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

Shane M. Troy[ab], Peadar G. Lawlor[a], Cornelius J. O' Flynn[b] and Mark G. Healy[b*]

[a] Teagasc, Pig Development Department, Animal & Grassland Research & Innovation Centre, Moorepark, Fermoy, Co. Cork, Ireland.

[b] Civil Engineering, National University of Ireland, Galway, Co. Galway, Ireland

*Corresponding author. Tel.: +353 91 495364 fax: +353 91 494507, e-mail address: mark.healy@nuigalway.ie

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_2), nitrous oxide (N_2O) and methane (CH_4) following the addition, at a rate of 18 t ha^{-1}, 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 ^{o}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^{-1} and 36 kg phosphorus ha^{-1}, 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_2O 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_2 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_2) 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_2 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,

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

Biochar application to agricultural soils has the potential for long-term C sequestration, due to the stability of biochar in soil environments. Biochar is composed of a range of different forms of C, from recalcitrant aromatic ring structures, which can persist in soil for millennia, to more easily degradable aliphatic and oxidised C structures, which mineralise to CO_2 more rapidly through degradation by biotic and abiotic oxidation (Schmidt and Noack, 2000, Cheng et al., 2006; Liang et al., 2008). Increased CO_2 emissions, following biochar addition to soil, have been attributed to increased mineralisation rates in the biochar-amended soil due to (1) mineralisation of applied biochar C (Major et al., 2010a; Smith et al., 2010) or (2) enhanced soil organic C mineralisation (Rogovska et al., 2011). In a two-year experiment, Major et al. (2010a) found that only 3 % of applied biochar C was lost as CO_2, with 75 % of the biochar mineralisation occurring in the first year, which suggested that the stimulatory effects were short-term. The stability and resistance of the biochar against oxidation is known to vary depending on the feedstock and pyrolysis procedures and temperatures (Schmidt and Noack, 2000; Liang et al., 2008). Mukherjee and Zimmerman (2013) showed that the loss of biochar C, N and P to leaching water correlated with biochar volatile matter content and was greater from biochar made at lower temperatures than from high temperature biochar. Rogovska et al. (2011) found accelerated soil organic C mineralisation with biochar addition to soil, and hypothesised that the increases may 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_2) in the soil and, hence, the emissions of nitrous oxide (N_2O) 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_2 (IPCC, 2007). Emissions of N_2O 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_4) in a
110 soil, thereby reducing the pool of inorganic-N for the N_2O-producing mechanisms. Clough et al.
111 (2010) attributed higher N_2O emissions from biochar-amended soil to greater nitrite (NO_2)
112 concentrations brought about by nitrification inhibitors on biochar, which slowed nitrate (NO_3)
113 formation. Yanai et al. (2007) found an 89 % suppression of N_2O 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_2O emissions at 83 % WFPS. The authors attributed this

116 increase to better soil aeration and the stimulation of N_2O-producing activity due to the
117 neutralisation of soil pH. Studies have shown that biochar addition to soil may also influence
118 methane (CH_4) emissions, which have a global warming potential estimated as being 23 times
119 that of CO_2 (IPCC, 2007). Soil CH_4 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_4, 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^{-1} increased CH_4
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_2, N_2O and
128 CH_4 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 ^{o}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 ^{o}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^{-1} 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^{-1} 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 ^{o}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^{-1}, 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^{-1}. This application rate
168 corresponds with the general land spreading limit of 170 kg N ha^{-1} yr^{-1} 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_4 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^{-1} 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

weight; R is a gas constant, 8314 J mol^{-1} 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: kg CO_2-C ha^{-1} h^{-1}, g CH_4-C ha^{-1} h^{-1}, g N_2O-N ha^{-1} 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 (ρ_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 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 μm filter and analysed colorimetrically for total oxidised N and NO_2 using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Vantaa, Finland). Nitrate was calculated by subtracting 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 N_2O-N, CO_2-C, and CH_4-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: N_2O-N, CO_2-C, and CH_4-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 N_2O-N, CO_2-C, and CH_4-C over the 28-day sampling period was performed using the MIXED procedure in SAS. N_2O-N, CO_2-C, and CH_4-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

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_2O-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_2O-N emissions were similar for all treatments
278 ($p>0.05$).

