C for soil treated with cow manure effluents (pH 12 and 7) was significantly higher than the rest of soil amendments and control.

Keywords: organic wastes; cow manure; CO_2 effluxes; ammonia stripping; C: N ratio

1. Introduction

Agriculture is considered the primary source of ammonia emission globally (Bouwman and Van Der Hoek, 1997) and regionally in, e.g., Europe (Sutton et al., 2011) and USA (Pinder et al., 2004). Ammonia and its inorganic derivatives, nitrite, and nitrate are easily percolated to the ground and surface water, resulting in a deterioration of water quality and risk hazards in drinking water (Dubrovsky and Hamilton, 2010).

Regarding CO_2 efflux from soil treated with organic amendments, FAO (2014) showed that the total annual emissions of greenhouse gases (GHG) from agriculture to the atmosphere in 2011 were 5,335 Mt CO_2 eq. Twenty-five percent of this amount is released into the atmosphere due to manure storage, management, and amendments. Soil CO_2 efflux, as described by Kuzyakov (2006) is efflux that comes from the root and

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rhizomicrobial respiration, decomposition of plant residues, the priming effect induced by root exudation or by addition of plant residues, and basal respiration by microbial decomposition of soil organic matter (SOM). Many key factors control the CO_2 efflux from the soil, such as climatic factors, temperature and water content (Sallam, 2002), clay content (FAO, 2014), water holding capacity (Schjønning et al., 1999), C: N ratio (Kowalska et al., 1994). Risse et al. (2006) reported that among many applied fertilizers to maize in China, CO_2 and NO_2 emissions were significantly correlated to pig manure and inorganic fertilizer due to their low C: N ratio. An incubation experiment (Yuan et al., 2014) showed that the biochar amendments to soils reduced N-gases volatilization and decreased CO_2 emissions from soils due to the low C: N ratio in the used biochar.

Therefore several pretreatments have been suggested to reduce the C: N ratio of N-rich wastes such as manure and produce organic amendments with a reduced C: N ratio and higher soil carbon stability. These methods include composting (Paré et al., 1998), pyrolysis process to produce biochar (Ameloot, et al., 2015), and ammonia recovery from manure (Mohammed-Nour et al., 2019).

Composting animal manure and nitrogen-rich wastes is a technique to reduce nitrogen release from organic materials to soils. During composting, the C/N of mixed organic materials decreases due to the biochemical oxidation of organic matter (van Vliet et al., 2007). Composting of 'struvite' food waster reduced N loss by 18% compared to the use of raw wastes (SAAF, 2007). In a lysimeter study, it was found that the application of poultry manure and paper mill sludge blends resulted in a pulse of NO_3-N (170 and 156 mg N/L) that occurred three months following application. At the same time, compost treatments showed no such pulse (Dere and Stehouwer, 2011). Another study by Sparks et al. (1996) found that composting of cattle manure doubled the soil humic substances compared with the raw manure. They concluded that composting of cattle manure resulted in more stable and less decomposable organic compounds in soils. On the other hand, during the composting process, an appreciable amount of nitrogen is lost through the volatilization of ammonia (Steiner et al., 2010).

Another method for increasing the C/N of the organic material is the pyrolysis of wastes to produce biochar. The pyrolysis process involves the heating of plant biomass in the absence of oxygen gas (Lehmann, 2007). The pyrolysis process increased carbon percentage due to the increasing degree of carbonization. However, hydrogen and oxygen content tends to decline (Al-Wabel et al., 2013). Enders et al. (2012) found that during the pyrolysis of different feedstock to produce biochar, fixed carbon significantly increased. The N recovery was negatively correlated to a pyrolysis temperature.

The conversion of plant residues to biochar is an attractive strategy for mitigating atmospheric carbon dioxide emissions and enhancing carbon storage in soil (Xiang et al., 2015).

Sigurnjak (2019) recently showed that nitrogen recovered from wastes could be used as a nitrogen fertilizer for crop cultivation. Mohammed-Nour et al., (2019) achieved a 90% recovery of the ammonia in cow manure through alkalization and thermal treatment. They suggested the use of ammonia stripping technique to reduce the environmental risks associated with ammonium volatilization from manure. The chemical properties of the produced effluents from the ammonia recovery process are different from manure. Therefore, its chemical behaviour as a soil amendments is not clear.

Soil stable organic carbon is one of the parameters used to evaluate the sustainability and efficiency of soil carbon sequestration. Bastida et al. (2012) mentioned that different carbon fractions, such as the total organic carbon, water-soluble carbon, and microbial biomass carbon, were increased in amended soils compared to the control. Also, Lima et al. (2009) stated an increase in lignin and lignin-like products in the soil amended with compost.

The study's primary objectives were to investigate the effects of cow manure stripped ammonia effluents (CMSAEs) on temporal changes in soil CO_2 flux, nitrogen forms (NH_4^+,

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NO_3^- and total N), estimate the microbial biomass C as an indicator for microbial activity during incubation.

2. Materials and Methods

2.1. Soil and Organic Materials Characterization

2.1.1. Soil

Topsoil (0–30 cm) was collected from an agricultural field located in Aloyyna, Riyadh, Saudi Arabia (24°54'27.36″ N and 46 °23'35.49″ E). Collected soil was homogenized, and sieved to less than 2 mm, then it was air-dried for the physicochemical characterization according to standard methods (Estefan, 2017). pH was determined in 1:5 water extract (w/v) using pH meter, Orion star A211, Electrical conductivity (EC) was measured in the filtrated extracts using YSI, USA.

2.1.2. Soil amendments

2.1.2.1 Cow manure (CM)

Cow manure (CM) was collected from ALSAFI dairy farm situated in Al-Kharj, Saudi Arabia.

2.1.2.2. Cow manure stripped ammonia effluents (CMSAEs)

CMSAEs are the byproduct of ammonia recovery from cow manure through the alkalization and distillation process (Mohammed-Nour et al., 2019). In this experiment, two effluents from different alkalization degrees (pH 9 and 12) were studied.

