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**Impact of biochar addition to soil on greenhouse gas emissions following pig manure application**

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## **ABSTRACT**

The application of biochar produced from wood and crop residues, such as sawdust, straw, sugar bagasse and rice hulls, to highly weathered soils under tropical conditions has been shown to influence soil greenhouse gas (GHG) emissions. However, there is a lack of data concerning GHG emissions from soils amended with biochar derived from manure, and from soils outside tropical and subtropical regions. The objective of this study was to quantify the effect on emissions of carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) following the addition, at a rate of 18 t ha<sup>-1</sup>, of two different types of biochar to an Irish tillage soil. A soil

column experiment was designed to compare three treatments (n=8): (1) non-amended soil (2) soil mixed with biochar derived from the separated solid fraction of anaerobically digested pig manure and (3) soil mixed with biochar derived from Sitka Spruce (*Picea sitchensis*). The soil columns were incubated at 10 °C and 75 % relative humidity, and leached with 80 mL distilled water, twice per week. Following 10 weeks of incubation, pig manure, equivalent to 170 kg nitrogen ha<sup>-1</sup> and 36 kg phosphorus ha<sup>-1</sup>, was applied to half of the columns in each treatment (n=4). Gaseous emissions were analysed for 28 days following manure application. Biochar addition to the soil increased N<sub>2</sub>O emissions in the pig manure-amended column, most likely as a result of increased denitrification caused by higher water filled pore space and organic carbon (C) contents. Biochar addition to soil also increased CO<sub>2</sub> emissions. This was caused by increased rates of C mineralisation in these columns, either due to mineralisation of the labile C added with the biochar, or through increased mineralisation of the soil organic matter.

Keywords: biochar, pig manure, soil, nitrous oxide, carbon dioxide, methane

## 1. Introduction

Increasing amounts of greenhouse gases (GHG) in the atmosphere are causing changes in world climate (IPCC, 2007). The production of biochar and renewable energy through pyrolysis is seen as one prospective strategy, which could result in reduced global carbon dioxide (CO<sub>2</sub>) concentrations. Roberts et al. (2010) found negative values for the net GHG emissions following the pyrolysis of corn stover and yard waste and the application of the biochar to soil (-864 and -885 kg CO<sub>2</sub> equivalent emissions reduction per tonne dry feedstock, respectively), compared with ethanol production from the corn stover and compost production from the yard waste. The majority (62 - 66 %) of these GHG emission reductions were realised through C sequestration within the soil. Gaunt and Lehmann (2008) found that when biochar was applied to agricultural land, the potential reduction in GHG emissions was between 2 and 5 times greater than when it was burned to offset fossil fuel usage. These potential reductions in GHG emissions following biochar application to soil are primarily due to the sequestration of carbon (C) within the soil (Gaunt and Lehmann, 2008; Roberts et al., 2010), with other potential reductions due to savings in fertiliser requirement, reductions in fossil fuel usage, and reductions in soil emissions (Gaunt and Lehmann, 2008).

In Ireland, recent landspreading legislation (Nitrates Directive, 91/676/EEC) has limited the magnitude, timing and placement of organic manure to land. Currently, the amount of livestock manure that can be applied to land has been limited to 170 kg of nitrogen (N) per hectare per yr. The land available for landspreading will further be restricted, starting in 2013, and culminating in 2017, when land spreading of pig manure can no longer exceed the crop's phosphorus (P) requirements for growth (S.I. 610 of 2010). The implication of this will be that an additional ~50 % land area will be required for manure application than is the case in 2012,

70 thereby increasing the cost of manure handling. The resulting increase in manure transport costs  
71 for farmers, along with the potential of surface and groundwater pollution from the  
72 landspreading of manure, has resulted in the need to examine practical solutions for pig manure  
73 treatment. The production of biochar from pig manure may be a solution for some farmers living  
74 in very pig dense regions.

75 Biochar application to agricultural soils has the potential for long-term C sequestration,  
76 due to the stability of biochar in soil environments. Biochar is composed of a range of different  
77 forms of C, from recalcitrant aromatic ring structures, which can persist in soil for millennia, to  
78 more easily degradable aliphatic and oxidised C structures, which mineralise to CO<sub>2</sub> more  
79 rapidly through degradation by biotic and abiotic oxidation (Schmidt and Noack, 2000, Cheng et  
80 al., 2006; Liang et al., 2008). Increased CO<sub>2</sub> emissions, following biochar addition to soil, have  
81 been attributed to increased mineralisation rates in the biochar-amended soil due to (1)  
82 mineralisation of applied biochar C (Major et al., 2010a; Smith et al., 2010) or (2) enhanced soil  
83 organic C mineralisation (Rogovska et al., 2011). In a two-year experiment, Major et al. (2010a)  
84 found that only 3 % of applied biochar C was lost as CO<sub>2</sub>, with 75 % of the biochar  
85 mineralisation occurring in the first year, which suggested that the stimulatory effects were short-  
86 term. The stability and resistance of the biochar against oxidation is known to vary depending on  
87 the feedstock and pyrolysis procedures and temperatures (Schmidt and Noack, 2000; Liang et al.,  
88 2008). Mukherjee and Zimmerman (2013) showed that the loss of biochar C, N and P to leaching  
89 water correlated with biochar volatile matter content and was greater from biochar made at lower  
90 temperatures than from high temperature biochar. Rogovska et al. (2011) found accelerated soil  
91 organic C mineralisation with biochar addition to soil, and hypothesised that the increases may  
92 be due to (1) increased aerobic microbial activity as a result of higher soil aeration due to the

lower bulk density of the biochar-amended soil and (2) enhanced microbial colonisation, causing accelerated decomposition of organic compounds.

The long-term effects of biochar can be seen in fertile Anthrosols found around the Amazonian basin. These soils have very high biochar contents due to the charring of forest wood by the indigenous people thousands of years ago (Lehmann et al., 2003). Nutrient leaching has been shown to be minimal from these soils despite their high nutrient content, which has resulted in high soil fertility in contrast to the low fertility adjacent acid soils. Biochar potentially has a superior ability to retain nutrients in comparison to other forms of organic matter (OM) (Lehmann, 2007). Previous experiments have shown that the ability of biochar to retain nutrients in the soil can influence nutrient leaching (Novak et al., 2009; Laird et al., 2010a), nutrient availability (Laird et al. (2010b) and plant growth rates (Asai et al., 2009; Major et al., 2010b).

