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5 **Impact of biochar addition to soil on greenhouse gas emissions following pig manure**  
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7  
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9  
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15  
16 **ABSTRACT**

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

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

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

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47 **1. Introduction**

48           Increasing amounts of greenhouse gases (GHG) in the atmosphere are causing changes in  
49 world climate (IPCC, 2007). The production of biochar and renewable energy through pyrolysis  
50 is seen as one prospective strategy, which could result in reduced global carbon dioxide (CO<sub>2</sub>)  
51 concentrations. Roberts et al. (2010) found negative values for the net GHG emissions following  
52 the pyrolysis of corn stover and yard waste and the application of the biochar to soil (-864 and -  
53 885 kg CO<sub>2</sub> equivalent emissions reduction per tonne dry feedstock, respectively), compared  
54 with ethanol production from the corn stover and compost production from the yard waste. The  
55 majority (62 - 66 %) of these GHG emission reductions were realised through C sequestration  
56 within the soil. Gaunt and Lehmann (2008) found that when biochar was applied to agricultural  
57 land, the potential reduction in GHG emissions was between 2 and 5 times greater than when it  
58 was burned to offset fossil fuel usage. These potential reductions in GHG emissions following  
59 biochar application to soil are primarily due to the sequestration of carbon (C) within the soil  
60 (Gaunt and Lehmann, 2008; Roberts et al., 2010), with other potential reductions due to savings  
61 in fertiliser requirement, reductions in fossil fuel usage, and reductions in soil emissions (Gaunt  
62 and Lehmann, 2008).

63           In Ireland, recent landspreading legislation (Nitrates Directive, 91/676/EEC) has limited  
64 the magnitude, timing and placement of organic manure to land. Currently, the amount of  
65 livestock manure that can be applied to land has been limited to 170 kg of nitrogen (N) per  
66 hectare per yr. The land available for landspreading will further be restricted, starting in 2013,  
67 and culminating in 2017, when land spreading of pig manure can no longer exceed the crop's  
68 phosphorus (P) requirements for growth (S.I. 610 of 2010). The implication of this will be that  
69 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

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

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

104 Biochar addition to soil has been shown to influence the concentrations of inorganic-N,  
105 organic C and oxygen (O<sub>2</sub>) in the soil and, hence, the emissions of nitrous oxide (N<sub>2</sub>O) from the  
106 soil (Clough et al., 2010; Singh et al., 2010). Nitrous oxide has a global warming potential  
107 estimated as being 296 times that of CO<sub>2</sub> (IPCC, 2007). Emissions of N<sub>2</sub>O have been reported to  
108 either increase (Clough et al., 2010) or decrease (Singh et al., 2010), following biochar  
109 application to soil. Singh et al. (2010) found that wood biochar adsorbed ammonium (NH<sub>4</sub>) in a  
110 soil, thereby reducing the pool of inorganic-N for the N<sub>2</sub>O-producing mechanisms. Clough et al.  
111 (2010) attributed higher N<sub>2</sub>O emissions from biochar-amended soil to greater nitrite (NO<sub>2</sub>)  
112 concentrations brought about by nitrification inhibitors on biochar, which slowed nitrate (NO<sub>3</sub>)  
113 formation. Yanai et al. (2007) found an 89 % suppression of N<sub>2</sub>O emissions at 73-78 % soil  
114 water filled pore space (WFPS) due to the adsorption of water by biochar. However, the same  
115 study found a 51 % increase in N<sub>2</sub>O emissions at 83 % WFPS. The authors attributed this

116 increase to better soil aeration and the stimulation of N<sub>2</sub>O-producing activity due to the  
117 neutralisation of soil pH. Studies have shown that biochar addition to soil may also influence  
118 methane (CH<sub>4</sub>) emissions, which have a global warming potential estimated as being 23 times  
119 that of CO<sub>2</sub> (IPCC, 2007). Soil CH<sub>4</sub> emissions have been reported to either increase (Zhang et al.,  
120 2010) or decrease (Rondon et al., 2005), following biochar addition. Rondon et al. (2005)  
121 credited a near complete suppression of CH<sub>4</sub>, following biochar addition to soil, to a reduction in  
122 anaerobic conditions and increased soil aeration. However, in a field experiment in a rice paddy,  
123 Zhang et al. (2010) found that soil amended with biochar at 40 tonne ha<sup>-1</sup> increased CH<sub>4</sub>  
124 emissions by 34 % when N fertiliser was applied, and by 41 % without N fertilization.