Effluents were prepared by treating 100 g of fresh CM with either 2.44 or 0.5 ml of 15 N KOH to bring pH to 12 or 9. Then 100 ml of deionized water was added to manure paste in a one-lit round glass bottle. Mixtures were heated up to 95 °C for 5 h. Ammonia was recovered in 25ml of 0.5 N sulfuric acid. CMSAEs were collected, then slowly cooled down to 25 °C.

2.1.2.3. Composted Cow manure (CMC)

Composted cow manure (CMC) was obtained from (ALSAFI dairy products facility, Riyadh, Saudi Arabia), CMC was stored at 4°C.

2.1.2.4. Cow manure biochar (CMB)

One kg of dry cow manure (CM) was pyrolyzed at 400°C for 4 h. Cow manure biochar (CMB) was produced as mentioned by Al-Wabel et al. (2013).

CMC and CMB were used in the incubation experiment as reference material to evaluate the C stability from CMSAEs of CM. Before application time, all organic materials were air-dried, grained, and sieved to 1mm.

2.2. Chemical analysis of soil amendments

Total nitrogen and carbon were determined using a EuroVector Elemental Analyzer EA3000 equipped with Callidus software (EuroVectorSpA, Milan, Italy). To determine total phosphorus, potassium, calcium, magnesium, and other micronutrients in manure, 0.2 g of dried manure were treated with 10 mL of concentrated nitric acid and digested according to the procedure of Creed et al., (1994) using microwave digestion (MARS, CEM Corporation, USA). The total concentration was determined in the digestate using an inductivity coupled plasma optical emission spectrophotometer (ICP-OES, PerkinElmer Optima 4300 DV, USA).

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2.3. Incubation Experiment

A long-term incubation experiment was carried out under laboratory conditions for 90 days. The experiment consists of six organic materials; CM, CMC, CMB, plus the control (pH12 and T95°C) CMSAE and (pH9 and T95 °C) CMSAE. CMC and CMB were used to compare C, and N dynamics with that of CMSAEs.100 g of 2mm sieved calcareous soil (texture: sandy loam), placed into 250-mL jars. Experimental soil was pre-incubated for 15 days at 25°C to allow the soil to equilibrate after sieving and handling. The moisture of the soil samples was initially adjusted to 75% of the water holding capacity (WHC) through the addition of deionized H_2O at regular intervals (1to 2 weeks). The WHC was determined by saturating a sample of soil in filter paper placed in a glass funnel. Then, the water was drained for two h before the gravimetric soil moisture content (for 100% WHC) was determined by drying for 24 h at 105°C. Amendments were added to the soil at a 50 mg $C.g^{-1}$ soil based on the elemental C analysis of the used amendments—total added N amendments estimated before the experiment. A blank without N and C addition was used as a control. The jars were fastened airtight and incubated in a growth chamber at 30°C. The samples' moisture was periodically adjusted to the value of field capacity (27% v/w). The CO_2 efflux from soil was measured at 1, 2, 4, 5, 10, 13, 18, 30, 40, 50, 60, 70, 80, and 90 days, using 10 mL of 1N NaOH solutions as the captured solution. At all sampling time, 10 g soil was extracted with 50 mL of 0.5 M K_2SO_4 before and after fumigation with chloroform. The extracts were titrated with Fe $(NH_4)_2(SO_4)$ 0.2 N to determine the amount of microbial biomass carbon during the 90 day incubation period, according to (Anderson and Domsch, 1978). For available nitrogen determinations, 10 g of fresh soil were extracted with 2 M KCl, distilled with Kjeldahl instrument, the nitrogen was received at 3% boric acid. Standard H_2SO_4 0.01N were used to back titrate boric acid and have mineral nitrogen content (NH_4^+ and NO_3^-) for pH and EC determination suspension of (1:5) soil: water was made, Orion Star (A211) pH meter was used to determine soil pH. Electrical conductivity (EC) was measured in the filtrated extracts using an EC meter (YSI, USA). Finally, for available phosphorus and micronutrients, an extract of 0.005 M ammonium bicarbonate (DTPA) was prepared, and the inductivity coupled plasma optical emission spectrophotometer (ICP-OES, PerkinElmer Optima 4300 DV, USA) were used to estimate the available concentration of extracting solution.

2.4. Statistical analysis

The presented data are averages of three replicates. The measured soil chemical properties, carbon efflux rate, and microbial carbon were statistically compared using Duncan's multiple range test. Nutrient release from different organic amendments at different time intervals was statistically analyzed by completely randomized design under two (days of incubation and organic amendment) factorial arrangement. Statistical analysis of the data, simple correlation, and regression analyses were performed using SPSS 19.0 software. The significance test was conducted at 5 and 1% level of significance ($p \leq 0.05$ and $p \leq 0.01$).

3. Results and Discussion

3.1. Experimental Soil

The soil used in this study was agricultural soil with sandy loam texture, pH of 8.5; electrical conductivity of 0.6 dS m^{-1}, total carbon 4.8%, total nitrogen (N) content of 0.1% and calcium carbonate content was 29.9%.

3.1.1. Soil pH

There were significant differences ($p \leq 0.01$) in soil pH among the organic amendments and incubation time. Almost all treatments increased pH after seven days of incubation except for CMB (Figure1). The highest pH value was 9.7, which was obtained by CMSAE (pH12&T95°C), while the lowest pH was 8, which was obtained by CMSAE

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(pH9&T95ºC). The soil pH of CM, CMC CMB, and CMSAE (pH9&95ºC) was lower than form 7 days was increased and the pH was stable afterward. Higher pH values of CMSAE (pH12&T95ºC) could by explain by the addition of more KOH before ammonia stripping, compared to CMSAE (pH9&T95ºC). At the start, the CMB had the highest pH. The increase of basic metals in the biochar might be the reason to raise soil pH after biochar application (Kookana et al., 2011), (Streubel et al., 2011) reported 0.8 to 0.1 unit rise in the soil pH as a result of biochar application to the soil.