Biochar addition to soil has been shown to influence the concentrations of inorganic-N, organic C and oxygen ( $O_2$ ) in the soil and, hence, the emissions of nitrous oxide ( $N_2O$ ) from the soil (Clough et al., 2010; Singh et al., 2010). Nitrous oxide has a global warming potential estimated as being 296 times that of  $CO_2$  (IPCC, 2007). Emissions of  $N_2O$  have been reported to either increase (Clough et al., 2010) or decrease (Singh et al., 2010), following biochar application to soil. Singh et al. (2010) found that wood biochar adsorbed ammonium ( $NH_4$ ) in a soil, thereby reducing the pool of inorganic-N for the  $N_2O$ -producing mechanisms. Clough et al. (2010) attributed higher  $N_2O$  emissions from biochar-amended soil to greater nitrite ( $NO_2$ ) concentrations brought about by nitrification inhibitors on biochar, which slowed nitrate ( $NO_3$ ) formation. Yanai et al. (2007) found an 89 % suppression of  $N_2O$  emissions at 73-78 % soil water filled pore space (WFPS) due to the adsorption of water by biochar. However, the same study found a 51 % increase in  $N_2O$  emissions at 83 % WFPS. The authors attributed this

increase to better soil aeration and the stimulation of N<sub>2</sub>O-producing activity due to the neutralisation of soil pH. Studies have shown that biochar addition to soil may also influence methane (CH<sub>4</sub>) emissions, which have a global warming potential estimated as being 23 times that of CO<sub>2</sub> (IPCC, 2007). Soil CH<sub>4</sub> emissions have been reported to either increase (Zhang et al., 2010) or decrease (Rondon et al., 2005), following biochar addition. Rondon et al. (2005) credited a near complete suppression of CH<sub>4</sub>, following biochar addition to soil, to a reduction in anaerobic conditions and increased soil aeration. However, in a field experiment in a rice paddy, Zhang et al. (2010) found that soil amended with biochar at 40 tonne ha<sup>-1</sup> increased CH<sub>4</sub> emissions by 34 % when N fertiliser was applied, and by 41 % without N fertilization.

There are few studies concerning GHG emissions from biochar from feedstocks other than wood, and data from soils outside tropical and subtropical regions are also required (Verheijen et al., 2010). Therefore, the objectives of this study were to investigate CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions from Irish tillage soil, amended with biochar derived from either pig manure or wood (Sitka Spruce), with and without fertilisation with pig manure.

## **2. Materials and Methods**

### **2.1. Soil Column Preparation**

The soil used in this study was an Acid Brown Earth (Regan et al., 2010) collected to a depth of 0.2 m from a tillage farm near Fermoy, County Cork. The 0.2m depth was chosen as this is an average plough depth for tillage soil. The soil was air dried, passed through a 2 mm sieve, and mixed to ensure homogeneity. Two types of biochar were used for this study: pig manure biochar and wood biochar. Pig manure biochar was produced from the solid fraction of pig manure after anaerobic digestion, which had been separated using a decanter centrifuge. The

separated manure was then mixed with Sitka Spruce (*Picea sitchensis*) sawdust (at a 4:1 ratio by wet weight), dried, and subjected to slow pyrolysis in a custom-built laboratory pyrolysis reactor operated at 600 °C, with a residence time of 15 minutes. After pyrolysis, the biochar was moved to a cooling area of the reactor before removal from the reactor. Sawdust was added to the manure as separation, drying and pyrolysis of pig manure alone is not economically viable, and does not produce a positive energy balance (Troy et al., unpublished results). Wood biochar was produced by slow pyrolysis of Sitka Spruce (*Picea sitchensis*) wood in a large-scale pyrolysis reactor at 600 °C and a residence time of 15 minutes. Both biochars were ground to pass through a 2 mm sieve. The characteristics of the biochars are given in Table 1.

Soil columns were constructed using 0.3 m-deep and 0.104 m-internal diameter pipes, which were sealed at the base with perforated PVC end-caps to ensure that the soil remained free-draining. Pea gravel from a commercial supplier, manually sieved to a particle size of between 5 and 10 mm, was placed at the base of each column to a depth of 0.05 m. The three treatments (n=8) examined in this study were: (1) non-amended soil (the study control) (2) soil mixed with pig manure biochar (PM600) and (3) of soil mixed with wood biochar (W600). Batches of air-dried sieved soil (<2 mm) were mixed with sieved biochar (<2 mm) at biochar application rates equivalent to 18 t ha<sup>-1</sup> to a soil depth of 0.2 m. The unamended columns contained 1868 g of soil (dry weight), while the biochar-amended columns contained 1868 g of soil and 15.3 g biochar (dry weight). Distilled water was added to bring the mixtures to a water content (WC) of approximately 26 % (the WC of the soil in the field at the time of sampling), and the mixture was thoroughly mixed by hand. The soil was packed in 0.05-m-depth increments (with a dry bulk density of 1.1 g cm<sup>-1</sup> equivalent to field conditions) to ensure uniform packing of soil, to a total depth of 0.2 m. The soil columns were incubated at a constant temperature (10



°C) and relative humidity (75 %), based on typical climatic conditions in Ireland (Walsh, 2012). All columns were leached with 160 mL of distilled water, applied twice weekly in two 80-mL doses over two hours. This is equivalent to 980 mm of rainfall  $\text{yr}^{-1}$ , which is in the mid-range of average annual rainfall amounts in Ireland (Walsh, 2012). Following 10 weeks of incubation, pig manure, collected from an integrated pig farm in Fermoy, Co. Cork, was applied to the surface of four columns of each treatment at a rate equivalent to 170 kg N  $\text{ha}^{-1}$ . This application rate corresponds with the general land spreading limit of 170 kg N  $\text{ha}^{-1} \text{yr}^{-1}$  from livestock manure imposed by the Irish Statutory Instrument (S.I.) 610 of 2010. The 10-week lag time was applied before manure application to avoid a burst in microbial activity, associated with drying and re-wetting of soil during the construction of the columns. Drying and re-wetting of soil has been shown to cause a burst in microbial activity and a sharp increase in C and N mineralisation (Bengtsson et al., 2003; Borken and Matzner, 2009), which would have resulted in artificially high emissions. The characteristics of the pig manure are given in Table 2. The treatments which received pig manure were then known as Control+PM, PM600+PM and W600+PM.

## **2.2. Gas Sampling and Analysis**

Gas analysis began following 10 weeks of incubation (after pig manure application) and continued for 28 days, with samples being taken on Days 1, 2, 3, 4, 5, 6, 7, 9, 11, 13, 15, 19, 24 and 28 following pig manure application. The emissions from columns which did not receive pig manure were also sampled on Days 1, 4, 7, 11, 15, 19, 24 and 28. The 10-week lag period before gas sampling began allowed for the effect of drying and re-wetting of the soil on the gaseous emissions to be negated. Large rubber stoppers, placed on top of each column, sealed the headspace (0.08 m) above the soil, which allowed gas samples to be collected from this

headspace *via* rubber septum stoppers, located at the side of each column. As part of the ongoing watering during the gas analysis, each column was leached with 80 mL of distilled water on Days 4, 8, 11, 15, 18, 22 and 25. On days when the columns received water, gas samples were taken 1 hour after water application.

Gas was sampled after Singh et al. (2010): ten minutes before sampling, the headspace in the column above the soil was fanned to remove accumulated gases. Then, just before sealing the top of the column with the rubber stopper, the headspace was again fanned gently for 15 seconds and a gas sample (20 ml) was withdrawn from the headspace. This sample represented the zero minute sampling time. Subsequent to sealing the headspace, gas samples were extracted from the enclosed headspace 5, 10 and 20 minutes after the headspace was sealed. These gas samples were immediately injected into pre-evacuated 6-mL Exetainer vials (Labco, Buckinghamshire, UK). This allowed the vials to be over pressurised, removing the possibility of contamination of the samples with external air.

