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5  
6 **The impact of biochar addition on nutrient leaching and soil properties of tillage soil**  
7 **amended with pig manure**

8  
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10  
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15  
16 **ABSTRACT**

17 The application of pig manure to a tillage soil can result in pollution of surface and  
18 groundwater bodies. Countries in the European Union (EU) are required to comply with the  
19 Water Framework Directive, which states that all EU countries should attain at least 'good  
20 status' surface and ground water quality by 2015. Amendment of soil with biochar has  
21 previously been shown to reduce nutrient leaching and improve soil properties. The objectives of  
22 this laboratory study were to investigate if the application of two types of biochar at a rate of 18 t  
23 ha<sup>-1</sup>: (1) reduced leaching of carbon (C), nitrogen (N) and phosphorus (P) from a low P Index

24 tillage soil amended with pig manure and (2) affected the soil properties before and after pig  
25 manure application. Three treatments were examined: (1) non-amended soil (the study control),  
26 (2) soil mixed with biochar from the separated solid fraction of anaerobically digested pig  
27 manure and (3) of soil mixed with biochar from Sitka Spruce. Columns, filled with sieved soil  
28 (<2 mm) and biochar (<2 mm), were incubated for 30 weeks at 10 °C and 75 % relative humidity  
29 and leached with 160 mL distilled water per week. Pig manure, equivalent to 170 kg N ha<sup>-1</sup> and  
30 36 kg P ha<sup>-1</sup>, was applied to half of the columns in each treatment after 10 weeks of incubation.  
31 Leachate from each soil column was analysed weekly, while soil properties were examined by  
32 destructively sampling columns every 10 weeks. Amendment with pig manure biochar increased  
33 the Morgan's P content of the soil, while leaching of P and C also increased, indicating the  
34 unsuitability of pig manure biochar as an amendment to soils which may be used as pig manure  
35 spreadlands. However, the addition of wood biochar increased soil water, C and organic matter  
36 contents, while reducing nitrate and organic C leaching. The addition of wood-derived biochar to  
37 tillage soil which will receive pig manure may be justifiable, as it reduces nutrient leaching from  
38 the soil, sequesters C and may allow for higher application rates of pig manure.

39

40 Keywords: black carbon, water framework directive, nitrate, landspreading, phosphorus, carbon

41

## 42 **1. Introduction**

43 The European Union (EU) Water Framework Directive (WFD) (2000/60/EC; EC, 2000)  
44 aims to achieve at least 'good status' of all surface and groundwater by 2015. To meet this  
45 objective, Programmes of Measures (POM) must be implemented in all EU member states. In  
46 Ireland, POM are enacted by the Nitrates Directive (91/676/EEC; EEC, 1991), which limits the

47 magnitude and timing of inorganic fertilizer and organic manure applications to land. To address  
48 the requirements of the WFD, the quantity of livestock manure which can be applied to land  
49 cannot exceed  $170 \text{ kg ha}^{-1} \text{ year}^{-1}$  for nitrogen (N) and  $49 \text{ kg ha}^{-1} \text{ year}^{-1}$  for phosphorus (P). This  
50 limit is dependent on soil test phosphorus (STP; based on plant available Morgan's P (Pm))  
51 concentration in the soil. The Soil P Index is used to categorise STP concentrations, with a range  
52 from Soil P Index 1 (deficient in STP) to 4 (excessive STP) (Schulte et al., 2010). The amount by  
53 which these application limits can be exceeded will be reduced gradually to zero by January 1,  
54 2017. Many grassland soils which have previously been used as spreadlands for pig manure are  
55 likely to have become high in STP and, therefore, be unsuitable for this purpose in the future  
56 (Hackett, 2007). The implication of this will be that pig farmers may require additional  
57 spreadlands than is currently the case, thereby increasing the need for pig slurry export, thus  
58 increasing costs. The addition of biochar to soil may provide an answer to this problem. Previous  
59 studies have shown that biochar can increase the nutrient retention capacity of soil, reducing  
60 leaching, sequestering carbon (C), improving soil properties, and allowing for higher application  
61 rates of organic manures (Laird et al., 2010a, 2010b; Singh et al., 2010).

62 Biochar is produced from the pyrolysis of organic feedstocks such as wood and crop  
63 residues, sludge, digestate and manures (Troy et al., 2013a). During the pyrolysis process, the  
64 organic portion of the feedstocks is converted to solid (char), liquid (pyrolysis oil) and gaseous  
65 fractions. When applied to soil as a soil conditioner, the char is known as biochar. Biochar  
66 addition to soil has been shown to influence soil physico-chemical properties, such as pH,  
67 porosity, bulk density, pore-size distribution, water holding capacity, soil surface area, drainage  
68 and aeration (Glaser et al., 2002; Chan et al., 2007; Downie et al., 2009; Laird et al., 2010b). The  
69 response of soils to biochar amendment depends on the biochar properties, soil properties, and on

70 further nutrient addition to soil (Lehmann and Rondon, 2006). The feedstock and pyrolysis  
71 conditions used to produce the biochar can also have a significant impact on the effects of the  
72 biochar when applied to soils; differences in feedstock nutrient concentrations can persist even  
73 after pyrolysis (DeLuca et al., 2009), while the pyrolysis temperature can also affect the  
74 concentrations of these nutrients (Chan et al., 2008; Gaskin et al., 2008).