Soil pH after 20 days tends to increase then fall at 60 days except for CMC, decreasing earlier at 20 days incubation time. This was also reported by McCauley et al., (2009) they stated that the cation exchange capacity increases as a result of organic matter decomposition, therefore increasing the soil buffering capacity. The high buffering capacity of the soil increased by the increasing decomposition of organic material, releasing of OH^- and CO_2 and pH increased. Hence the lack of effect of the organic materials on soil pH may most likely be approved by the findings of Gramss et al., (2003). At 90 days pH tends to equilibrate, while row caw manure and by CMSAE (pH12 and T 95ºC) tend to increase. The second pH increase could be attributed to the breakdown of organic matter, which results in H+ ions to be released into the soil from the functional groups which led to pH decrease (Van Ranst, 2006).

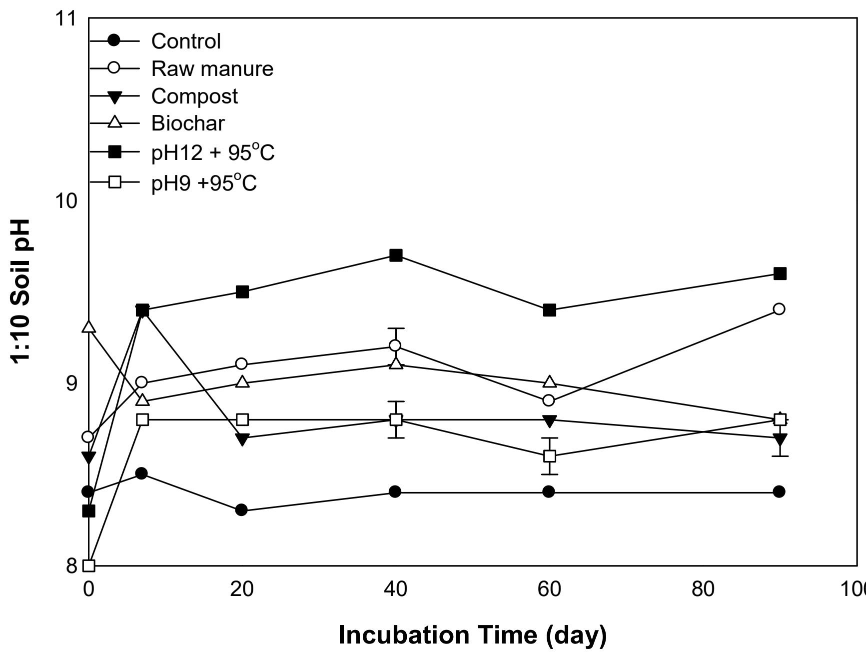

Figure 1. Variation in soil pH treated with different organic amendments derived from cow manure at incubation times.

3.1.2. soil EC

There was a statistically significant difference in soil EC due to the addition of the different amendments. The incubation time did not affect soil EC. Application of various organic amendments resulted in an initial rise in soil EC followed by steady afterward. All amendments EC were less than two dS m^{-1} except for CMC of 3 dS m^{-1} (Figure 2). The soil incubated with CMC showed the highest EC. The soil EC of CMB was increased during 0- 40 days. The CMSAEs showed less EC as compared to CMC but similar to that of the CMB. Higher CM soil EC related to initial EC. The increase of soil salinity due to cow manure application was reported by Hao and Chang (2003). They considered manure as an essential source of soil salinity. The same observation was reported by Goff (2006), who found that huge manure quantities induced soil salinity. These quantities increased salt content and soil EC to be increased. CM can increase salinity due to the presence of water-soluble nutrients ammonium, Na, Ca, Mg, K, Cl, SO_4, and HCO_3 and the use of nutritional salts (NaCl).

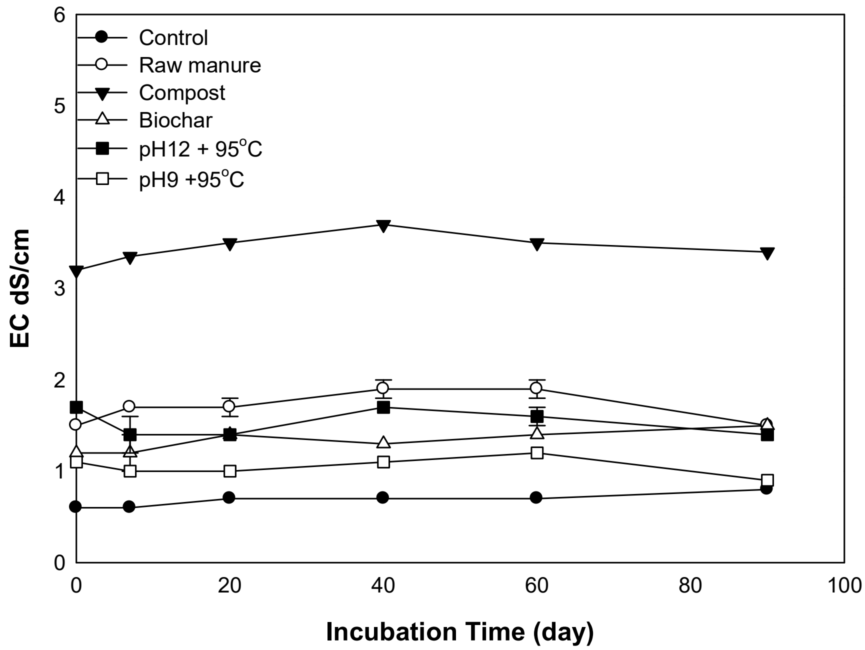

Figure 2. Variation in soil EC as affected by different organic amendments derived from cow manure at different incubation time.

3.1.3. Available phosphorus

The results for available phosphorus (P) affected by different organic amendments derived from CM were shown in Figure 3. There was a statistically significant difference in available P as a result of organic amendments and incubation time. The available P in soils treated with CM, CMC and CMSAE (pH12&T95°C) decreased between 0 to 7 days and then tended to increase as the incubation time increases. This decrease may result from CaCO3, which is reported to retain P as dicalcium phosphate and octacalcium phosphate (Von Wandruszka, 2006). Soil treated with CMSAE (pH12&T95°C) showed the highest available P between days 20 to 90. This increase in soil available P might be due to the high humic acid content in manure effluents compared to CM and CMB, as found by (Delgado et al., 2002). They indicated that the presence of humic acid slows the precipitation of poorly soluble Ca phosphates.