Nitrous oxide and CH<sub>4</sub> were measured in the samples collected at sampling times 0, 10 and 20 minutes using a Shimadzu Gas Chromatographer (GC-2014) (Shimadzu Scientific Instruments, Maryland, USA). Carbon dioxide was measured in the samples collected at sampling times 0, 5 and 10 minutes using a Agilent Gas Chromatograph System (7890A) (Agilent Technologies, California, USA). All GHGs were measured using linear regression. Fluxes were calculated from the change in headspace concentration over measured period using:

$$\frac{dGas}{dt} * 10^{-6} * \frac{V_{chamber} * p * 100 * MW}{R * T} * 10^6 * \frac{1}{A}$$

where:  $dGas/dt$  is measured in ppm h<sup>-1</sup> to get the change in concentration over time;  
 $V_{chamber}$  is the volume of the chamber used;  $p$  is atmospheric pressure;  $MW$  is the molecular

weight;  $R$  is a gas constant,  $8314 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $T$  is temperature in Kelvin; and  $A$  is the area of the chamber.

Each gas was extrapolated over a hectare and converted to the following:  $\text{kg CO}_2\text{-C ha}^{-1} \text{ h}^{-1}$ ,  $\text{g CH}_4\text{-C ha}^{-1} \text{ h}^{-1}$ ,  $\text{g N}_2\text{O-N ha}^{-1} \text{ h}^{-1}$ , similar to Collins et al. (2011) and Zhang et al. (2010). Negative fluxes of gases indicated uptake of gas by soil and positive fluxes indicated net emissions from the soil. Cumulative fluxes were determined by multiplying each gas flux by the interval between sampling days. These cumulative fluxes were then summed to find the cumulative emissions of each gas over the 28-day sampling period.

### 2.3. Soil and Leachate Analyses

Extra soil columns ( $n=4$ ) were set up so that they could be destructively sampled after 10 weeks of incubation, just before the beginning of the gas analysis. Analyses were conducted at depth increments of 0-0.05, 0.05-0.1, and 0.1–0.2 m below the soil surface. The soil from each depth increment was air-dried and sieved to a particle size of 2 mm, or less, before analyses. The OM content of the soil was determined using the loss on ignition test (B.S.1377-3; BSI, 1990). Soil total C and total N were determined by high temperature combustion using a LECO Truspec CN analyser (LECO Corporation, St. Joseph, MI, USA). Soil pH was determined using a pH probe (WTW, Weilheim, Germany) at a 2:1 ratio of deionised water-to-soil. Bulk density ( $\rho_b$ ) and total porosity ( $n$ ) were calculated according to Haney and Haney (2010). Water-filled pore space was estimated from WC, bulk density, and total porosity in accordance with Haney and Haney (2010):

$$WFPS = \frac{WC * \rho_b}{n}$$

A sample of leached water was collected from the base of each column once per week during the 28-day gas sampling period. This leachate sample was analysed for total organic C (TOC) and  $\text{NO}_3$  to help interpret the C and N cycling processes occurring in the soil columns. Unfiltered leachate samples were analysed for TOC using a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Limited, Cork, Ireland). Sub-samples of leachate were passed through a  $0.45\ \mu\text{m}$  filter and analysed colorimetrically for total oxidised N and  $\text{NO}_2$  using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Vantaa, Finland). Nitrate was calculated by subtracting  $\text{NO}_2$  from total oxidised N.

#### **2.4. Statistical Analysis**

Emissions data were analyzed using the Statistical Analyses System (SAS Institute, 2004) with each column as the experimental unit. For all analyses, significance was given as  $p < 0.05$ . The hourly flux of  $\text{N}_2\text{O-N}$ ,  $\text{CO}_2\text{-C}$ , and  $\text{CH}_4\text{-C}$  were analysed as repeated measures using a repeated measures ANOVA using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were:  $\text{N}_2\text{O-N}$ ,  $\text{CO}_2\text{-C}$ , and  $\text{CH}_4\text{-C}$ . For all the above analyses, the fixed effects were: treatment, sampling day and column. Sampling day was the repeated measure. Comparison of cumulative emissions of  $\text{N}_2\text{O-N}$ ,  $\text{CO}_2\text{-C}$ , and  $\text{CH}_4\text{-C}$  over the 28-day sampling period was performed using the MIXED procedure in SAS.  $\text{N}_2\text{O-N}$ ,  $\text{CO}_2\text{-C}$ , and  $\text{CH}_4\text{-C}$  were the dependent variables. Treatment was included as a fixed effect.

Soil data were also analyzed using the Statistical Analyses System (SAS Institute, 2004) with each column as the experimental unit. pH, WFPS, OM, N and C contents, and C:N ratio were analysed as repeated measures using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were: pH, WFPS, OM, N and C

contents, and C:N ratio. For all the above analyses, the fixed effects were: treatment, depth and column. Depth was the repeated measure. Statistical significance was given as  $p < 0.05$ .

### **3. Results**

#### **3.1 Soil Characteristics**

The characteristics of the soil and soil/biochar mixtures, after 10 weeks of incubation, are given in Table 3. The biochar-amended soils had higher C and OM contents than the Control. There was an increase of between 4 and 7 % in the WFPS of the biochar-amended soils compared with the Control. The N content of the PM600 soil was higher than that of the Control or W600 soils due to the high N content of the applied pig manure biochar ( $p < 0.05$ ). There was no difference in pH between soil treatments ( $p > 0.05$ ).

#### **3.2. Nitrous Oxide Emissions**

The 28-day  $\text{N}_2\text{O}$ -N flux, illustrated in Figure 1a, remained low from the non-manure-amended treatments throughout the study ( $-0.12$  to  $0.13 \text{ g N}_2\text{O-N ha}^{-1} \text{ hour}^{-1}$ ). The addition of biochar to these treatments had no effect on  $\text{N}_2\text{O}$ -N emissions on any particular sampling day ( $p > 0.05$ ). Similarly, there was no difference between non-manure-amended treatments in their cumulative emissions over 28 days ( $p > 0.05$ ) (Figure 2a). The addition of pig manure to the soil influenced  $\text{N}_2\text{O}$ -N emissions: one week following pig manure application, there was a significant increase in  $\text{N}_2\text{O}$ -N emissions from all the manure-amended treatments. The greatest emissions occurred 11 days after manure application ( $0.89$ ,  $1.02$  and  $0.99 \text{ g N}_2\text{O-N ha}^{-1} \text{ hour}^{-1}$  for Control+PM, PM600+PM and W600+PM, respectively). This compares to emissions of  $0.05$ ,  $0.07$  and  $0.07 \text{ g N}_2\text{O-N ha}^{-1} \text{ hour}^{-1}$  for Control, PM600 and W600, respectively, on Day 11. The

N<sub>2</sub>O-N emissions from the manure-amended treatments decreased rapidly from their peak on Day 11 and returned to the level of the treatments which did not receive manure by Day 19. From Day 19 until the end of the study, the N<sub>2</sub>O-N emissions were similar for all treatments ( $p>0.05$ ).