75 Previous studies have documented reduced leaching from soil amended with biochar  
76 (Lehmann et al., 2003, Novak et al., 2009; Laird et al., 2010a; Singh et al., 2010). The retention  
77 of nutrients in the soil has been attributed to the higher sorption capacity of biochar (Novak et  
78 al., 2009; Singh et al., 2010), increased water retention, which reduces leaching of mobile  
79 nutrients, increased growth rate of microorganisms (Ishii and Kadoya, 1994; Steiner et al.,  
80 2008b), and alterations to the N cycling process within the soil (Steiner et al., 2008a; DeLuca et  
81 al., 2009; Clough et al., 2010; Laird et al., 2010a; Clough et al., 2013). However, these studies  
82 mostly occurred in tropical and subtropical areas. Research on biochar application to soils in  
83 temperate regions is severely lacking (Verheijen et al., 2010). There is also a paucity of data  
84 concerning biochar from feedstocks other than wood, and future research needs to focus on  
85 biochar production from crop residues, manures, sewage and green wastes (Verheijen et al.,  
86 2010). The use of manure biochars may have additional benefits to farmers. The addition of  
87 biochar from chicken manure has been shown to increase N availability in soil (Chan et al.,  
88 2008). The P and potassium (K) contents of manure are almost completely recovered in the  
89 biochar, leading to higher concentrations in the biochar than in the original manure (Ro et al.,  
90 2010). Due to its higher N, P and K concentrations, biochar from manure may offer additional  
91 benefits as a low-grade fertilizer, even when used without other forms of fertilisation.

92           Therefore, the objectives of this laboratory study were to investigate if biochar derived  
93 from both pig manure and wood (Sitka Spruce): (1) reduced nutrient leaching from a low P Index  
94 tillage soil amended with pig manure and (2) affected the soil properties before and after pig  
95 manure application.

96

## 97 **2. Materials and Methods**

98

### 99 **2.1. Soil and Biochar**

100           Surface soil to a depth of 0.2 m was collected from a tillage farm near Fermoy, County  
101 Cork. The soil was free-draining and classified as an Acid Brown Earth (Regan et al., 2010). A  
102 low P Index tillage soil was chosen as this type of soil will be the most likely recipient of pig  
103 manure, once the new fertiliser application limits are in force. The soil was air dried, passed  
104 through a 2 mm sieve, and mixed to ensure homogeneity. This unstructured soil consisted of 57  
105 % sand, 29 % silt and 14 % clay, giving it a sandy loam texture.

106           Two types of biochar were used for this study: pig manure biochar and wood biochar. Pig  
107 manure biochar was produced from the solid fraction of separated pig manure after anaerobic  
108 digestion, which was then mixed with Sitka Spruce sawdust (at a 4:1 ratio by wet weight), and  
109 subjected to slow pyrolysis in a laboratory pyrolysis reactor operated at 600 °C, similar to the  
110 methods described in Troy et al. (2013a). Wood biochar was produced by slow pyrolysis of Sitka  
111 Spruce wood in a large-scale pyrolysis reactor at 600 °C. Both biochars were ground to pass  
112 through a 2 mm sieve. The characteristics of the biochars are given in Table 1.

113

### 114 **2.2. Preparation of Soil Columns**

115 The experiment was conducted in 0.3 m-deep and 0.104 m-internal diameter PVC  
116 columns, which were sealed at the base with perforated PVC end-caps to allow for the outflow of  
117 leachate, ensuring the soil remained free-draining. The three treatments (n=8), examined over a  
118 study duration of 30 weeks, were: (1) non-amended soil (the study control), (2) soil mixed with  
119 pig manure biochar (PM600) and (3) of soil mixed with wood biochar (W600). Batches of air-  
120 dried sieved soil (<2 mm) were mixed by hand with sieved biochar (<2 mm) at biochar  
121 application rates equivalent to 18 t ha<sup>-1</sup> to a soil depth of 0.2 m. Prior to placing the soil in the  
122 columns, distilled water was added to bring the mixtures to a water content (WC) of  
123 approximately 26 % (the WC of the soil in the field at the time of sampling) and the mixture was  
124 thoroughly mixed by hand. Pea gravel, 5 – 10 mm in size, was placed at the base of each column  
125 to a depth of 0.05 m, and was overlain by soil mixtures (with a dry bulk density of 1.1 g cm<sup>-1</sup>) to  
126 a depth of 0.2 m. The soil was packed in 0.05-m-deep increments to ensure uniform packing of  
127 soil. The characteristics of the soil and the soil and biochar mixes before leaching are given in  
128 Table 2.

129

### 130 **2.3. Soil Column Incubation and Leaching**

131 The temperature (10 °C) and relative humidity (75 %) at which the columns were stored  
132 were based on climatic conditions in Ireland (Walsh, 2012). All columns were leached with 160  
133 mL of distilled water, applied twice weekly in two 80-mL doses over two hours, each week for  
134 30 weeks. The rate of water addition was designed to simulate a weekly total rainfall of 19 mm  
135 per week; 980 mm per year, which is in the mid-range of average yearly precipitation in Ireland  
136 (Walsh, 2012). On week 10 of the study, pig manure, collected from an integrated pig farm in  
137 Fermoy, Co. Cork, was applied to the surface of four columns of each treatment at a rate

138 equivalent to 170 kg N ha<sup>-1</sup> and 36 kg P ha<sup>-1</sup>. The treatments which received pig manure were  
139 then known as Control+PM, PM600+PM and W600+PM. The pig manure had a dry matter  
140 content of 3 % and total N (TN), ammonium (NH<sub>4</sub>-N) and total P (TP) contents of 2.94, 1.74 and  
141 0.62 kg m<sup>-3</sup>, respectively.