There were irritating results for P as general this could be explained as P adsorption, and desorption biochar and other carbonaceous materials are governed mainly by soil pH (Initiative, 2012). In addition, P availability in soil is controlled by Ca and Mg ions under high pH conditions. Thus, the decline in the availability of P mainly qualified to the high content of $CaCO_3$ and high soil pH by forming less soluble compounds.

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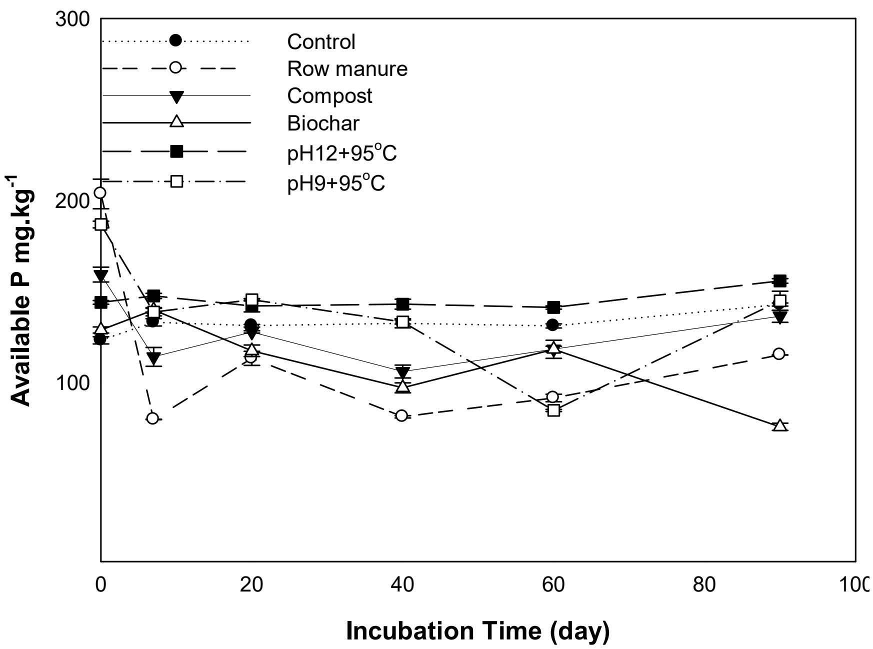

Figure 3. Available phosphorus is affected by different organic amendments derived from cow manure at incubation times.

3.1.4. Available iron

There was a significant difference in soil available Fe as a result of organic amendments addition. The Fe declined as incubation time decreased (Figure 4). The Fe content values are plotted in two areas: sharp Fe decrease in CMC and CMB, gradual Fe decrease: in CMSAEs and CM. After 60 days, Fe content depleted to the lowest value for all treatments. The Fe content of soils treated with CM and CMSAEs was higher compared to other amendments. This may be related to the high Fe content of CM. and CMASEs had high humic substance content that may contribute to Fe availability via the formation of water-soluble Fe- Humic substance complexes, which quickly move in the soil (Garcia-Mina et al., 2004). Uptake of 59Fe from 59Fe-complex was measured even at pH values compatible with those found in calcareous soils (Colombo et al., 2012). Although calcareous soils tend to reduce Fe availability due to high pH in this soil (Abadía et al., 2011; Bavaresco and Poni, 2003). The high pH increases the hydroxyl functional group, and subsequently, Fe hydroxide precipitated (Zeng et al., 2014).

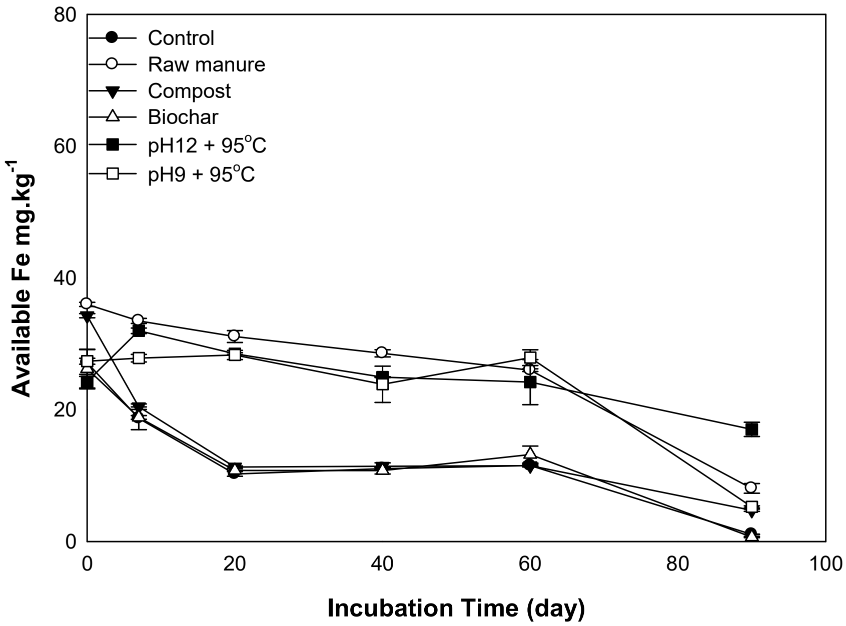

Figure 4. Soil available iron as affected by different organic amendments derived from cow manure at different incubation times.

3.1.5. Available cupper

There was a significant difference in Cu content as result of organic amendments. The Cu content declined with increasing incubation time. The Cu values were also plotted in two areas: a sharp decrease in CMC and CMB, a gradual decrease in CM and CMSAEs. The Cu content of 0 to 20 days decreased in all amendments with the exception of CM; afterward, Cu contents were almost stable until 60 days, and then its content decreased at 90 days (Figure 5). The highest Cu content at start explained by low soil pH as showed in (Figure1). The Cu content CMSAEs was higher than CMC and CMB; the reason behind this was the temperature of CMSAEs preparation, which promoted Cu containing tissue of CM to degradation, consequently produce more Cu in soil solution (Aaltonen et al., 2019).

(Cuske et al., 2013) stated copper could be binding to low molecular weight organic acids into a shape of movable complexes. The low Cu values at the end of the experiment might be due to the buffering capacity of this soil.