The patterns of N<sub>2</sub>O-N emissions were similar for the three manure-amended treatments. There was no difference between N<sub>2</sub>O-N emissions from PM600+PM and W600+PM compared with Control+PM on any sampling day ( $p>0.05$ ). This is due to a high variability between columns in the same treatment. However, over the 28-day sampling period, the cumulative emissions from PM600+PM were significantly higher compared with Control+PM ( $p<0.05$ ), while W600+PM also tended to have higher N<sub>2</sub>O-N emissions than Control+PM ( $p<0.1$ ). Cumulative N<sub>2</sub>O-N emissions from PM600+PM and W600+PM were 79 and 68 % higher, respectively, than Control+PM. Cumulative emissions from W600+PM and PM600+PM were similar ( $p=1.0$ ) (Figure 2a).

Figure 3 shows the amount of NO<sub>3</sub> leached from each treatment during the 28-day gas sampling period. The quantity of NO<sub>3</sub> leached from the soils was significantly lower from W600 and PM600 than the Control ( $p<0.05$ ), and from W600+PM and PM600+PM compared with Control+PM ( $p<0.001$ ). The addition of pig manure did not significantly increase the amount NO<sub>3</sub> leached from any of the biochar-amended soils ( $p>0.05$ ). However, the quantity of NO<sub>3</sub> increased significantly from Control+PM compared with the Control ( $p<0.01$ ).

### **3.3. Carbon Dioxide Emissions**

The CO<sub>2</sub>-C emissions, shown in Figure 1b, remained low from the non-manure-amended treatments throughout the study duration (0.03 to 0.54 kg CO<sub>2</sub>-C ha<sup>-1</sup> hour<sup>-1</sup>). Soil CO<sub>2</sub>-C fluxes

from the manure-amended treatments were significantly higher than the non-manure-amended treatments on the day of manure application (Day 1) ( $p < 0.001$ ), and on Day 1 were 3.5, 3.5 and 4.0 kg CO<sub>2</sub>-C ha<sup>-1</sup> hour<sup>-1</sup> for Control+PM, PM600+PM and W600+PM, respectively. However, from Day 4 until the end of the study, there was no significant difference between any treatment ( $p < 0.05$ ). The manure-amended treatments had higher cumulative emissions than the treatments which did not receive manure, largely due to the high CO<sub>2</sub>-C emissions on the day of manure application (Figure 2b).

The addition of biochar to the non-manure-amended treatments had no effect on CO<sub>2</sub>-C emissions on any particular sampling day ( $p > 0.05$ ). However, the biochar-amended treatments had higher cumulative emissions over the 28-day sampling period ( $p < 0.1$ ) (Figure 2b), with 94 and 99 kg ha<sup>-1</sup> more CO<sub>2</sub>-C emitted from PM600 and W600, respectively, compared with the Control. This represents an increase of 87 and 91 % in cumulative emissions of CO<sub>2</sub>-C over the sampling period for PM600 and W600, respectively, compared with the Control. The addition of biochar to the manure-amended treatments also had no effect on CO<sub>2</sub>-C emissions on any particular sampling day ( $p > 0.05$ ). However, W600+PM had 45 % higher cumulative emissions than Control+PM over the 28-day study period ( $p < 0.1$ ). PM600+PM also had 31 % higher cumulative emissions than Control+PM, but the difference was not significant ( $p = 0.39$ ). Cumulative emissions from W600+PM and PM600+PM were similar ( $p = 0.92$ ) (Figure 2b).

Figure 4 shows the amount of TOC leached from each treatment during the 28-day gas sampling period. Leaching of TOC from W600, with and without manure addition, was significantly lower than the Control ( $p < 0.001$ ), despite the fact that the C content of the W600 soil was higher than that of the Control at all depths (Table 3). However, leaching of TOC from PM600 was significantly higher than both the Control and W600, irrespective of whether or not

manure was applied. The addition of pig manure did not increase TOC leaching in any of the treatments ( $p>0.05$ ).

### **3.4. Methane Emissions**

Similar to the  $\text{CO}_2\text{-C}$  fluxes, the  $\text{CH}_4\text{-C}$  emissions from the pig manure-amended treatments were high on the day of manure application ( $108 - 115 \text{ g CH}_4\text{-C ha}^{-1} \text{ hour}^{-1}$ ), but quickly reduced to the levels of the non-pig manure-amended treatments (Figure 1c). From Day 4 until the end of the study, there was no significant difference between the treatments which received manure and those which did not. Emissions of  $\text{CH}_4\text{-C}$  were low throughout the study, apart from Days 1 and 2 for the manure-amended treatments. Excluding these, the flux of  $\text{CH}_4\text{-C}$  was between  $-1.6$  and  $0.9 \text{ g ha}^{-1} \text{ hour}^{-1}$  for every treatment on every sampling day. The pig manure-amended treatments had significantly greater cumulative emissions than the non-pig manure-amended treatments, due to the high  $\text{CH}_4\text{-C}$  emissions on the day of manure application ( $p<0.0001$ ) (Figure 2c).

## **4. Discussion**

### **4.1. Nitrous Oxide Emissions**

Nitrous oxide is emitted during the microbial processes of nitrification and denitrification (Bateman and Baggs, 2005; Rivett et al., 2008). The supply of  $\text{O}_2$  dictates the contribution of each process to the amount of  $\text{N}_2\text{O}$  emissions (Brady and Weil, 1996; Bateman and Baggs, 2005; Rivett et al., 2008). The rate of denitrification is also influenced by the soil inorganic-N concentrations (especially  $\text{NO}_3$ ) and the presence of dissolved organic C in the soil (Dobbie and Smith, 2001; Rivett et al., 2008). Mineralisation of the organic-N in the pig manure resulted in an increase in inorganic N concentrations in the soil after pig manure application. This increase in



inorganic N concentrations and the increase in organic C concentration from the manure resulted in the peak in N<sub>2</sub>O emissions observed in the manure-amended treatments (Figure 1a).

There was no difference in N<sub>2</sub>O emissions between the biochar-amended treatments and the Control for the treatments that did not receive pig manure. Emissions of N<sub>2</sub>O were low from these columns, indicating low denitrification rates, due to the lack of available inorganic N. However, when pig manure was applied to the soil, the cumulative emissions from biochar-amended treatments tended to have higher N<sub>2</sub>O emissions than the Control. The quantity of NO<sub>3</sub> leached from the soils amended with biochar was also lower than the Control soil (Figure 3). The addition of biochar to the soil resulted in 46 -50 % reductions in NO<sub>3</sub>-N leaching in the manure-amended soils, and reductions of 26 – 30 % in the soils which did not receive manure. This result, coupled with the higher N<sub>2</sub>O emissions, indicated the occurrence of higher denitrification rates in the biochar-amended treatments. The increase in denitrification can be attributed to (1) higher WFPS and (2) greater organic C availability in the biochar-amended soils. Organic C may be used as an electron donor during denitrification, with the oxygen lost during the denitrification process being used to form CO<sub>2</sub> (Rivett et al., 2008). In a study measuring N<sub>2</sub>O losses through denitrification from intact soil cores fertilised with NO<sub>3</sub>, Jahangir et al. (2012) found N<sub>2</sub>O emissions were significantly increased with the addition of dissolved organic C to the soil. They suggested that adding C sources to the subsoil could increase NO<sub>3</sub> depletion via denitrification (Jahangir et al., 2012). The greater WFPS in the biochar-amended columns may also have resulted in increased denitrification, by causing the development of anaerobic zones within the soil, resulting in reduced aerobic microbial activity (Brady and Weil, 1996; Porporato et al., 2003; Rivett et al., 2008). Denitrification has been shown to be sensitive to soil WFPS. In

an incubation study, using arable soil fertilised with ammonium nitrate, Dobbie and Smith (2001) found a 30-fold increase in N<sub>2</sub>O emissions by increasing the WFPS from 60 to 80 %.