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

130

## 131 **2. Materials and Methods**

### 132 **2.1. Soil Column Preparation**

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

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

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



162 °C) and relative humidity (75 %), based on typical climatic conditions in Ireland (Walsh, 2012).  
163 All columns were leached with 160 mL of distilled water, applied twice weekly in two 80-mL  
164 doses over two hours. This is equivalent to 980 mm of rainfall yr<sup>-1</sup>, which is in the mid-range of  
165 average annual rainfall amounts in Ireland (Walsh, 2012). Following 10 weeks of incubation, pig  
166 manure, collected from an integrated pig farm in Fermoy, Co. Cork, was applied to the surface of  
167 four columns of each treatment at a rate equivalent to 170 kg N ha<sup>-1</sup>. This application rate  
168 corresponds with the general land spreading limit of 170 kg N ha<sup>-1</sup> yr<sup>-1</sup> from livestock manure  
169 imposed by the Irish Statutory Instrument (S.I.) 610 of 2010. The 10-week lag time was applied  
170 before manure application to avoid a burst in microbial activity, associated with drying and re-  
171 wetting of soil during the construction of the columns. Drying and re-wetting of soil has been  
172 shown to cause a burst in microbial activity and a sharp increase in C and N mineralisation  
173 (Bengtsson et al., 2003; Borken and Matzner, 2009), which would have resulted in artificially  
174 high emissions. The characteristics of the pig manure are given in Table 2. The treatments which  
175 received pig manure were then known as Control+PM, PM600+PM and W600+PM.

176

## 177 **2.2. Gas Sampling and Analysis**

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

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

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

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

$$204 \frac{dGas}{dt} * 10^{-6} * \frac{V_{chamber} * p * 100 * MW}{R * T} * 10^6 * \frac{1}{A}$$

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

207 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  
208 chamber.

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

215

### 216 **2.3. Soil and Leachate Analyses**

217 Extra soil columns ( $n=4$ ) were set up so that they could be destructively sampled after 10 weeks  
218 of incubation, just before the beginning of the gas analysis. Analyses were conducted at depth  
219 increments of 0-0.05, 0.05-0.1, and 0.1–0.2 m below the soil surface. The soil from each depth  
220 increment was air-dried and sieved to a particle size of 2 mm, or less, before analyses. The OM  
221 content of the soil was determined using the loss on ignition test (B.S.1377-3; BSI, 1990). Soil  
222 total C and total N were determined by high temperature combustion using a LECO Truspec CN  
223 analyser (LECO Corporation, St. Joseph, MI, USA). Soil pH was determined using a pH probe  
224 (WTW, Weilheim, Germany) at a 2:1 ratio of deionised water-to-soil. Bulk density ( $\rho_b$ ) and total  
225 porosity ( $n$ ) were calculated according to Haney and Haney (2010). Water-filled pore space was  
226 estimated from WC, bulk density, and total porosity in accordance with Haney and Haney  
227 (2010):

$$228 \quad WFPS = \frac{WC * \rho_b}{n}$$

229 A sample of leached water was collected from the base of each column once per week  
230 during the 28-day gas sampling period. This leachate sample was analysed for total organic C  
231 (TOC) and NO<sub>3</sub> to help interpret the C and N cycling processes occurring in the soil columns.  
232 Unfiltered leachate samples were analysed for TOC using a BioTector TOC TN TP Analyzer  
233 (BioTector Analytical Systems Limited, Cork, Ireland). Sub-samples of leachate were passed  
234 through a 0.45 µm filter and analysed colorimetrically for total oxidised N and NO<sub>2</sub> using a  
235 nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Vantaa, Finland). Nitrate was  
236 calculated by subtracting NO<sub>2</sub> from total oxidised N.