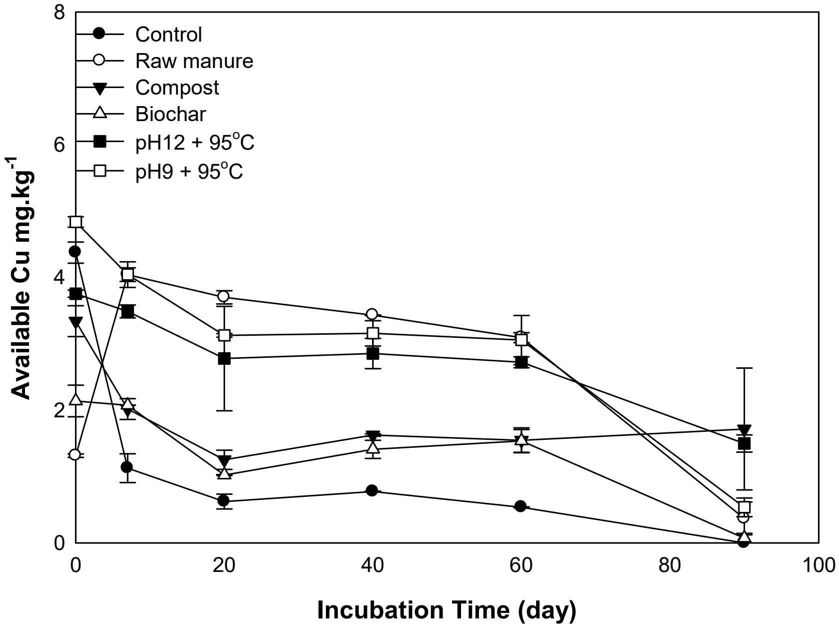

Figure 5. Soil available cupper as affected by different organic amendments derived from cow manure at different incubation times.

3.1.6. Available zinc

There were significant differences in Zn content was observed as a result of organic amendments application. Zn content generally declined with increasing incubation time (Figure 6). The highest recorded Zn content was (39.7 mg kg^{-1}) for CMC treatment, while the lowest Zn content was (1.1 mg kg^{-1}) in control soils after 90 days. Higher soil pH and CO_3 content negatively affected Zn content and decreased its availability. The results of (Smith, 2009) showed that aerobic composting processes increase the heavy metals complex with organic materials by forming strongly bound to the compost, affecting their solubility.

High pH values increase soil hydroxyl functional groups, and subsequently, zinc hydroxide and zinc carbonate are expected to be precipitate and reduce Zn availably (Zeng et al., 2014).

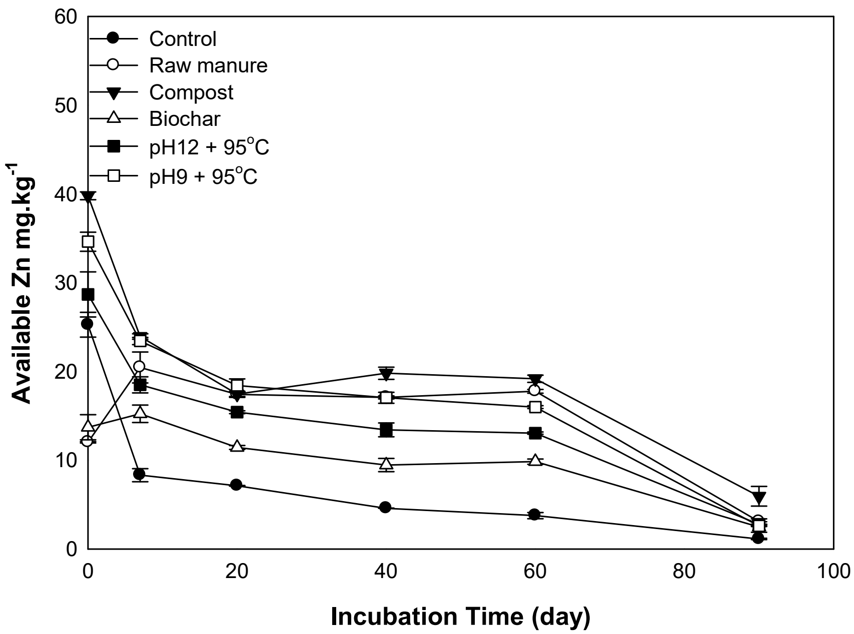

Figure 6. Soil available Zinc as affected by different organic amendments derived from cow manure at different incubation times.

3.1.7. Available manganese

Higher Mn content was observed at the start of the incubation. Afterward, Mn concentration tends to sharply decrease for all organic amendments in 20 days, except for a gradual decline for CMSAE (pH9&T95°C), which reached 9.6 mg kg^{-1} at 40 days. The highest Mn content was 86 mg kg^{-1} which was observed at CMSAE (pH9&T95°C), while the lowest Mn concentration was 0.38 mg kg^{-1} which was observed at CMB with 90 days. Mn concentration was reduced in CMB three times than CMSAE (pH9&T95°C) at seven days incubation time. At the same time, its content decreased by (1:8) ratio at 20 days (Figure 7). Low Mn content may have resulted from the mass losses that happened after the decomposition of organic matter (Ingelmo et al., 2012). Similar results were also obtained by (Zeng et al., 2014), who found the Mn content was below the critical level when soil pH was increased.

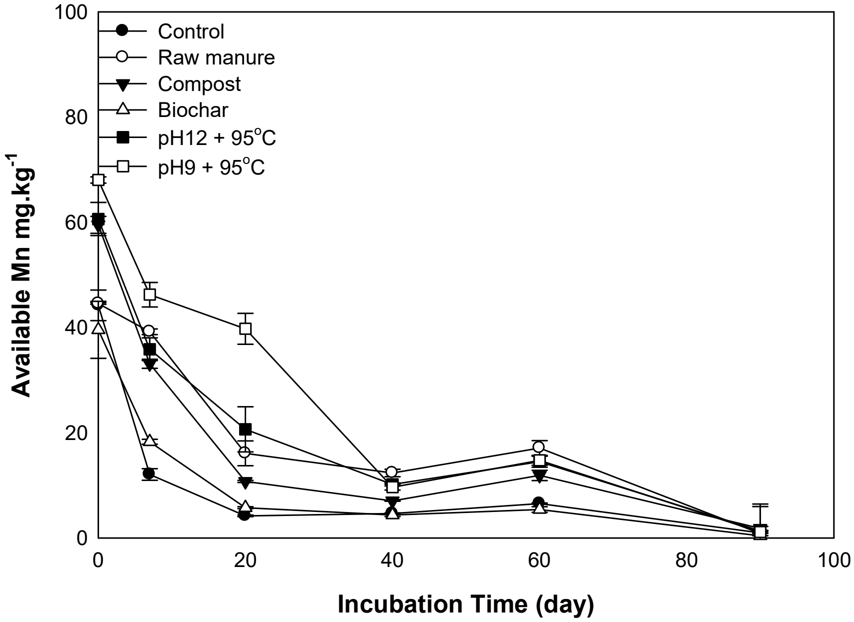

Figure 7. Soil available Mn as affected by different organic amendments derived from cow manure at different incubation times.