142

#### 143 **2.4. Leachate Analyses**

144 A sample of leached water was collected from the base of each column once per week for  
145 analysis. Unfiltered leachate samples were analysed for total organic C (TOC) and TN using a  
146 BioTector TOC TN TP Analyzer (BioTector Analytical Systems Limited, Cork, Ireland). Sub-  
147 samples of leachate were passed through a 0.45 µm filter to remove particulates and analysed  
148 colorimetrically for total oxidised N, NH<sub>4</sub>, nitrite (NO<sub>2</sub>) and dissolved reactive P (DRP) using a  
149 nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate was calculated by  
150 subtracting NO<sub>2</sub> from total oxidised N. Filtered and unfiltered samples were tested for total  
151 dissolved P (TDP) and TP using acid persulfate digestion. Particulate P (PP) was calculated by  
152 subtracting TDP from TP. Dissolved unreactive P (DUP) was calculated by subtracting DRP  
153 from TDP.

154

#### 155 **2.5. Analysis of Soil and Biochar Properties**

156 Columns (n=4) from each treatment were destructively sampled at time increments of 10,  
157 20 and 30 weeks. Analyses were conducted at depth increments of 0-0.05, 0.05-0.1, and 0.1-0.2  
158 m below the soil surface. The soil from each depth increment was air-dried and sieved to a  
159 particle size of 2 mm, or less, before analyses. The organic matter (OM) content of the soil was  
160 determined using the loss on ignition test (B.S.1377-3; BSI, 1990). Bulk density ( $\rho_b$ ) and total



161 porosity ( $n$ ) were calculated according to Haney and Haney (2010). Water-filled pore space  
162 (WFPS) was estimated from WC, bulk density, and total porosity in accordance with Haney and  
163 Haney (2010):

$$164 \quad WFPS = \frac{WC * \rho_b}{n}$$

165 Water extractable P (WEP) was measured by shaking 5 g of soil in 25 mL of distilled  
166 water for 30 min, filtering (0.45  $\mu$ m) the supernatant water and determining P colorimetrically  
167 (McDowell and Sharpley, 2001). Morgan's P was determined using Morgan's extracting solution  
168 (Morgan, 1941). Soil total C and TN were determined by high temperature combustion using a  
169 LECO Truspec CN analyser (LECO Corporation, St. Joseph, MI, USA). Water soluble organic C  
170 (WSOC) was determined by shaking a 1:10 extract of soil/biochar-to-deionised water (w/v) for  
171 30 min (Yanai et al., 2007), filtering (0.45  $\mu$ m) the supernatant water and determining TOC using  
172 a BioTector TOC TN TP Analyzer (BioTector Analytical Systems Limited, Cork, Ireland).

173 The ability of the biochar and soil to adsorb P was assessed using a batch experiment  
174 (Fenton et al., 2009; O'Flynn et al., 2013). In graduated containers, 90 ml of ortho-phosphorus  
175 ( $PO_4$ -P) solutions, prepared using dissolved potassium phosphate ( $KH_2PO_4$ ) in distilled water,  
176 ranging in concentration from 3 to 30 mg P L<sup>-1</sup>, were added to 5 g samples of biochar or soil. The  
177 mixtures were shaken using an end-over-end shaker for 24 hours. Sub-samples of the supernatant  
178 were passed through 0.45  $\mu$ m filters and analysed colorimetrically for DRP using a nutrient  
179 analyser. A Langmuir isotherm was used to estimate the mass of P adsorbed per mass of the soil  
180 or biochar (Fenton et al., 2009):

$$181 \quad \frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{b}$$

182 where  $C_e$  is the concentration of P in solution at equilibrium ( $\text{mg L}^{-1}$ ),  $x/m$  is the mass of P  
183 adsorbed per unit dry weight of soil or biochar ( $\text{g kg}^{-1}$ ),  $a$  is a constant related to the binding  
184 strength of molecules onto soil or biochar, and  $b$  is the maximum adsorption capacity ( $\text{g kg}^{-1}$ ).

185

## 186 **2.6. Statistical Analysis**

187 Soil and leachate data were analyzed using the Statistical Analyses System (SAS  
188 Institute, 2004) with each column as the experimental unit. For all analyses, statistical  
189 significance was given as  $p < 0.05$ . Water content, OM, Morgan's P, WEP, N and C contents, and  
190 C:N ratio were analysed as repeated measures using the MIXED procedure of SAS with Tukey-  
191 Kramer adjustment for multiple comparisons. The dependent variables were: WC, OM,  
192 Morgan's P, WEP, N and C contents, and C:N ratio. For all the above analyses, the fixed effects  
193 were: treatment, week, depth and column. Comparison of cumulative leaching of TN,  $\text{NO}_3$ ,  $\text{NO}_2$ ,  
194  $\text{NH}_4$ , TP, TDP, DRP, DUP, PP and TOC (between both week 1 and 30, and week 11 and 30) was  
195 performed using the MIXED procedure in SAS. Total nitrogen,  $\text{NO}_3$ ,  $\text{NO}_2$ ,  $\text{NH}_4$ , TP, TDP, DRP,  
196 DUP, PP and TOC were the dependent variables. Treatment was included as a fixed effect. Total  
197 organic C and  $\text{NO}_3$  were analysed as repeated measures using the MIXED procedure of SAS  
198 with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were: TOC  
199 and  $\text{NO}_3$ . The fixed effects were: treatment, week and column.