Despite the increase in denitrification with biochar addition to the soil, the overall amount of N lost through N<sub>2</sub>O-N emissions is low (<10 % for the manure-amended treatments, <1 % for the non-manure-amended treatments) compared with N lost through NO<sub>3</sub>-N leaching. However, biochar addition may also have increased the rate of complete denitrification to N<sub>2</sub> within the soil, although this was not studied in this experiment. Carbon availability in soil has been shown previously to promote the reduction of N<sub>2</sub>O to N<sub>2</sub> (Miller et al., 2009). Jahangir et al. (2012) found that the N<sub>2</sub> flux from the top 0.10 m of a soil fertilised with NO<sub>3</sub> was increased by 78 % with the addition of dissolved organic C to the soil. The present study is a laboratory-based study and results may differ to those in the field. The growth of plants in the soil could have a large impact on N<sub>2</sub>O emissions, with N uptake by the plants resulting in a reduction in NO<sub>3</sub> available for denitrification.

## **4.2. Carbon Dioxide Emissions**

The manure-amended treatments had higher cumulative emissions than the treatments which did not receive manure. This was largely due to the significantly higher emissions of CO<sub>2</sub> on the first sampling day. The addition of manure slurries to soil has been shown to cause a short-lived spike in microbial activity and CO<sub>2</sub> emissions (Dumale et al., 2009; Collins et al, 2011). The amount of pig manure C mineralised during the sampling period was estimated as the difference between the cumulative CO<sub>2</sub>-C emissions from the manure-amended and non-manure-amended treatments (Rogovska et al., 2011). Between 150 and 180 kg ha<sup>-1</sup> of the total CO<sub>2</sub>-C emissions were caused by the mineralisation of C in the manure, with no significant difference

between treatments. This corresponds to 44 - 54 % of the total applied manure C being mineralised in the 28 days after application, with the vast majority of this mineralisation occurring in the first day. In a column study investigating GHG emissions from pig manure, Dendooven et al. (1998) reported that 62 % of the C applied in the pig slurry was mineralized within 28 days, if no priming effect was assumed.

The soil CO<sub>2</sub>-C emissions from the non-manure-amended treatments show the decomposition of the soil (and biochar) OM and microbial respiration (Collins et al., 2011). The trend for higher CO<sub>2</sub>-C emissions from biochar-amended soils than from non-biochar-amended soils is similar to the results of other studies (Major et al., 2010a; Smith et al., 2010; Rogovska et al., 2011). In the current study, the increase in CO<sub>2</sub>-C emissions due to the addition of biochar may be due to mineralisation of labile C added with the biochar (Cross and Sohi, 2011), enhanced mineralisation, or priming of the soil organic C (Major et al., 2010a). Priming is the accelerated mineralisation of soil OM due to stimulation caused by the addition of a labile C source (Zimmerman et al., 2011). However, in the current study, it is not clear how much CO<sub>2</sub>-C emissions came from the biochar C mineralisation and how much came from enhanced mineralisation of soil OM. In a field experiment using biochar applied at 23.2 tonne ha<sup>-1</sup>, Major et al. (2010a) found that increased CO<sub>2</sub> emissions recorded from the biochar-amended soil were mostly caused by increased non-biochar-C respiration. However, Cross and Sohi (2011) found that higher CO<sub>2</sub> mineralisation in biochar-amended soils was from the utilisation of the small labile component of the biochar, and not from the loss of the native soil OM due to the priming effect of biochar addition. The labile fraction of biochar, which can be easily mineralised in soil, has been shown to depend on the feedstock and pyrolysis conditions used, with higher temperatures, similar to those used in the current study, generally resulting in increased

carbonisation and less labile C in the resulting biochar (Bruun et al., 2011; Cross and Sohi, 2011). As a result of this reduction in labile C, the priming effect on CO<sub>2</sub> evolution has also been shown to be lower from biochar produced at high temperatures compared with biochar produced at lower temperatures (Zimmerman et al., 2011).

In a 500-day column incubation study, Rogovska et al. (2011) found that biochar application significantly increased CO<sub>2</sub> emissions on all sampling days compared with the soil which did not receive biochar. The authors attributed the increase in CO<sub>2</sub> emissions to an accelerated rate of soil OM mineralisation caused by (1) increased soil aeration due to the lower bulk density of the biochar-amended soil, which resulted in higher aerobic microbial activity and (2) enhanced microbial colonisation, causing accelerated decomposition of organic compounds. However, in the current study, the WFPS was higher in the biochar-amended treatments (Table 3), which suggested reduced aeration. Therefore, the acceleration in mineralisation rates in the current study was more likely to have been caused by mineralisation of the biochar C. Any increase in CO<sub>2</sub>-C emissions corresponding to the increased denitrification rates in the biochar-amended treatments between Days 7 and 19 was small compared with the CO<sub>2</sub>-C emitted from mineralisation.

The increased CO<sub>2</sub>-C emissions from PM600 and W600 compared with the Control represented 0.83 and 0.67 %, respectively, of the total applied biochar C, assuming that there was no priming effect on soil C. This compares to 44 - 54 % mineralisation of the applied manure C, again using the assumption that there were no priming effects. This shows that the application of biochar C to soil leads to a much higher percentage of sequestered C compared with other forms of OM, such as manure, which are quickly mineralised and released as CO<sub>2</sub>. In a study using soil amended with both wheat straw and biochar from the slow pyrolysis of wheat straw, Bruun et al.

(2012) found that 2.9 % of the biochar C was lost as CO<sub>2</sub> over 65 days of soil incubation, while 53 % of wheat straw C was lost. Major et al. (2010a) found that 2.2 % of biochar C was lost by respiration in the first 2 years after soil application. However, the stimulatory effect on CO<sub>2</sub>-C emissions, provided by biochar addition, reduced considerably in the second year of the study, suggesting that losses by mineralisation would decrease further with time (Major et al., 2010a).