279 The patterns of N_2O-N emissions were similar for the three manure-amended treatments.
280 There was no difference between N_2O-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_2O-N emissions than Control+PM ($p<0.1$).
285 Cumulative N_2O-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_3 leached from each treatment during the 28-day gas
289 sampling period. The quantity of NO_3 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_3 leached from any of the biochar-amended soils ($p>0.05$). However, the quality of NO_3
293 increased significantly from Control+PM compared with the Control ($p<0.01$).
294

295 **3.3. Carbon Dioxide Emissions**

296 The CO_2-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_2-C ha^{-1} $hour^{-1}$). Soil CO_2-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_2-C ha^{-1} $hour^{-1}$ 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_2-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_2-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^{-1} more CO_2-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_2-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_2-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 CO_2-C fluxes, the CH_4-C emissions from the pig manure-amended treatments were
326 high on the day of manure application (108 – 115 g CH_4-C ha^{-1} $hour^{-1}$), 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 CH_4-C were low throughout the study, apart from Days 1 and
330 2 for the manure-amended treatments. Excluding these, the flux of CH_4-C was between -1.6 and
331 0.9 g ha^{-1} $hour^{-1}$ 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 CH_4-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 O_2 dictates the contribution of
339 each process to the amount of N_2O emissions (Brady and Weil, 1996; Bateman and Baggs, 2005;
340 Rivett at al., 2008). The rate of denitrification is also influenced by the soil inorganic-N
341 concentrations (especially 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_2O emissions observed in the manure-amended treatments (Figure 1a).
346 There was no difference in N_2O emissions between the biochar-amended treatments and
347 the Control for the treatments that did not receive pig manure. Emissions of N_2O 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_2O emissions than the Control. The quantity of NO_3
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_3-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_2O 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_2 (Rivett et al., 2008). In a study measuring N_2O
359 losses through denitrification from intact soil cores fertilised with NO_3, Jahangir et al. (2012)
360 found N_2O 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_3 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_2O 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_2O-N emissions is low (<10 % for the manure-amended treatments, <1 % for
370 the non-manure-amended treatments) compared with N lost through NO_3-N leaching. However,
371 biochar addition may also have increased the rate of complete denitrification to N_2 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_2O to N_2 (Miller et al., 2009). Jahangir et al. (2012)
374 found that the N_2 flux from the top 0.10 m of a soil fertilised with NO_3 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_2O emissions, with N uptake by the plants resulting in a reduction in NO_3 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_2
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_2 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_2-C emissions from the manure-amended and non-manure-
387 amended treatments (Rogovska et al., 2011). Between 150 and 180 kg ha^{-1} of the total CO_2-C
388 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_2-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_2-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_2-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_2-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^{-1}, Major et al. (2010a) found that increased CO_2 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_2 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

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_2 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_2 emissions on all sampling days compared with the soil
418 which did not receive biochar. The authors attributed the increase in CO_2 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_2-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_2-C emitted from
427 mineralisation.

428 The increased CO_2-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_2. 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_2 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_2-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^{-1}, Figure 2) compared with
447 the C lost through mineralisation to CO_2 (100 – 400 kg CO_2-C ha^{-1}, Figure 4).
448
449 **4.3. Methane Emissions**
450 Adding biochar to the soil did not significantly affect daily or cumulative CH_4-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_4-C emissions on the day of manure application
453 ($p<0.0001$). Elevated CH_4 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_4 emissions are attributed to the release of dissolved CH_4-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_4 emissions following biochar addition. Reductions in anaerobic conditions were credited
459 with the near complete suppression of CH_4, 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_4 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_2
467 and CH_4 emissions, and at 11 days for N_2O 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_2O emissions (only when pig manure was
471 also added) and CO_2 emissions (with and without pig manure addition). Increased N_2O 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_3-N
474 leaching from the biochar-amended columns. The increase in CO_2 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_4 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 ± SD)[2]