200

## 201 **3. Results and Discussions**

202

### 203 **3.1. Water Content and Organic Matter**

204 The columns remained free draining throughout the experiment. No leachate passed  
205 through the columns on the first week of leaching. On week 2, the leachate volume collected was  
206  $133\pm 15.7$ ,  $89\pm 9.0$  and  $75\pm 6.2$  mL for Control, PM600 and W600 columns, respectively. From  
207 week 5 onwards, except for week 11 when the manure was added, the average leachate volume  
208 was greater than 147 mL for all columns. The average leachate volume collected from week 12-  
209 30 was  $151\pm 2.2$ ,  $152\pm 2.4$  and  $154\pm 1.8$  mL for Control, PM600 and W600, respectively, while  
210 the averages from week 12-30 were  $151\pm 1.6$ ,  $152\pm 1.5$  and  $153\pm 1.9$  for Control+PM,  
211 PM600+PM and W600+PM, respectively.

212 The WC of all treatments increased significantly between week 0 and week 10 ( $p < 0.01$ )  
213 (Figure 1). The WC on week 0 was between 25.5 and 26.7 %, but by week 10, the WC had risen  
214 to  $>31$  % for all treatments at all sampling depths. After week 10, there was no further significant  
215 increase in WC ( $p > 0.05$ ). There was an increase in WC with sampling depth: soil sampled at the  
216 0.1–0.2 m depth had a significantly higher WC than soil at the 0–0.05 m depth for all treatments  
217 on every sampling week ( $p < 0.0001$ ). There was an increase in the WC of the biochar-amended  
218 treatments when compared with the Control on most sampling weeks. On week 30, the WC of  
219 biochar-amended treatments at each sampling depth was 7.2–13.6 % greater than that at the  
220 corresponding sampling depth of the Control. Previous studies have shown that biochar-amended  
221 soil can have a higher water holding capacity than unamended soil due to blockages of soil pores by  
222 the smallest sized fraction of biochar, increased net surface area with biochar addition, or the  
223 increased OM content of biochar-amended soils (Downie et al., 2009; Laird et al., 2010b;  
224 Streubel et al., 2011). Soil WC can impact many soil processes, including mineralization, plant  
225 uptake, leaching and denitrification (Porporato et al., 2003). The addition of pig manure had no  
226 effect on soil WC ( $p > 0.05$ ).

227 The OM contents of the soils are shown in Figure 2. The biochar-amended soils had  
228 significantly higher OM contents than the Control on the majority of sampling days and  
229 sampling depths ( $p < 0.05$ ). There was no difference in OM content with depth for any treatment  
230 on any sampling week ( $p > 0.05$ ). The addition of pig manure to the columns had no effect on the  
231 OM content of the soil on week 20 or 30 ( $p > 0.05$ ). In general, there was a decrease in OM  
232 content from week 0 to week 30 ( $p < 0.05$ ).

233

### 234 **3.2. Carbon Leaching and Soil Content**

235 The quantity of TOC leached from the treatments is shown in Figure 3. The total amount  
236 of TOC leached from PM600 over the 30-week experiment were greater than the Control  
237 ( $p < 0.001$ ) and W600 ( $p < 0.001$ ). The WSOC of PM600 was higher than the Control and W600  
238 (Table 2), indicating more mobile C in the pig manure biochar. Biochar from wood has a higher  
239 aromaticity than biochar from manures due to the higher lignin and cellulose content of the  
240 wood. Biochars produced from manures and crop residues are more readily degradable (Collison  
241 et al., 2009). Therefore, a greater proportion of C in the pig manure biochar is likely to be lost  
242 through mineralisation and leaching, compared with the wood biochar. Gaskin et al. (2008), in a  
243 study using biochars from both pine chips and poultry manure, produced at 500 °C, found that  
244 leaching of total dissolved C from the manure-based biochar was seven times higher than that  
245 leached from the wood-based biochar (0.85 and 0.12 g kg<sup>-1</sup>, respectively).

246 There was significantly less TOC being leached from W600, compared with the Control  
247 ( $p < 0.001$ ), on weeks 2-18. This occurred despite the fact that W600 had a higher WSOC content  
248 than the Control at the beginning of the experiment (Table 2). The reduction in TOC leaching in  
249 this study is likely to be due to enhanced mineralisation in the wood-biochar-amended

250 treatments. Some of the organic C may also be used as an electron donor for denitrification. This  
251 reduction in TOC leaching is not seen in the PM600 treatment compared with the Control, due to  
252 the high WSOC of this treatment (Table 2). Laird et al. (2010a) also found reduced TOC  
253 leaching through the addition of wood-based biochar to soil compared with unamended soil.  
254 They suggested that TOC leaching was reduced through the ability of wood biochar to adsorb  
255 organic C. However, this was not the case in the current study, as the cation exchange capacity  
256 (CEC) of the biochar-amended treatments was similar to that of the Control (Table 2). Pig  
257 manure addition did not result in increased TOC leaching ( $p>0.05$ ) in the manure-amended  
258 treatments.

259 The C content of the biochar-amended soils was higher than the Control soil on every  
260 sampling week (Table 3). The addition of pig manure did not increase the soil C content  
261 ( $p>0.05$ ). In a companion study using the same soil columns, Troy et al. (2013b) found that  
262 between 44 and 54 % of the total applied manure C was mineralised to  $\text{CO}_2$  in the 28 days after  
263 manure application. The soil C:N ratio in the W600 treatment was generally greater than that of  
264 the Control on all sampling weeks and depths ( $p<0.05$ ) (Table 3). The soil C:N ratio of the  
265 PM600 soil was also greater than that of the Control on the majority of sampling days and  
266 depths. The addition of pig manure did not increase the soil C:N ratio in the manure-amended  
267 treatments, except for the 0-5 cm depth in W600+PM on week 20 (Table 3).