3.2. Nitrogen dynamic

3.2.1. Available nitrate

Nitrate -nitrogen is considered one of the measurements for soil nitrogen availability. The results showed that the addition of different organic materials caused an increase in the KCl extract NO_3^- of nitrogen concentrations as incubation time increased. The maximum nitrification was recorded at 60 and 90 days after incubation. The maximum NO_3^- accounted for 1124 ±4.2 and 870 ±2 mg kg^{-1} soil for CM and CMSAE (pH12 + 95^{o}C) respectively (Figure 8).

Generally incubation time increased NO_3^- content. After 20 days increase in soil NO_3^- might be related to biological oxidation of ammonia to nitrate through nitrification process (Grunditz and Dalhammar, 2001) and (Vadivelu et al., 2007)

$2NH_4^+ + 3O_2 = 2HNO_2 + 2H^+ + 2H_2O$ (Nitrosomas sp)

$2HNO_2 + O_2 = 2NO_3^- + 2H^+$ (Nitrobacter sp)

Environmental factors that affect ammonification and nitrification are temperature, water status, C: N ratio (Agehara and Warncke, 2005); (Kampschreur et al., 2007). Ammonium nitrification could be a reason for the increase in NO_3^- the content of soil incubated with an organic compound. The rise in nitrification at 60 days was also found by Usman et al. (2013) stated that the poultry manure addition to soil resulted in NO_3^- accumulation at 60 says. This was mainly due to the increased activity of nitrifying bacteria. These findings agree with those results found by Preusch et al. (2002), who found that the ammonium content extracted from soil treated with fresh poultry litter declined during the first 30 days of incubation there was a rapid increase in NO_3^- contents.

Also, high soil pH could be a reason for the inhibition of nitrifying bacteria growth, resulting in incremental NO_3 content (Pichtel, 1990). It is essential to highlight the importance of NO_3^- management while applying cow manure to prevent NO_3^- peculation through the soil profile. The CMC and CMSAE (pH12 + 95^{o}C) showed the highest NO_3 at incubation. This increase is due to the appreciable content of NO_3^- in CMC. Paul and Beauchamp (1994) found that the soil amended with CMC contains more than 206 mg N per kg soil compared to fresh CM. Hence, if CM is added to the soil under field conditions, we suggest that the best management practice would be to avoid the environmental risk of NO_3-N leaching.

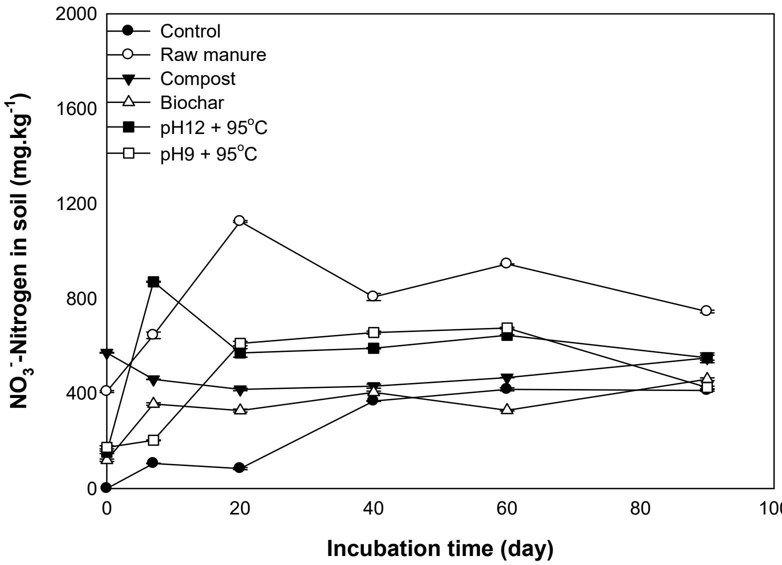

Figure 8. Available NO_3^- mg kg^{-1} as affected by different organic amendments derived from cow manure at different incubation time.

3.2.2. Available ammonium

Ammonium nitrogen is considered one of the measurements for soil nitrogen availability to plants. The results showed that the addition of different organic materials caused a significant difference in extracted NH_4^+ nitrogen content. At zero time, the available ammonium was relatively high, as much as incubation time, increased the NH_4^+ content tend to decrease, these results point out the added manures increased available NH_4^+. Extracted ammonium increased immediately after manure applications, which was also found by Whalen et al., (2000), who reported a concentration of 1100 mg kg^{-1} ammonium following manure application. Microbes quickly degrade simple organic compounds such as simple carbohydrate and amino acids in a short time. Therefore, soil available ammonium increases (Cai et al., 2019).

Over time, ammonium content decreased up to 60 days. This reduction was mainly due to the nitrification process where ammonium is converted to NO_3^- as stated by (Hampel et al., 2018). The NH_4 content was high due to CM addition results showed by (Nyawade et al., 2019) had the same manner when organic matter was added to cultivated soil. This may be due to dissolved organic matter, which increased the ammonium content (Haroon et al., 2018). These findings are consistent with those of Preusch et al., (2002); they found that the NH_4-N concentration extracted from soil treated with fresh manure declined during the first 30 days of incubation, but that there was a rapid increase in NO3-N concentrations. NH_4-N immobilization by soil microbes and/or N losses such as ammonia volatilization might also be responsible for the rapid decrease in net N mineralization after 20 days of incubation (Wang et al., 2018). The reduction in ammonium content may also be attributed to wide C/N, as stated by (Kirckner et al., 1993). Also (Sharifnia et al., 2016) noted that the retention of ammonium into the negative charge of clay might be attributed to lower NH_4^+ content.