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

654 [1] db, dry basis; [2] SD, standard deviation

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669 Table 2: Characteristics of the pig manure added to the soil (Means ± SD)[1]

		Total applied	
	kg m^{-3}	kg ha^{-1}	mg $column^{-1}$
Dry Matter	21.0 ± 0.98	1214	1030
Total N	2.94 ± 0.156	170	144
NH_4-N	1.74 ± 0.08	78.2	66.4
Total C	5.86 ± 0.08	340	289

670 [1] 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 (%)[1]	0-5	61.6[a]	63.7[ab]	65.6[b]	0.45	<0.001
	5-10	63.6[a]	67.5[b]	67.8[b]	0.45	<0.001
	10-20	69.9[a]	73.5[a]	73.1[a]	0.45	<0.001
Organic Matter ($\%_{db}$)[2]	0-5	4.89[a]	5.14[ab]	5.28[b]	0.02	<0.001
	5-10	4.88[a]	5.18[b]	5.20[b]	0.02	<0.001
	10-2	4.85[a]	5.26[b]	5.18[b]	0.02	<0.001
Carbon ($\%_{db}$)	0-5	1.81[a]	2.25[b]	2.42[b]	0.035	<0.001
	5-10	1.80[a]	2.30[b]	2.45[b]	0.035	<0.001
	10-20	1.81[a]	2.29[b]	2.39[b]	0.035	<0.001
Nitrogen ($\%_{db}$)	0-5	0.217[ab]	0.227[b]	0.206[a]	0.0020	<0.001
	5-10	0.181[a]	0.203[b]	0.176[a]	0.0020	<0.001
	10-2	0.172[a]	0.194[b]	0.170[a]	0.0020	<0.001
C:N[3]	0-5	8.34[a]	9.90[ab]	11.75[b]	0.338	<0.001
	5-10	9.92[a]	11.31[ab]	13.91[b]	0.338	<0.001
	10-20	10.52[a]	11.81[b]	14.08[b]	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 [1] WFPS, water filled pore space; [2] db, dry basis; [3] C:N, carbon to nitrogen ratio;

690 **Captions for Figures**

691 Figure 1: Emissions of N_2O-N (a) CO_2-C (b) and CH_4-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.

695

696 Figure 2: Cumulative emissions of N_2O-N (a) CO_2-C (b) and CH_4-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.