268

### 269 **3.3. Nitrogen Leaching and Soil Content**

270 Generally, there were no significant differences in soil N content between the treatments  
271 on any time of destructive sampling (Table 3). The addition of pig manure did not increase the  
272 soil N content in the manure-amended treatments ( $p>0.05$ ).

273 The total amount of N leached from the soil columns over the 30-week experiment is  
274 shown in Figure 4. Over 90 % of the total mass of TN leached from the columns over the entire  
275 study duration was in the form of NO<sub>3</sub>. Following pig manure application, between weeks 10 and  
276 11, there was a significant increase in the total amount of TN leached from the manure-amended  
277 columns compared with the other columns (p<0.001 for all three treatments). Of the 144 mg of  
278 pig TN added as pig manure, 66-70 mg had leached by week 30, with no significant differences  
279 between treatments.

280 The amount of NO<sub>3</sub> and NO<sub>2</sub> in the leachate exiting the soil columns each week is shown  
281 in Figure 5 (a) and (b). High concentrations of NO<sub>3</sub> were leached from all treatments for the first  
282 number of weeks, peaking at >110 mg L<sup>-1</sup> for all treatments on week 3. There was a swift decline  
283 in the concentration of NO<sub>3</sub> in the leachate after week 4, and by week 9, the concentration of  
284 NO<sub>3</sub> in the leachate had decreased to <35 mg L<sup>-1</sup> for all treatments and remained below this  
285 value for all the non-manure-amended columns for the duration of the experiment. Drying and  
286 re-wetting of soil during the construction of the columns may have caused a burst in microbial  
287 activity and a sharp increase in C and N mineralisation (Van Gestel et al., 1991; Bengtsson et al.,  
288 2003; Borken and Matzner, 2009), resulting in surplus available NH<sub>4</sub> and high levels of  
289 nitrification. The soil used in this experiment also had a low C:N ratio of 8.2. Soil with C:N  
290 ratios below 20 can be characterised as having a surplus of available NH<sub>4</sub> for nitrification  
291 (Bengtsson et al., 2003).

292 Biochar amendment to the soil reduced the amount of NO<sub>3</sub> leached from the columns by  
293 24 and 26 %, respectively, for PM600 and W600, compared with the Control. The reduction in  
294 NO<sub>3</sub> leached per week from the biochar-amended soils was only significant (p<0.05) in the first  
295 12 weeks of the study. The application of pig manure resulted in a peak in the leaching of NO<sub>3</sub>

296 (Figure 5a), which reached maximum values for all treatments on weeks 17-18. For 4 weeks  
297 after pig manure application, PM600+PM and W600+PM leached significantly less NO<sub>3</sub> than the  
298 Control+PM. The amount of NO<sub>2</sub> leaching was small when compared with NO<sub>3</sub>. The  
299 concentration of NO<sub>2</sub> in the leachate was <0.1 mg L<sup>-1</sup> from week 2-9. This corresponds with the  
300 peak in NO<sub>3</sub> leaching (Figure 5a). This low amount of NO<sub>2</sub> leached from all treatment may also  
301 be due to the drying and re-wetting effect described earlier. The burst of microbial activity  
302 caused by re-wetting may have ensured that almost complete nitrification to NO<sub>3</sub> occurred for  
303 the first 9 weeks. The quantity of the NO<sub>2</sub> leached increased significantly from week 9 to week  
304 18 across all treatments, irrespective of whether soil was amended with biochar or pig manure.  
305 This temporary build-up of NO<sub>2</sub> in the soil may be due to a time lag between NO<sub>3</sub> reduction and  
306 NO<sub>2</sub> reduction during the denitrification process, due to the preference of denitrifiers to NO<sub>3</sub>,  
307 even when both NO<sub>2</sub> and NO<sub>3</sub> are present (Rivett et al., 2008).

308         The amount of NH<sub>4</sub> leached was low compared with NO<sub>3</sub>. This indicates high  
309 nitrification across all treatments and the high CEC of the soil. Throughout the leaching  
310 experiment, the quantity of NH<sub>4</sub> leached from each column on most sampling weeks remained  
311 between 0.005 and 0.015 mg. There was no significant difference between the amount of NH<sub>4</sub>  
312 leached from the columns which received manure and those which did not. There was also no  
313 difference between amount of NH<sub>4</sub> leached from the biochar-amended columns and the Control  
314 (p>0.05).

315         Many different reasons have been given for reductions in N leaching due to biochar  
316 addition to soil, including adsorption of NH<sub>4</sub> or NO<sub>3</sub> onto biochar, and enhanced immobilisation  
317 and denitrification of N (Clough et al., 2013). Laird et al. (2010a) attributed significantly reduced  
318 NO<sub>3</sub> leaching from pig manure-amended soil + biochar treatments compared with manure-