237

#### 238 **2.4. Statistical Analysis**

239 Emissions data were analyzed using the Statistical Analyses System (SAS Institute, 2004)  
240 with each column as the experimental unit. For all analyses, significance was given as p<0.05.  
241 The hourly flux of N<sub>2</sub>O-N, CO<sub>2</sub>-C, and CH<sub>4</sub>-C were analysed as repeated measures using a  
242 repeated measures ANOVA using the MIXED procedure of SAS with Tukey-Kramer adjustment  
243 for multiple comparisons. The dependent variables were: N<sub>2</sub>O-N, CO<sub>2</sub>-C, and CH<sub>4</sub>-C. For all the  
244 above analyses, the fixed effects were: treatment, sampling day and column. Sampling day was  
245 the repeated measure. Comparison of cumulative emissions of N<sub>2</sub>O-N, CO<sub>2</sub>-C, and CH<sub>4</sub>-C over  
246 the 28-day sampling period was performed using the MIXED procedure in SAS. N<sub>2</sub>O-N, CO<sub>2</sub>-C,  
247 and CH<sub>4</sub>-C were the dependent variables. Treatment was included as a fixed effect.

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

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

254

### 255 **3. Results**

#### 256 **3.1 Soil Characteristics**

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

263

#### 264 **3.2. Nitrous Oxide Emissions**

265 The 28-day  $N_2O$ -N flux, illustrated in Figure 1a, remained low from the non-manure-  
266 amended treatments throughout the study ( $-0.12$  to  $0.13$  g  $N_2O$ -N  $ha^{-1}$   $hour^{-1}$ ). The addition of  
267 biochar to these treatments had no effect on  $N_2O$ -N emissions on any particular sampling day  
268 ( $p > 0.05$ ). Similarly, there was no difference between non-manure-amended treatments in their  
269 cumulative emissions over 28 days ( $p > 0.05$ ) (Figure 2a). The addition of pig manure to the soil  
270 influenced  $N_2O$ -N emissions: one week following pig manure application, there was a significant  
271 increase in  $N_2O$ -N emissions from all the manure-amended treatments. The greatest emissions  
272 occurred 11 days after manure application ( $0.89$ ,  $1.02$  and  $0.99$  g  $N_2O$ -N  $ha^{-1}$   $hour^{-1}$  for  
273 Control+PM, PM600+PM and W600+PM, respectively). This compares to emissions of  $0.05$ ,  
274  $0.07$  and  $0.07$  g  $N_2O$ -N  $ha^{-1}$   $hour^{-1}$  for Control, PM600 and W600, respectively, on Day 11. The

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

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

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

294

### 295 **3.3. Carbon Dioxide Emissions**

296 The CO<sub>2</sub>-C emissions, shown in Figure 1b, remained low from the non-manure-amended  
297 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

298 from the manure-amended treatments were significantly higher than the non-manure-amended  
299 treatments on the day of manure application (Day 1) ( $p < 0.001$ ), and on Day 1 were 3.5, 3.5 and  
300 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,  
301 from Day 4 until the end of the study, there was no significant difference between any treatment  
302 ( $p < 0.05$ ). The manure-amended treatments had higher cumulative emissions than the treatments  
303 which did not receive manure, largely due to the high CO<sub>2</sub>-C emissions on the day of manure  
304 application (Figure 2b).

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

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

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

323

### 324 **3.4. Methane Emissions**

325 Similar to the  $\text{CO}_2\text{-C}$  fluxes, the  $\text{CH}_4\text{-C}$  emissions from the pig manure-amended treatments were  
326 high on the day of manure application ( $108 - 115 \text{ g CH}_4\text{-C ha}^{-1} \text{ hour}^{-1}$ ), but quickly reduced to  
327 the levels of the non-pig manure-amended treatments (Figure 1c). From Day 4 until the end of  
328 the study, there was no significant difference between the treatments which received manure and  
329 those which did not. Emissions of  $\text{CH}_4\text{-C}$  were low throughout the study, apart from Days 1 and  
330 2 for the manure-amended treatments. Excluding these, the flux of  $\text{CH}_4\text{-C}$  was between  $-1.6$  and  
331  $0.9 \text{ g ha}^{-1} \text{ hour}^{-1}$  for every treatment on every sampling day. The pig manure-amended treatments  
332 had significantly greater cumulative emissions than the non-pig manure-amended treatments, due  
333 to the high  $\text{CH}_4\text{-C}$  emissions on the day of manure application ( $p<0.0001$ ) (Figure 2c).