700

701 Figure 3: Cumulative leaching of NO_3-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.

704

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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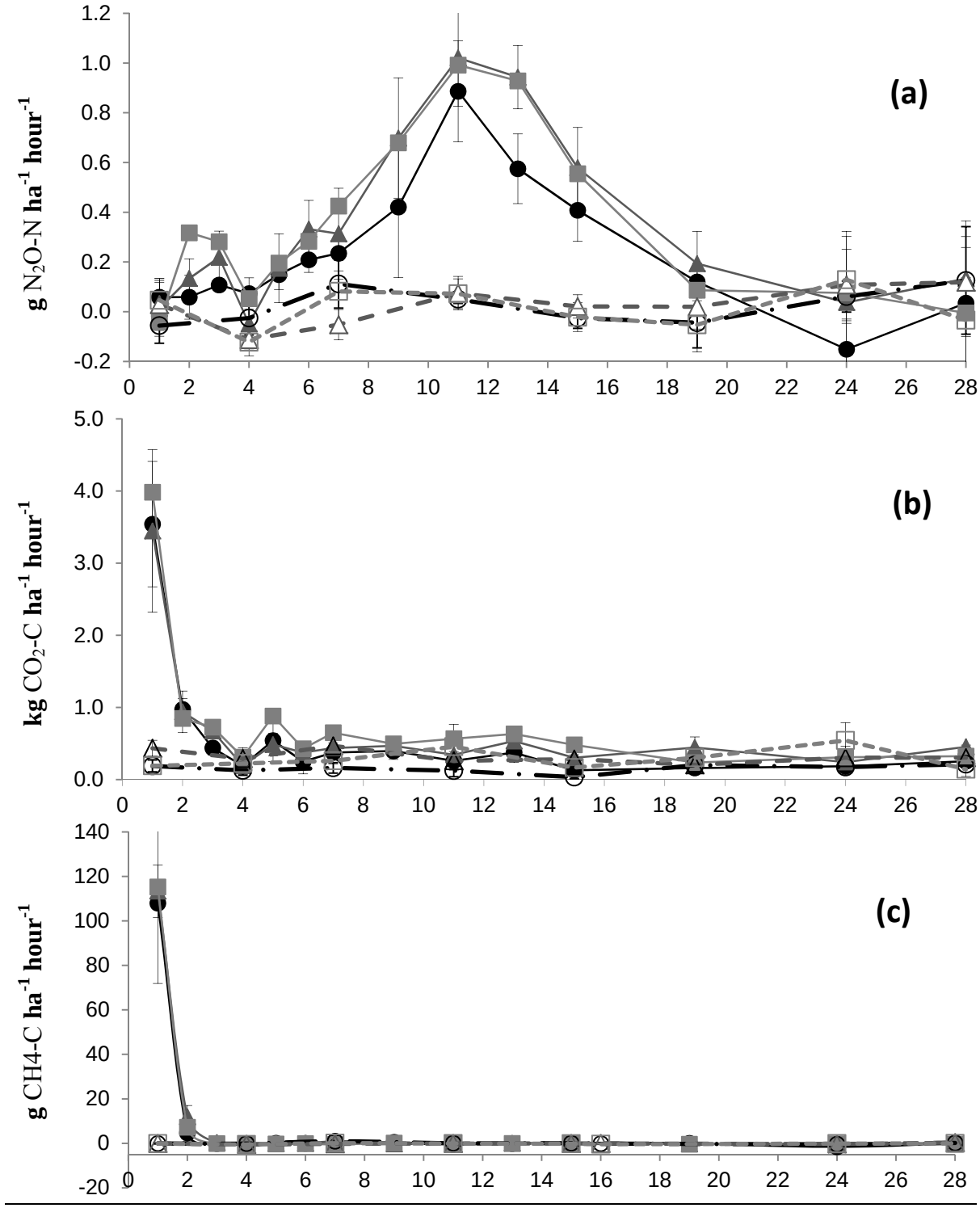
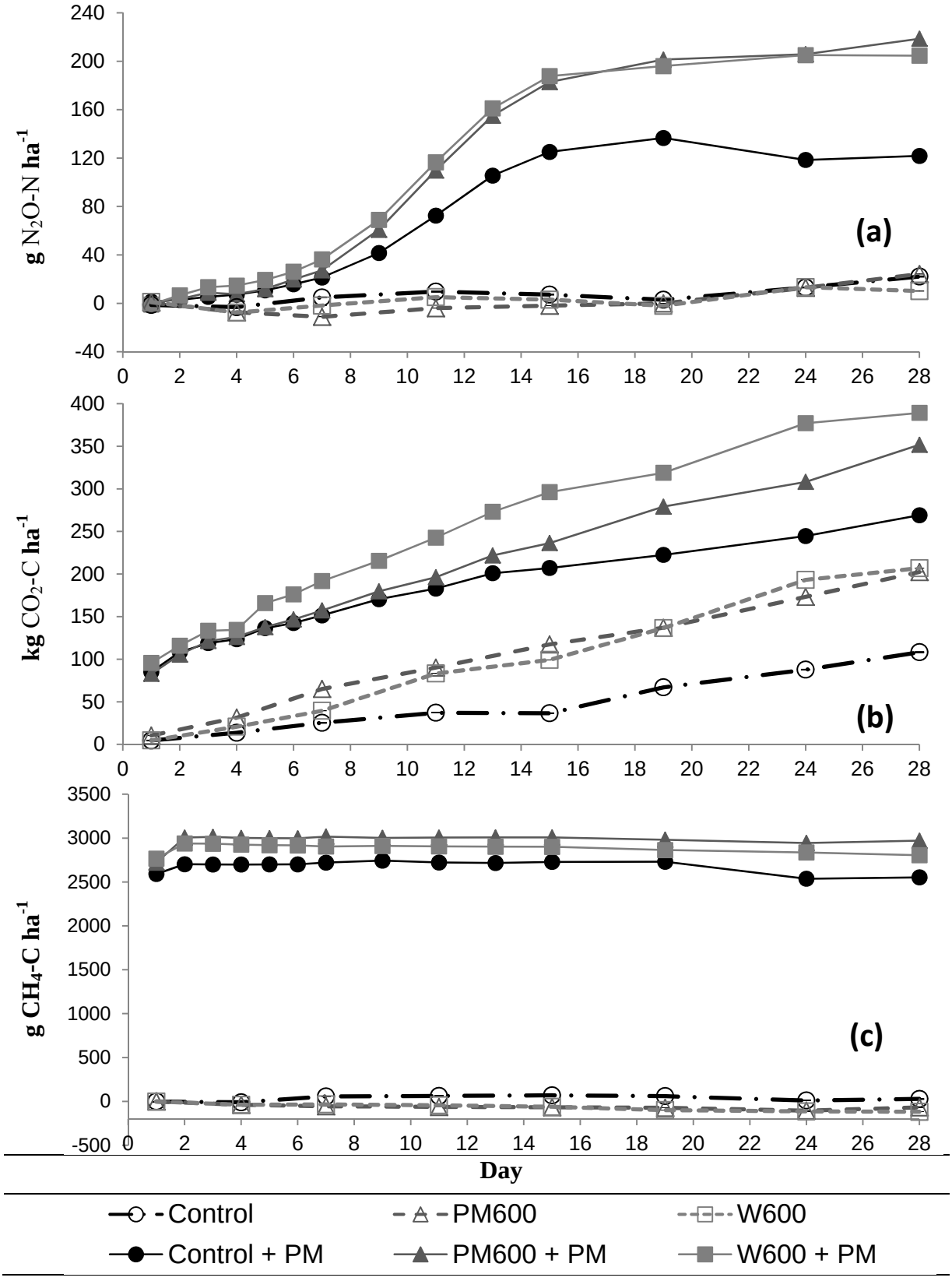
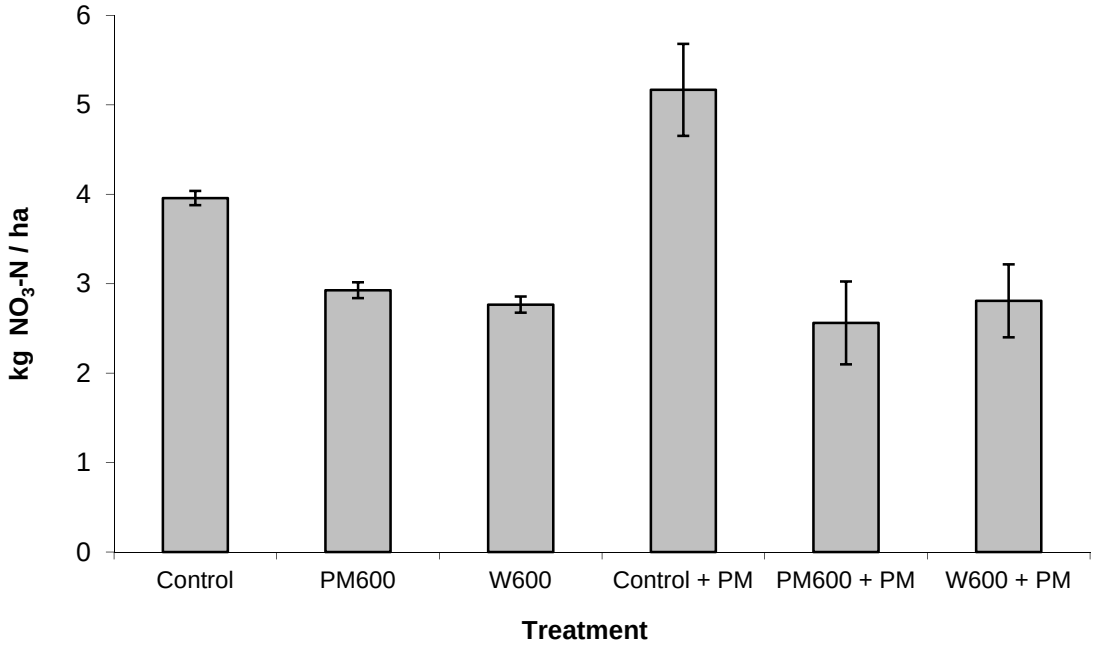
713 Figure 1