319 amended soil-only treatments to the adsorption of  $\text{NH}_4$  and soluble organic compounds within  
320 the soil, thus inhibiting mineralisation of organic N and/or nitrification of  $\text{NH}_4$ . The reductions in  
321  $\text{NO}_3$  leaching were not immediate; only after 23 weeks of biochar weathering was there any  
322 reduction in  $\text{NO}_3$  leaching (Laird et al., 2010a). Other studies have also shown the ability of  
323 biochar to adsorb  $\text{NH}_4$  (Dempster et al., 2012; Yao et al., 2012). However, the rationale given for  
324 the ability of biochar to enhance  $\text{NH}_4$  adsorption in soil is due to its higher CEC (Clough et al.,  
325 2013). However, the CEC of the biochar-amended soils in the current study was found to be  
326 similar to that of the Control (Table 2), and therefore, a reduction in  $\text{NO}_3$  leaching was unlikely,  
327 initially at least, to be caused by  $\text{NH}_4$  adsorption. The CEC of fresh biochar has previously been  
328 shown to be low (Busscher et al., 2010; Clough et al., 2010), with only weathered biochar being  
329 shown to have a high CEC due to oxidation and adsorption of other OM in the soil over time  
330 (Liang et al., 2006). The CEC of the biochar-amended treatments in the current study may have  
331 increased over time. However, biochar oxidation, which results in CEC increases, is temperature  
332 dependant (Cheng et al., 2006), and incubation at 10 °C is unlikely to have caused a dramatic  
333 increase in biochar CEC.

334         The reduction in  $\text{NO}_3$  leaching in this study was most likely caused by the impact of  
335 biochar on the rates of nitrification and denitrification within the soil due to (1) nitrification  
336 inhibitors present on unweathered biochar and (2) denitrification loss of  $\text{NO}_3$  due to being  
337 stimulated by higher WFPS and organic C contents in the biochar-amended treatments. In an  
338 incubation study using freshly made biochar, Clough et al. (2010) measured higher soil  $\text{NH}_4$   
339 concentrations in biochar-amended soil after the application of urine, compared with soil  
340 amended with urine only. This increase was attributed to nitrification inhibitors which slowed the  
341 rate of  $\text{NH}_4$  depletion. Unweathered biochar has been shown to contain microbially toxic



342 compounds (e.g. polyaromatic hydrocarbons), some of which may inhibit the *Nitrosomonas*  
343 bacteria responsible for nitrification (Kim et al., 2003; Clough and Condron, 2010). This  
344 inhibition of nitrification, due to toxic compounds is likely to be short-term: Clough et al. (2010)  
345 found that signs of nitrification inhibition had stopped 55 days after soil incubation, as  
346 weathering of the biochar decreased its ability to inhibit nitrification.

347 In general, the presence of anaerobic conditions and organic C as an electron donor  
348 facilitates denitrification (Rivett et al., 2008). In a companion study using the same soil columns,  
349 Troy et al. (2013b) found that nitrous oxide (N<sub>2</sub>O) emissions over a 28-period following manure  
350 addition were 79 and 68 % higher from PM600+PM and W600+PM, respectively, when  
351 compared with Control+PM. The increased WFPS in the biochar-amended columns may have  
352 caused the development of anaerobic zones within the soil, reducing nitrification and increasing  
353 denitrification. The WFPS measured at the 10-20 cm depth on weeks 20 and 30 was 69-72 % for  
354 the Control. The WFPS was 78 % and 77-79 %, respectively, for PM600 and W600. Increasing  
355 the WFPS beyond 60 % causes anaerobic conditions, resulting in reduced aerobic microbial  
356 activity and nitrification, and increased denitrification (Dobbie and Smith, 2001; Porporato et al.,  
357 2003; Bateman and Baggs, 2005; Yanai et al., 2007; Troy et al., 2013b). In an incubation study,  
358 using arable soil fertilised with ammonium nitrate, Dobbie and Smith (2001) found a 30-fold  
359 increase in N<sub>2</sub>O emissions by increasing the WFPS from 60 to 80 %, due to denitrification  
360 attributed to the development of anaerobic zones within the soil. In addition to a higher WFPS,  
361 the WSOC content of the biochar-amended treatments was higher than that of the Control (Table  
362 2), indicating higher organic C availability for denitrification. In a study measuring N<sub>2</sub>O losses  
363 through denitrification from intact soil cores fertilised with NO<sub>3</sub>, Jahangir et al. (2012) found  
364 N<sub>2</sub>O emissions were significantly increased with the addition of dissolved organic C to the soil.

365 They suggested that adding C sources to the subsoil could increase  $\text{NO}_3$  depletion via  
366 denitrification (Jahangir et al., 2012). Despite the increased WSOC of the biochar amended soils  
367 in the current study, leaching of TOC was lower in the W600 treatment than the Control, an  
368 indication that the organic C may have been used as an electron donor for denitrification.

369

### 370 **3.4. Phosphorus Leaching and Soil Content**

371 The amount of DRP, DUP and PP leached from the soil columns over the 30-week study  
372 period is shown in Figure 6. The trend for each treatment is similar with most of the TP leached  
373 from the columns being the dissolved fraction; for most of the weeks, the amount of PP leached  
374 from the columns was less than 0.004 mg per column. The concentration of P leached from the  
375 columns was low, indicating that the soil was P deficient. The maximum adsorption capacity of  
376 the soil was high at  $0.194 \text{ g P kg}^{-1}$ , whereas the maximum adsorption capacity of the wood  
377 biochar was  $0.134 \text{ g P kg}^{-1}$ . Therefore, the addition of the wood biochar to the soil was unlikely  
378 to impact the P absorbency.