334

## 335 **4. Discussion**

### 336 **4.1. Nitrous Oxide Emissions**

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



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

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

366 an incubation study, using arable soil fertilised with ammonium nitrate, Dobbie and Smith  
367 (2001) found a 30-fold increase in N<sub>2</sub>O emissions by increasing the WFPS from 60 to 80 %.

368 Despite the increase in denitrification with biochar addition to the soil, the overall amount  
369 of N lost through N<sub>2</sub>O-N emissions is low (<10 % for the manure-amended treatments, <1 % for  
370 the non-manure-amended treatments) compared with N lost through NO<sub>3</sub>-N leaching. However,  
371 biochar addition may also have increased the rate of complete denitrification to N<sub>2</sub> within the  
372 soil, although this was not studied in this experiment. Carbon availability in soil has been shown  
373 previously to promote the reduction of N<sub>2</sub>O to N<sub>2</sub> (Miller et al., 2009). Jahangir et al. (2012)  
374 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 %  
375 with the addition of dissolved organic C to the soil. The present study is a laboratory-based study  
376 and results may differ to those in the field. The growth of plants in the soil could have a large  
377 impact on N<sub>2</sub>O emissions, with N uptake by the plants resulting in a reduction in NO<sub>3</sub> available  
378 for denitrification.

379

#### 380 **4.2. Carbon Dioxide Emissions**

381 The manure-amended treatments had higher cumulative emissions than the treatments  
382 which did not receive manure. This was largely due to the significantly higher emissions of CO<sub>2</sub>  
383 on the first sampling day. The addition of manure slurries to soil has been shown to cause a  
384 short-lived spike in microbial activity and CO<sub>2</sub> emissions (Dumale et al., 2009; Collins et al,  
385 2011). The amount of pig manure C mineralised during the sampling period was estimated as the  
386 difference between the cumulative CO<sub>2</sub>-C emissions from the manure-amended and non-manure-  
387 amended treatments (Rogovska et al., 2011). Between 150 and 180 kg ha<sup>-1</sup> of the total CO<sub>2</sub>-C  
388 emissions were caused by the mineralisation of C in the manure, with no significant difference

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

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

412 carbonisation and less labile C in the resulting biochar (Bruun et al., 2011; Cross and Sohi,  
413 2011). As a result of this reduction in labile C, the priming effect on CO<sub>2</sub> evolution has also been  
414 shown to be lower from biochar produced at high temperatures compared with biochar produced  
415 at lower temperatures (Zimmerman et al., 2011).

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

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

435 (2012) found that 2.9 % of the biochar C was lost as CO<sub>2</sub> over 65 days of soil incubation, while  
436 53 % of wheat straw C was lost. Major et al. (2010a) found that 2.2 % of biochar C was lost by  
437 respiration in the first 2 years after soil application. However, the stimulatory effect on CO<sub>2</sub>-C  
438 emissions, provided by biochar addition, reduced considerably in the second year of the study,  
439 suggesting that losses by mineralisation would decrease further with time (Major et al., 2010a).

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

448

### 449 **4.3. Methane Emissions**

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

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

463

#### 464 **4. Conclusions**

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

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

478 The greenhouse gas emissions in this study were examined over a time period of one  
479 month following manure application. Longer-term studies would be necessary to give a true  
480 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;

690 **Captions for Figures**

691 Figure 1: Emissions of N<sub>2</sub>O-N (a) CO<sub>2</sub>-C (b) and CH<sub>4</sub>-C (c) from soil amended with biochar.

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

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

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696 Figure 2: Cumulative emissions of N<sub>2</sub>O-N (a) CO<sub>2</sub>-C (b) and CH<sub>4</sub>-C (c) from soil amended with

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

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

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701 Figure 3: Cumulative leaching of NO<sub>3</sub>-N during the 4 weeks of gas sampling. Control = soil

702 only. PM600 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended

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

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705 Figure 4: Cumulative leaching of TOC during the 4 weeks of gas sampling. Control = soil only.

706 PM600 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the

707 pig manure are shown with (+PM). Error bars show standard deviation.