The reduction in TOC leaching in W600 is also attributed to enhanced mineralisation of the organic C in the biochar-amended treatments. The reduction in TOC leaching was not observed in the PM600 treatment compared with the Control due to the high susceptibility of C in manure biochar to leaching. In a study investigating leaching of total dissolved C from biochar, Gaskin et al. (2008) found that leaching of dissolved organic C from poultry manure biochar was seven times higher than that leached from the pine chip biochar. Despite this, the leaching of TOC from all treatments was very low (< 13k kg TOC ha<sup>-1</sup>, Figure 2) compared with the C lost through mineralisation to CO<sub>2</sub> (100 – 400 kg CO<sub>2</sub>-C ha<sup>-1</sup>, Figure 4).

### **4.3. Methane Emissions**

Adding biochar to the soil did not significantly affect daily or cumulative CH<sub>4</sub>-C emissions irrespective of whether pig manure was added or not ( $p>0.05$ ). The pig manure-amended treatments had significantly greater CH<sub>4</sub>-C emissions on the day of manure application ( $p<0.0001$ ). Elevated CH<sub>4</sub> emissions in the days following the application of slurry to soil have been shown in previous studies (Chadwick et al., 2000; Sistani et al., 2010; Collins et al., 2011). These elevated CH<sub>4</sub> emissions are attributed to the release of dissolved CH<sub>4</sub>-C produced during storage of the manure prior to application (Collins et al., 2011). These results differ to previous results, which reported both increases (Zhang et al., 2010) and decreases (Rondon et al., 2005) in

CH<sub>4</sub> emissions following biochar addition. Reductions in anaerobic conditions were credited with the near complete suppression of CH<sub>4</sub>, following biochar addition to soil, in a study by Rondon et al. (2005). In the current study, biochar addition was shown to increase WFPS, therefore, increasing anaerobic conditions. However, the addition of biochar to soil did not cause an increase or a reduction in CH<sub>4</sub> emissions in this study.

#### **4. Conclusions**

The application of pig manure to soil increased GHG emissions. Although the peak effluxes occurred at various times after manure application (on the day after application for CO<sub>2</sub> and CH<sub>4</sub> emissions, and at 11 days for N<sub>2</sub>O emissions), the emissions of all measured gases from the pig manure-amended soils had reduced to that of the non-manure-amended soils by the end of the study.

The addition of biochar to the soil increased N<sub>2</sub>O emissions (only when pig manure was also added) and CO<sub>2</sub> emissions (with and without pig manure addition). Increased N<sub>2</sub>O emissions resulted from increased denitrification in the biochar-amended columns, caused by a higher WFPS and organic C contents. The increased denitrification rates also resulted in reduced NO<sub>3</sub>-N leaching from the biochar-amended columns. The increase in CO<sub>2</sub> emissions with biochar addition was most likely due to increased rates of C mineralisation in these columns. This may have been due to mineralisation of the labile biochar C or through increased mineralisation of the soil organic matter. Amendment of the soil with biochar had no effect of CH<sub>4</sub> emissions.

The greenhouse gas emissions in this study were examined over a time period of one month following manure application. Longer-term studies would be necessary to give a true picture of the overall effect of biochar addition on soil greenhouse gas emissions.

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653 Table 1: Characteristics of the biochars and soil used in the column experiment (Means  $\pm$  SD)<sup>2</sup>

	Pig manure biochar	Wood biochar	Soil
Organic Matter (% <sub>db</sub> ) <sup>1</sup>	72.5 $\pm$ 0.78	97.0 $\pm$ 1.24	4.62 $\pm$ 0.013
Ash Content (% <sub>db</sub> )	27.5 $\pm$ 0.78	3.0 $\pm$ 1.24	95.38 $\pm$ 0.013
Bulk Density (g cm <sup>-3</sup> )	0.19 $\pm$ 0.020	0.18 $\pm$ 0.016	1.10 $\pm$ 0.010
Total N (% <sub>db</sub> )	2.67 $\pm$ 0.042	0.42 $\pm$ 0.024	0.21 $\pm$ 0.008
Total C (% <sub>db</sub> )	62.7 $\pm$ 1.30	82.0 $\pm$ 1.15	1.75 $\pm$ 0.049
pH	9.6 $\pm$ 0.34	9.3 $\pm$ 0.19	6.9 $\pm$ 0.20

654 <sup>1</sup> db, dry basis; <sup>2</sup> SD, standard deviation

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669 Table 2: Characteristics of the pig manure added to the soil (Means  $\pm$  SD)<sup>1</sup>

	Total applied		
	kg m <sup>-3</sup>	kg ha <sup>-1</sup>	mg column <sup>-1</sup>
Dry Matter	21.0 $\pm$ 0.98	1214	1030
Total N	2.94 $\pm$ 0.156	170	144
NH <sub>4</sub> -N	1.74 $\pm$ 0.08	78.2	66.4
Total C	5.86 $\pm$ 0.08	340	289

670 <sup>1</sup> SD, standard deviation

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686 Table 3: Characteristics of the soil (Control), and the soil and biochar mixes (PM600 and W600)  
687 for 3 sampling depths (cm below surface) after 10 weeks of soil incubation and leaching, before  
688 pig manure was applied

	Depth	Control	PM600	W600	s.e.	p
WFPS (%) <sup>1</sup>	0-5	61.6 <sup>a</sup>	63.7 <sup>ab</sup>	65.6 <sup>b</sup>	0.45	<0.001
	5-10	63.6 <sup>a</sup>	67.5 <sup>b</sup>	67.8 <sup>b</sup>	0.45	<0.001
	10-20	69.9 <sup>a</sup>	73.5 <sup>a</sup>	73.1 <sup>a</sup>	0.45	<0.001
Organic Matter (% <sub>db</sub> ) <sup>2</sup>	0-5	4.89 <sup>a</sup>	5.14 <sup>ab</sup>	5.28 <sup>b</sup>	0.02	<0.001
	5-10	4.88 <sup>a</sup>	5.18 <sup>b</sup>	5.20 <sup>b</sup>	0.02	<0.001
	10-2	4.85 <sup>a</sup>	5.26 <sup>b</sup>	5.18 <sup>b</sup>	0.02	<0.001
Carbon (% <sub>db</sub> )	0-5	1.81 <sup>a</sup>	2.25 <sup>b</sup>	2.42 <sup>b</sup>	0.035	<0.001
	5-10	1.80 <sup>a</sup>	2.30 <sup>b</sup>	2.45 <sup>b</sup>	0.035	<0.001
	10-20	1.81 <sup>a</sup>	2.29 <sup>b</sup>	2.39 <sup>b</sup>	0.035	<0.001
Nitrogen (% <sub>db</sub> )	0-5	0.217 <sup>ab</sup>	0.227 <sup>b</sup>	0.206 <sup>a</sup>	0.0020	<0.001
	5-10	0.181 <sup>a</sup>	0.203 <sup>b</sup>	0.176 <sup>a</sup>	0.0020	<0.001
	10-2	0.172 <sup>a</sup>	0.194 <sup>b</sup>	0.170 <sup>a</sup>	0.0020	<0.001
C:N <sup>3</sup>	0-5	8.34 <sup>a</sup>	9.90 <sup>ab</sup>	11.75 <sup>b</sup>	0.338	<0.001
	5-10	9.92 <sup>a</sup>	11.31 <sup>ab</sup>	13.91 <sup>b</sup>	0.338	<0.001
	10-20	10.52 <sup>a</sup>	11.81 <sup>b</sup>	14.08 <sup>b</sup>	0.338	<0.001
pH	0-5	7.23	7.24	7.11	0.127	0.245
	5-10	7.34	7.33	7.20	0.127	0.245
	10-20	7.42	7.39	7.23	0.127	0.245

689 <sup>1</sup> WFPS, water filled pore space; <sup>2</sup> db, dry basis; <sup>3</sup> C:N, carbon to nitrogen ratio;

## Captions for Figures

Figure 1: Emissions of  $\text{N}_2\text{O}$ -N (a)  $\text{CO}_2$ -C (b) and  $\text{CH}_4$ -C (c) from soil amended with biochar.