379 The pig manure biochar had no capacity to adsorb P, and it had a higher WEP than the  
380 wood biochar (Table 1). Over the 30-week study period, there was significantly more TP  
381 ( $p < 0.001$ ) and TDP ( $p < 0.001$ ) leached from PM600 than the Control or W600. The increase in P  
382 leaching from PM600 was primarily due to increased DRP leaching ( $p < 0.001$ ). This was a result  
383 of higher WEP in the PM600 treatments when compared with the Control and W600 treatments  
384 on all sampling weeks and depths ( $p < 0.001$ ) (Table 4). The PM600 treatments also had  
385 significantly higher Morgan's P values when compared with the Control and W600 treatments  
386 on all sampling weeks and depths ( $p < 0.05$ ) (Table 5). The addition of PM600 caused the soil to  
387 change from a P Index 2 soil (low in STP) to a P index 4 (high STP) soil by week 10. This

388 indicates the unsuitability of this pig manure-derived biochar as an amendment of soil in receipt  
389 of animal manure. By increasing the P Index of the soil, the addition of pig manure-derived  
390 biochar has reduced the amount of manure which can be applied to the soil, thereby further  
391 increasing the costs of pig manure application. The amount of DRP leached from PM600 was  
392 between 0.004 mg and 0.01 mg per column from week 5 to 30. In contrast, the amount of DRP  
393 leached from both the Control and W600 peaked at between 0.002 and 0.004 mg per column per  
394 week between weeks 4 and 14. From week 14 until the end of the experiment, less than 0.002 mg  
395 was leached from the Control and W600 on most sampling weeks.

396         Laird et al. (2010a) found a large reduction in TDP in the leachate from hardwood  
397 biochar-amended columns after pig manure addition, compared with control columns after  
398 manure addition. They attributed this effect to adsorption of ortho-phosphate and organic P  
399 compound by the biochar. Laird et al. (2010b) found increased available P in the soil from the  
400 biochar-amended treatments. However, in the current study, there was no significant difference  
401 between the total quantities of P leached from W600 compared with the Control, irrespective of  
402 whether they were amended with pig manure or not. There was also no difference between the  
403 soil WEP (Table 4) or Morgan's P (Table 5) for the Control and W600 treatments. The soil in  
404 this study was low in WSP and the adsorption capacity of the soil was shown to be higher than  
405 that of the wood biochar. Therefore, no increase in P adsorption was expected. Approximately 30  
406 mg of P was added with the pig manure and the vast majority of this P remained in the soil; there  
407 was no increase in DRP and DUP leaching when manure was added to the treatments ( $p>0.05$ ).  
408 The addition of manure did increase WEP values for PM600+PM on week 20, and Control+PM  
409 and PM600+PM on week 30, compared with the treatments which did not receive manure  
410 (Table.4). The only effect pig manure addition had on Morgan's P was on PM600+PM on week

411 30 (Table 5). However, the addition of pig manure did result in the soil in the 0-5 cm top section  
412 of the Control+PM and W600+PM being classed as P Index 3, compared with P Index 2 in the  
413 Control and W600 treatments.

414

#### 415 **4. Conclusions**

416 The addition of both pig manure biochar and wood biochar to the low P Index tillage soil  
417 had significant effects on soil properties and nutrient leaching. Biochar addition increased the  
418 soil WFPS, OM and C contents, while reducing NO<sub>3</sub> leaching, compared with unamended soil.  
419 Amendment with pig manure biochar increased Morgan's P and WEP contents in the soil due to  
420 the higher concentration of easily extractable P in the manure-derived biochar. Leaching of P and  
421 C increased with the addition of pig manure biochar due to the higher concentrations of water  
422 soluble P and C in the pig manure biochar. Leaching of organic C was reduced in the wood  
423 biochar-amended treatments compared with the unamended soil.

424 The addition of wood-derived biochar to tillage soil which will receive pig manure may  
425 be justifiable, as it reduces nutrient leaching from the soil, while also sequestering C. This may  
426 allow for higher application rates of pig manure, reducing transports distances and costs of pig  
427 manure application. However, the application of pig manure biochar was not deemed  
428 appropriate, as the easily extractable P in this biochar increased Morgan's P, increasing the soil P  
429 Index, and thus reducing the amount of pig manure which can be applied.

430

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575 sorption and leaching of nitrate, ammonium, and phosphate in a sandy soil. *Chemosphere*, 89,  
576 1467–1471.

577 Table 1: Characteristics of the biochars used in the column experiment (mean  $\pm$  SD)

	Pig manure biochar	Wood biochar
Water Content (%)	0.39 $\pm$ 0.044	0.45 $\pm$ 0.039
Organic Matter (%)	72.5 $\pm$ 0.78	97.0 $\pm$ 1.24
Bulk Density (g cm <sup>-3</sup> )	0.19 $\pm$ 0.020	0.18 $\pm$ 0.016
Total N (%)	2.67 $\pm$ 0.042	0.42 $\pm$ 0.024
Total C (%)	62.7 $\pm$ 1.30	82.0 $\pm$ 1.15
Total H (%)	2.60 $\pm$ 0.184	1.82 $\pm$ 0.165
WEP (mg kg <sup>-1</sup> )	112.8 $\pm$ 5.36	3.6 $\pm$ 0.20
pH	9.6 $\pm$ 0.34	9.3 $\pm$ 0.19

578 WEP, water extractable phosphorus

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593 Table 2: Characteristics of the soil (Control), the soil and pig manure biochar mix (PM600) and  
 594 the soil and wood biochar mix (W600) on Week 0 of the experiment before leaching was applied  
 595 (mean  $\pm$  SD)