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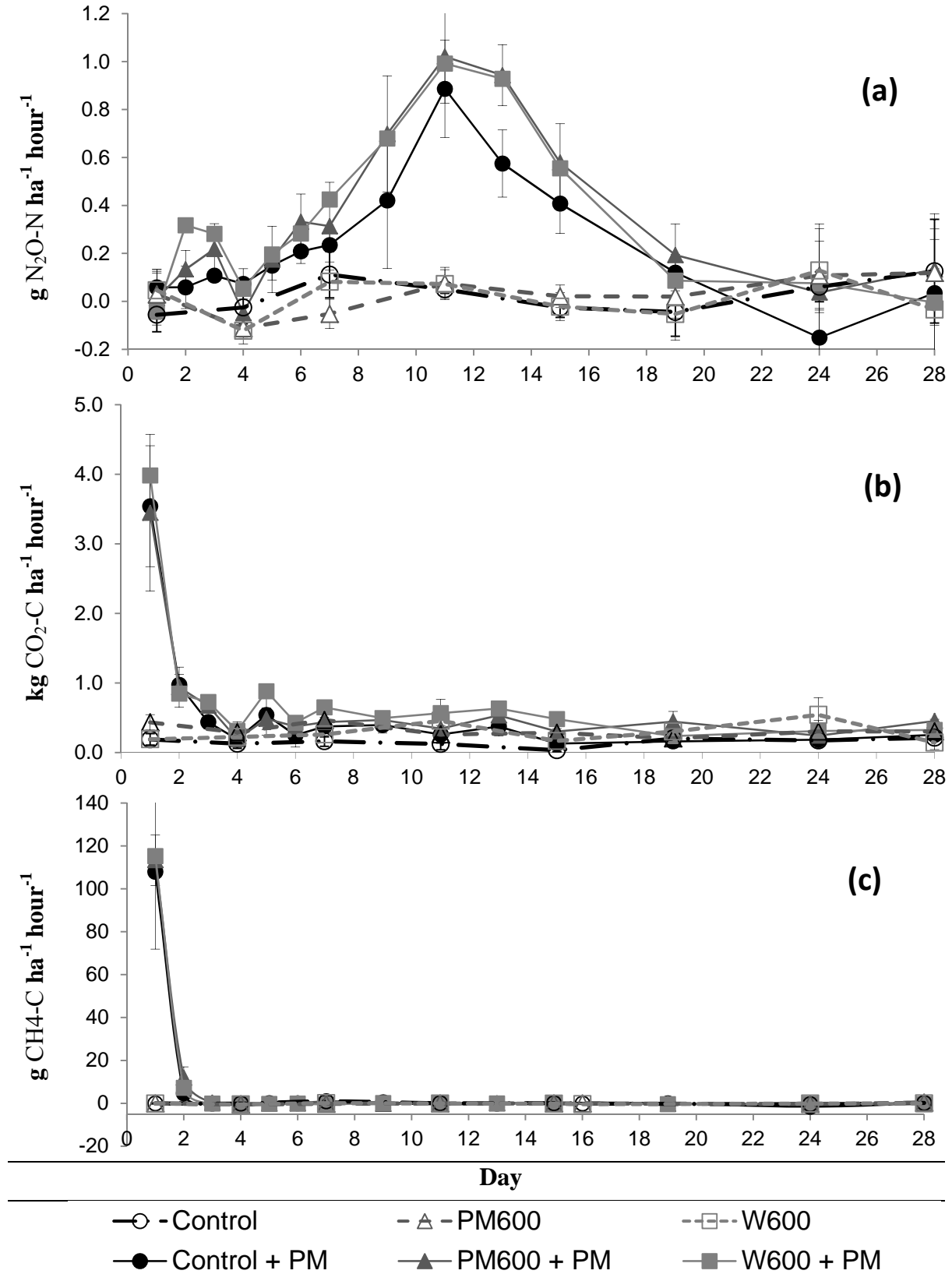
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