The maximum NH_4^+ content was observed at 90 days, with the exception of CMC and CMB (Figure 9). This seconded increase may be explained by the decomposition of the resistant material of CM and CMSAE such as protein, amino acids hemicelluloses (Narita et al., 2005) and produce NH_4^+.

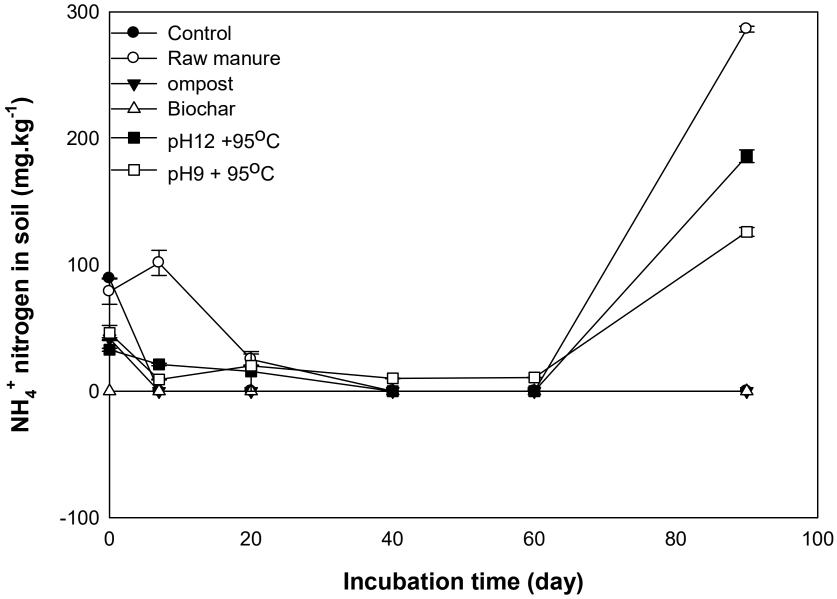

Figure 9. Available NH_4^+ mg kg^{-1} as affected by different organic amendments derived from cow manure at different incubation time.

3.3. Changes in microbial biomass carbon (MBC)

Microbial biomass carbon considered as a measurement for living component mass of the soil organic matter. The microbial biomass carbon plays a huge role in availability and transformation of soil organic matter and plants nutrients. (Figure 10) shows the effect organic materials and incubation time on microbial biomass carbon for 90 days. Most treatments showed increase of MBC at 7 days with exception of CMB and CMSAE (pH 9 and 95^{o}C). The CMSAE produced at pH12 showed the highest MBC at 7 days of incubation, the value was 11481±61 mg kg^{-1}. The MBC for control and CMB were the lowest as compare to other treatments.

The increase of MBC indicated the presence of inorganic nitrogen and consequently high microbial activity. Studies by Jara-Samaniego et al., (2017) showed the positive effect of organic materials addition which led to increase the MBC. The soil microorganisms largely depend on easy degradable materials to increase their numbers and decompose more organic material. After 20 days of incubation MBC content decline, this probably due to consuming soluble organic carbon by microbes. The CM reported to have amino-sugars, amino-acids, proteins and short-chain organic acids (Morvan and Nicolardot, 2009) that were reported to decompose fast in soil (Glanville et al., 2012 and Kögel-Knabner, 2002). The lowest Biochar MBC might be attributed to preparation temperature caused loss of many organic compounds that are consumed by microorganisms (Jindo et al., 2012).

The second stage of MBC have also been observed at 60 days it's also found at in other studies on sheep dung decomposition, and it is proposed that in the first peak of CO_2 emission (high MBC) is due to the decomposition of labile C from soil and easily degradable dung fractions, while in the second phase, the decomposers attack more recalcitrant material (Ma et al., 2013) so the MBC increased.

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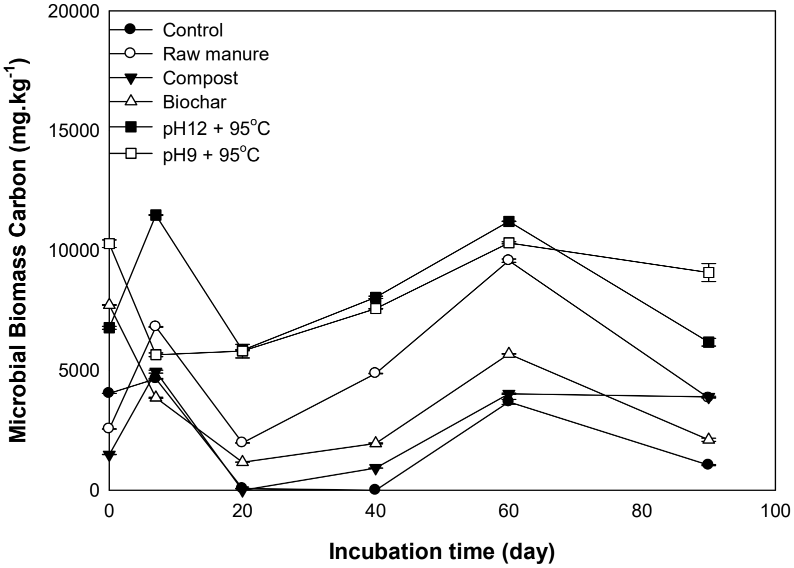

Figure 10. Extracted potassium sulfate microbial biomass carbon from soil as affected by different organic amendments derived from cow manure at different incubation time.