(a)
g N2O-N ha-1 hour-1
(b)
kg CO2-C ha-1 hour-1
(c)
g CH4-C ha-1 hour-1
Day
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM

714 Figure 2


g N2O-N ha-1
(a)
kg CO2-C ha-1
(b)
g CH4-C ha-1
(c)
Day
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM

715 Figure 3



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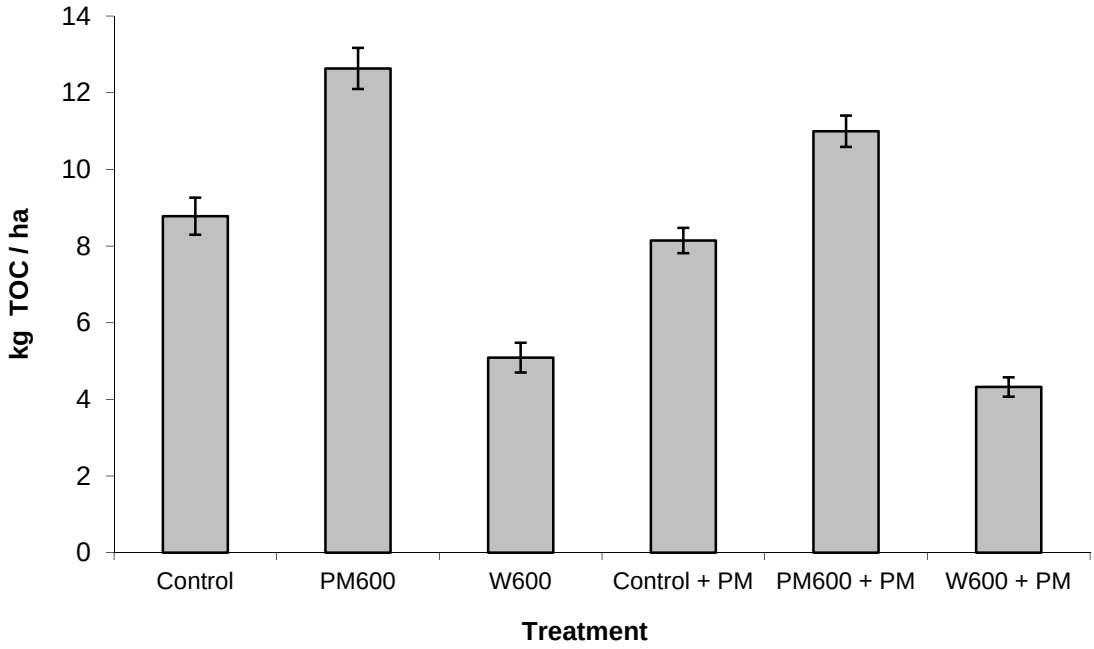
730 Figure 4



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