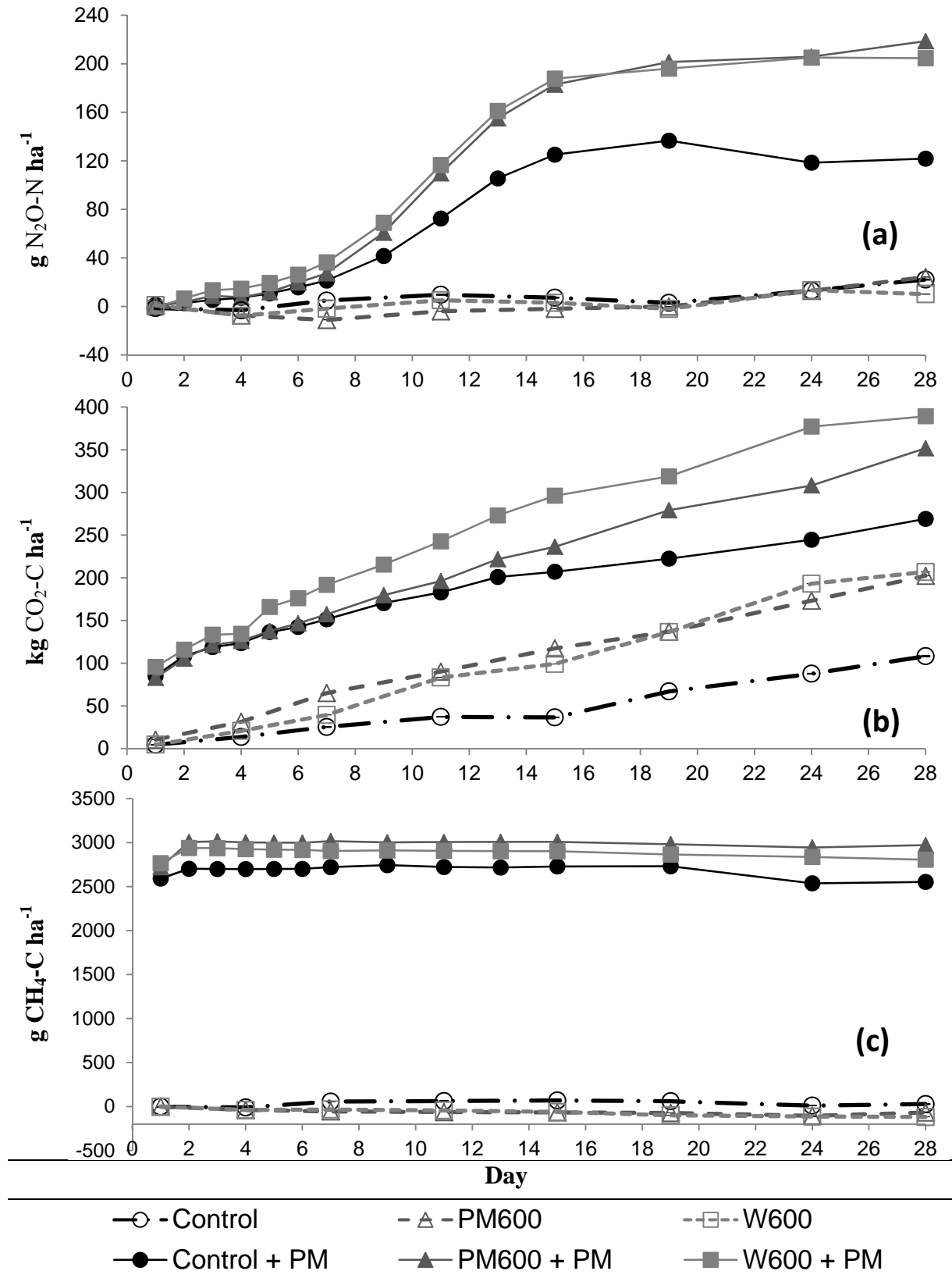
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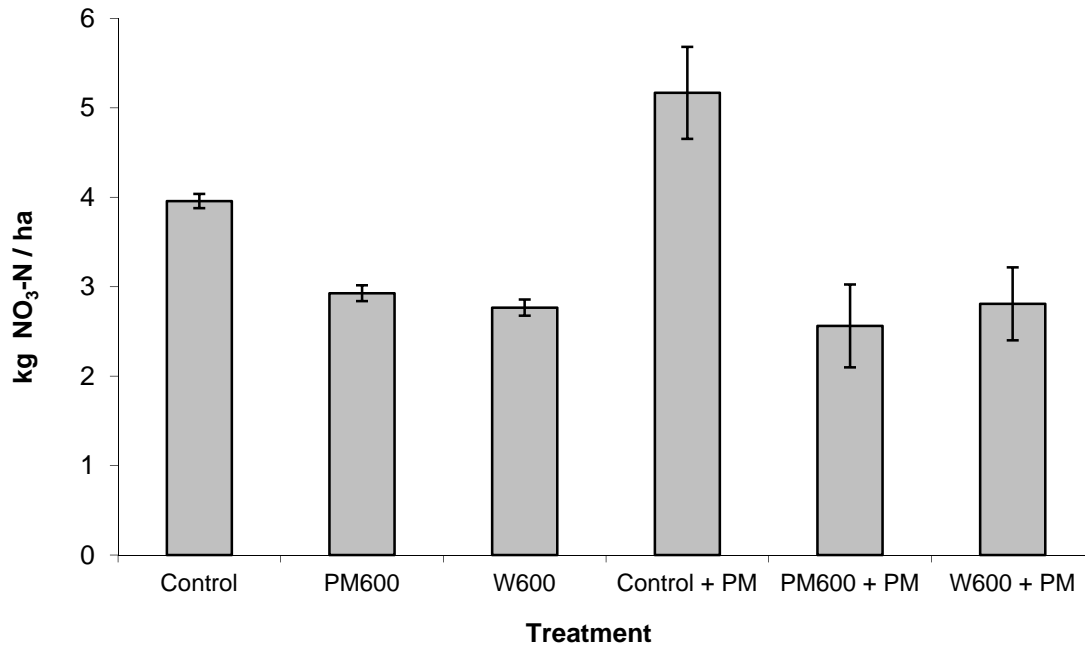
713 Figure 1