3.4. Changes in CO_2 efflux and cumulative CO_2

The maximum CO_2 efflux values were observed at the first seven days, after 20 days the values of the CO_2 efflux was decreased with increasing incubation time. The high values of CO_2 flux at start may be explained by addition of organic manures provide the soil with variety of essential nutrient for soil microorganisms activity and growth. The soil CO_2 efflux ranged from 0.231- 0.001 g kg^{-1} soil. The high CO_2 fluxes were observed in the CM it was 0.231 g kg^{-1} soil (Figure 11). The organic manures added the high soil pH expected to decrease for instance, although between 0 to 7 days no soil samples were extracted. It's known that the high $CaCO_3$ conditions and high pH conditions inhibits some of the neutral pH microorganisms growth (Rietz and Haynes, 2003). The addition of organic material in the short term provides additional substrates for the soil microorganisms and resulted in an increase in microorganism's activity. This substrate may also relieve osmotic and pH stress on the soil microorganisms, while improving soil chemical conditions (Chander et al., 1994).

The results reveal that the CMSAEs significantly increased the accumulated CO_2 efflux (Figure 12). The highest cumulative CO_2 flux values of CM almost similar 3.28 g kg $soil^{-1}$, while the CMB showed the smallest flux value was 2.7 g kg soil-1. Our study thus clearly shows that the CMSAE didn't decrease the accumulative CO_2 flux.

The low CO_2 flux rate possibly related to the low levels of MBC from 20 to 40 days. The previous studies found that the microbial population densities in the initial days at organic matter addition were higher as compared to the final days (Martin-Olmedo and Rees, 1999). It was observed that the CMB and CMC were proved to have less CO_2 efflux as compared to the CMSAE this is properly due to the high C/N ratio of these materials as well illustrated in literature (Cayuela et al., 2013; Huang et al., 2004). It was very clear that the CMSAEs efflux values were higher as compared to the other organic materials including the CM which expected to have low CO_2 flux, the reason behind this is mainly because the row manure was collected from the barn floor which is differ than that used to prepare CMSAE (fresh manure), furthermore the preparation temperature at ammonia string process may be attributed to promote the CMSAEs decomposition when added to the soil. The increase in MBC of soil treated with different organic material enhanced microbial activity.

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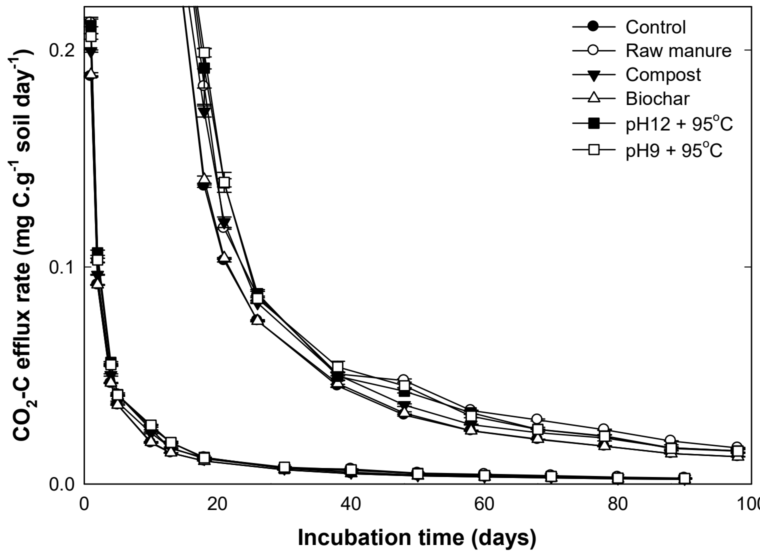

Figure 1. CO_2 efflux rate (mg C/g soil/day) as affected by different organic amendments derived from cow manure at different incubation time.

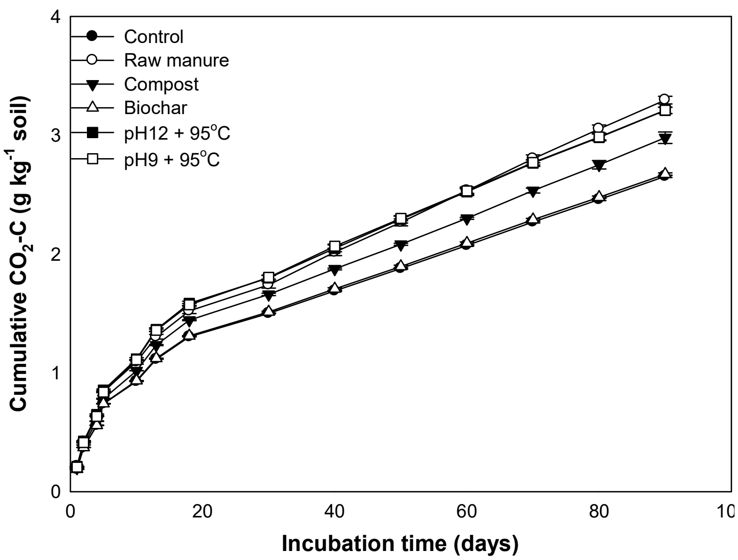

Figure 2. Cumulative CO_2 efflux (g/kg soil) as affected by different organic amendments derived from cow manure at different incubation time.

4. Conclusions

In this experiment, a calcareous sandy loam soil was treated with different organic amendments derived from cow manure for 90 days. The results showed that the addition of different organic materials caused an increase in the available NO_3^- nitrogen contents after 20 days of incubation time and decreased the available NH_4^+ concentration after seven days from the incubation start. MBC was significantly increased ($p \leq 0.05$) as the incubation time increased. The cow CMSAE produced at pH12 and 95°C, CM and CMC showed the highest MBC; these values accounted for 11481 ±61 and 6815 ±14 mg kg$^{-1,}$ respectively. At the same time, control and CMB reached their lowest MBC values after seven days.

Furthermore, the soil CO_2 efflux ranged from 0.231- 0.001 g kg^{-1} soil. The high CO_2 efflux was observed in the raw CM and CMSAEs of pH12 and T95°C; the values accounted

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for 0.231 and 0.211, respectively. Moreover, the results reveal that the CMSAEs at pH 12 and pH 9 with 95ºC decreased the accumulated CO_2 efflux, while the CMB showed the smallest efflux value (19.8). Our study thus clearly indicates that the CMSAE didn't reduce the accumulative CO_2 efflux. Finally, the organic materials significantly affected the soil micronutrient cations (Fe, Cu, Zn and Mn). The contents of available micronutrients were high at the beginning of incubation then decreased over time.

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