Control = soil only. PM600 = soil + pig manure biochar. W600 = soil + wood biochar.

Treatments amended with the pig manure are shown with (+PM). Error bars show standard deviation.

Figure 2: Cumulative emissions of  $\text{N}_2\text{O}$ -N (a)  $\text{CO}_2$ -C (b) and  $\text{CH}_4$ -C (c) from soil amended with

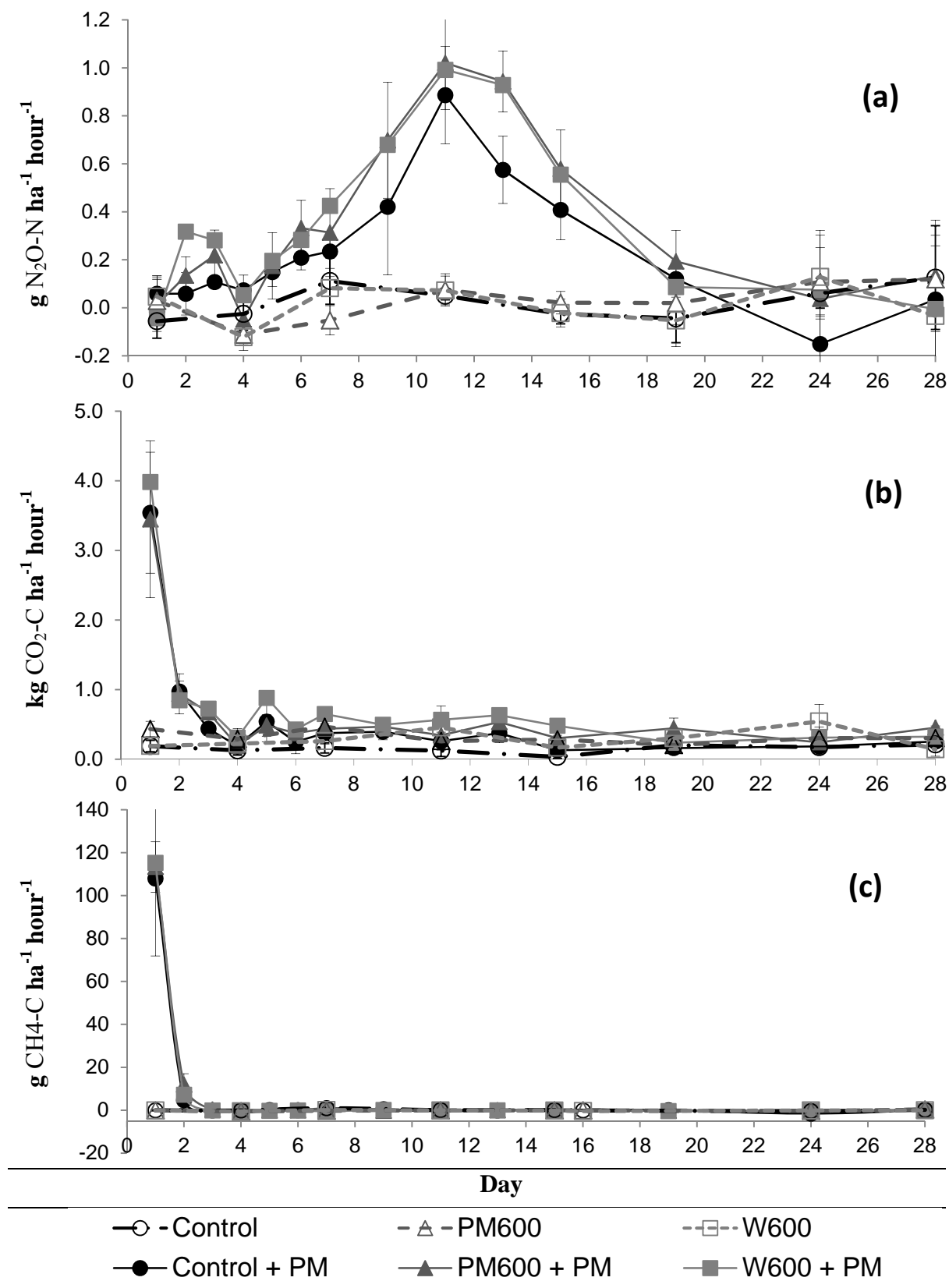
biochar. Control = soil only. PM600 = soil + pig manure biochar. W600 = soil + wood biochar.

Treatments amended with the pig manure are shown with (+PM). Error bars show standard deviation.