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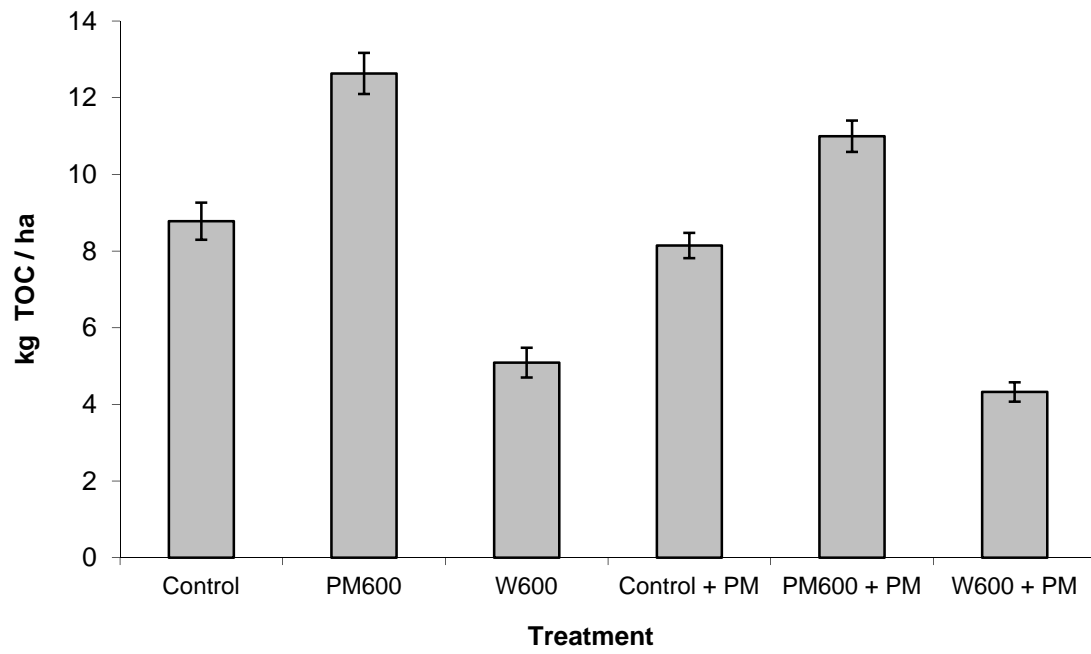
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730 Figure 4



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