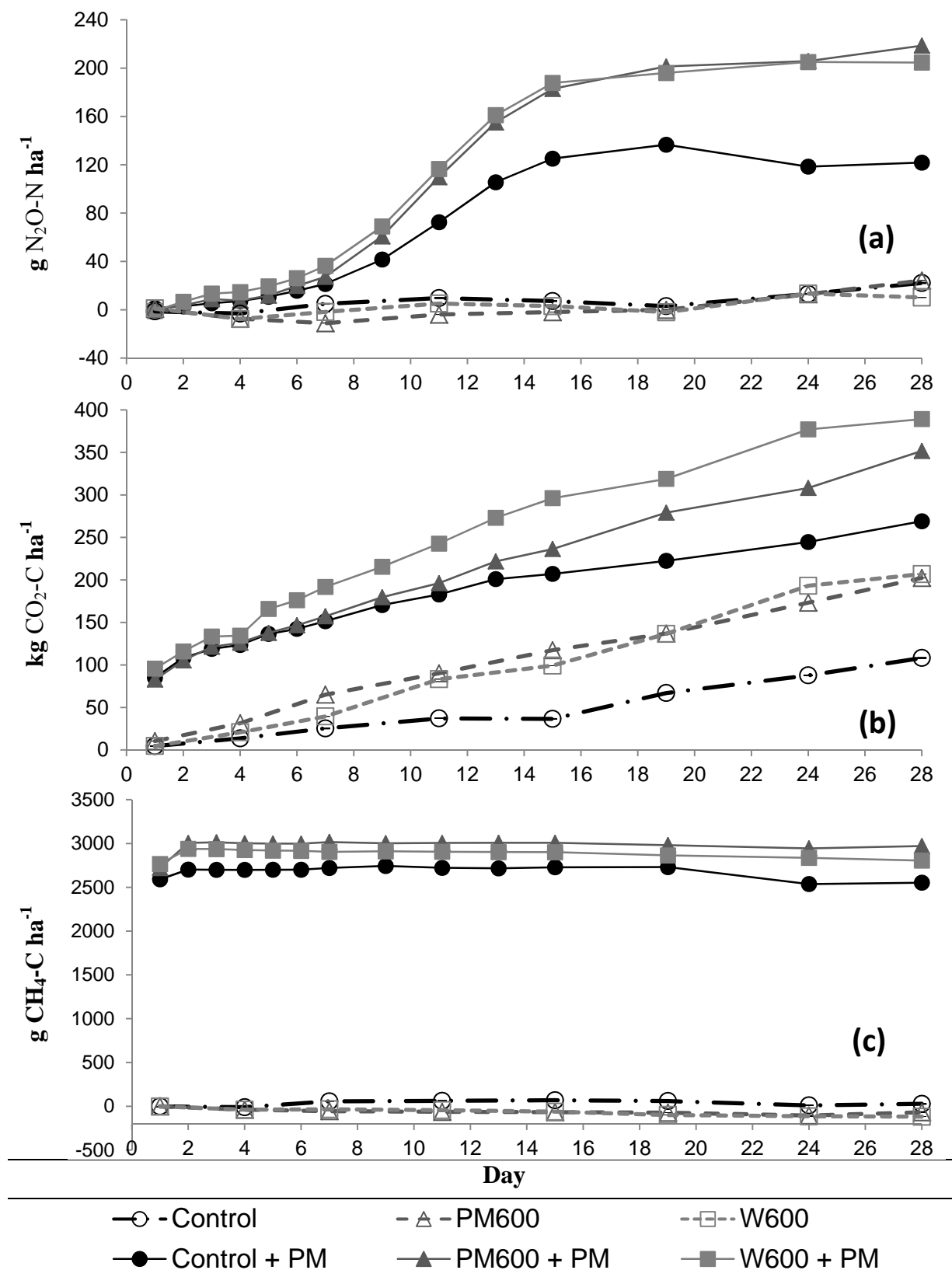
Figure 3: Cumulative leaching of  $\text{NO}_3$ -N during the 4 weeks of gas sampling. Control = soil only. PM600 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure are shown with (+PM). Error bars show standard deviation.

Figure 4: Cumulative leaching of TOC during the 4 weeks of gas sampling. Control = soil only. PM600 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure are shown with (+PM). Error bars show standard deviation.

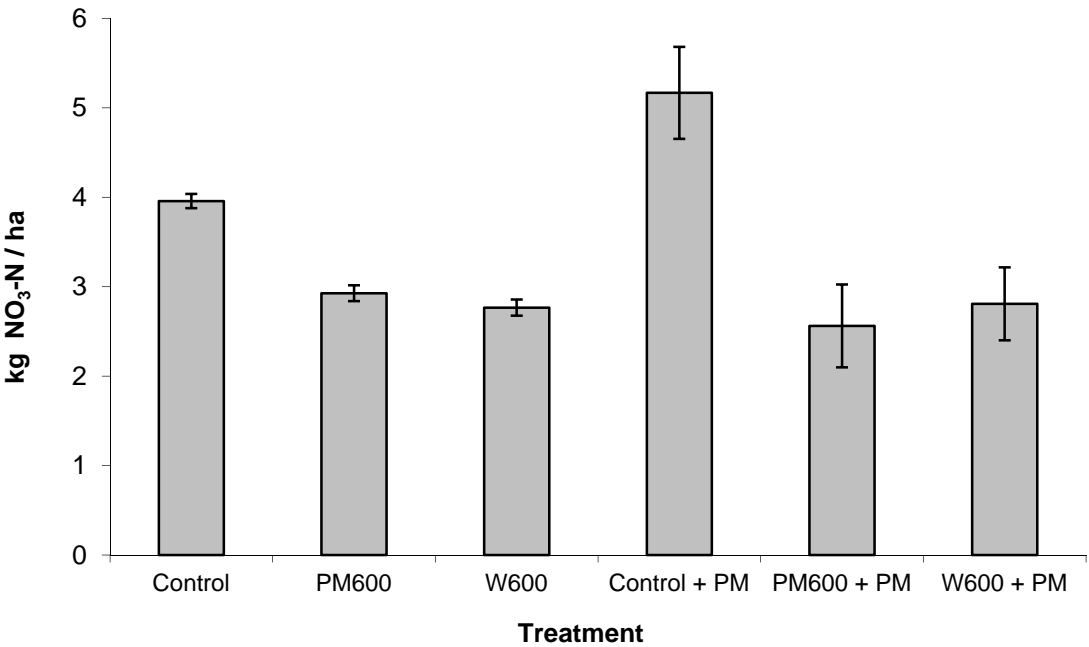
713 Figure 1



714 Figure 2

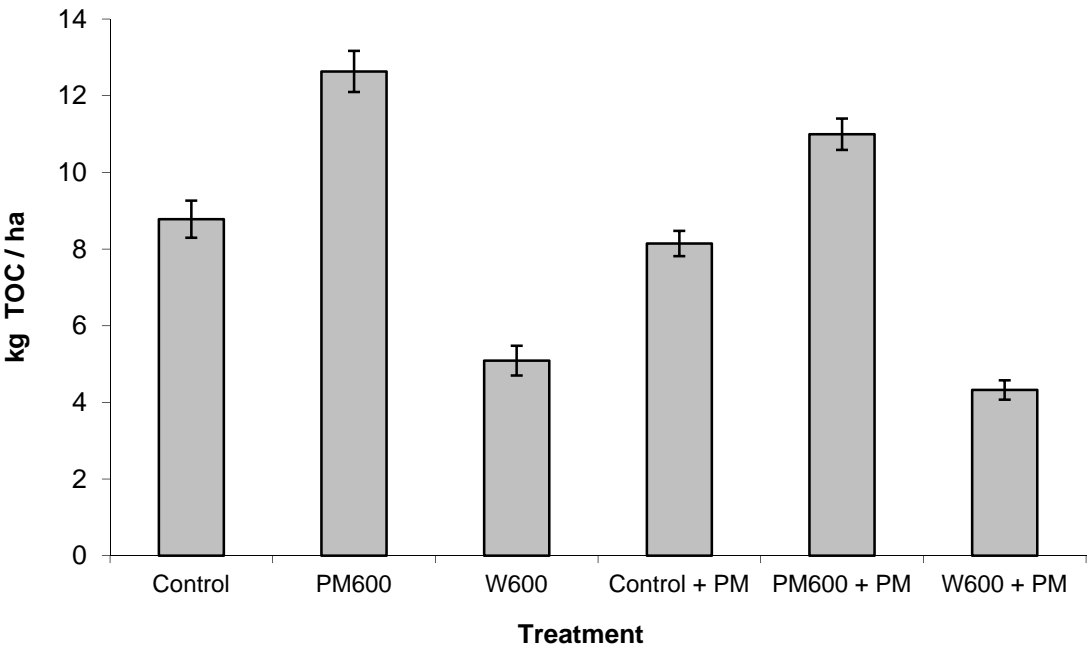


715    Figure 3



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730    Figure 4



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