	Control	PM600	W600
Water Content (%)	26.8 $\pm$ 0.24	25.5 $\pm$ 0.58	25.8 $\pm$ 0.36
Organic Matter (%)	4.62 $\pm$ 0.013	5.44 $\pm$ 0.194	5.40 $\pm$ 0.210
Bulk Density (g cm <sup>-3</sup> )	1.10 $\pm$ 0.010	1.11 $\pm$ 0.009	1.11 $\pm$ 0.017
Total N (%)	0.21 $\pm$ 0.008	0.22 $\pm$ 0.002	0.21 $\pm$ 0.013
Total C (%)	1.75 $\pm$ 0.049	2.18 $\pm$ 0.001	2.48 $\pm$ 0.170
WEP (mg kg <sup>-1</sup> )	0.36 $\pm$ 0.037	0.52 $\pm$ 0.008	0.39 $\pm$ 0.016
Morgan's P (mg L <sup>-1</sup> )	4.84 $\pm$ 0.269	7.53 $\pm$ 0.137	5.04 $\pm$ 0.184
WSOC (mg kg <sup>-1</sup> )	120 $\pm$ 1.9	196 $\pm$ 11.8	163 $\pm$ 9.4
K (cmol L <sup>-1</sup> )	0.36 $\pm$ 0.003	0.39 $\pm$ 0.000	0.33 $\pm$ 0.018
Ca (cmol L <sup>-1</sup> )	7.14 $\pm$ 0.105	6.74 $\pm$ 0.010	7.22 $\pm$ 0.154
Mg (cmol L <sup>-1</sup> )	0.30 $\pm$ 0.004	0.31 $\pm$ 0.004	0.31 $\pm$ 0.004
Na (cmol L <sup>-1</sup> )	0.23 $\pm$ 0.006	0.14 $\pm$ 0.075	0.11 $\pm$ 0.048
CEC (cmol L <sup>-1</sup> )	8.03 $\pm$ 0.111	7.58 $\pm$ 0.079	7.97 $\pm$ 0.084
pH	6.9 $\pm$ 0.20	6.9 $\pm$ 0.18	6.8 $\pm$ 0.04

596 WEP, water extractable phosphorus; WSOC, water soluble organic carbon; CEC, cation  
 597 exchange capacity.  
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606 Table 3: Carbon, nitrogen (%) and C:N ratio for the soil (Control), the soil and pig manure biochar mix  
 607 (PM600) and the soil and wood biochar mix (W600) at 3 depths (cm below surface) over 4 events

Week	Depth	Control	PM600	W600	Pig manure added week 10			s.e.	p
					Control	PM600	W600		
<b><u>Carbon</u></b>									
0		1.75 <sup>a</sup>	2.18 <sup>b</sup>	2.48 <sup>b</sup>				0.072	<0.05
10	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
20	0-5	1.67 <sup>a</sup>	2.14 <sup>b</sup>	2.29 <sup>b</sup>	1.79 <sup>a</sup>	2.17 <sup>b</sup>	2.28 <sup>b</sup>	0.039	<0.001
	5-10	1.72 <sup>a</sup>	2.17 <sup>b</sup>	2.26 <sup>b</sup>	1.66 <sup>a</sup>	2.19 <sup>b</sup>	2.16 <sup>b</sup>	0.039	<0.001
	10-20	1.71 <sup>a</sup>	2.23 <sup>b</sup>	2.35 <sup>b</sup>	1.70 <sup>a</sup>	2.27 <sup>b</sup>	2.26 <sup>b</sup>	0.039	<0.001
30	0-5	1.74 <sup>a</sup>	2.25 <sup>b</sup>	2.11 <sup>b</sup>	1.76 <sup>a</sup>	2.22 <sup>b</sup>	2.29 <sup>b</sup>	0.036	<0.001
	5-10	1.68 <sup>a</sup>	2.19 <sup>b</sup>	2.14 <sup>b</sup>	1.67 <sup>a</sup>	2.25 <sup>b</sup>	2.30 <sup>b</sup>	0.036	<0.001
	10-20	1.70 <sup>a</sup>	2.23 <sup>b</sup>	2.23 <sup>b</sup>	1.66 <sup>a</sup>	2.13 <sup>b</sup>	2.27 <sup>b</sup>	0.036	<0.001
<b><u>Nitrogen</u></b>									
0		0.214	0.220	0.210				0.0064	0.6176
10	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
	10-20	0.172 <sup>a</sup>	0.194 <sup>b</sup>	0.170 <sup>a</sup>				0.0020	<0.001
20	0-5	0.162 <sup>a</sup>	0.179 <sup>a</sup>	0.204 <sup>b</sup>	0.172 <sup>a</sup>	0.185 <sup>ab</sup>	0.174 <sup>a</sup>	0.0029	<0.001
	5-10	0.203 <sup>ab</sup>	0.226 <sup>b</sup>	0.203 <sup>ab</sup>	0.197 <sup>a</sup>	0.211 <sup>ab</sup>	0.200 <sup>a</sup>	0.0029	<0.001
	10-20	0.196	0.219	0.208	0.198	0.218	0.207	0.0029	<0.001
30	0-5	0.204 <sup>ab</sup>	0.216 <sup>b</sup>	0.194 <sup>a</sup>	0.211 <sup>ab</sup>	0.219 <sup>b</sup>	0.203 <sup>ab</sup>	0.0021	<0.001
	5-10	0.190 <sup>a</sup>	0.218 <sup>b</sup>	0.195 <sup>a</sup>	0.187 <sup>a</sup>	0.216 <sup>b</sup>	0.194 <sup>a</sup>	0.0021	<0.001
	10-20	0.191 <sup>a</sup>	0.203 <sup>ab</sup>	0.196 <sup>ab</sup>	0.188 <sup>a</sup>	0.210 <sup>b</sup>	0.196 <sup>ab</sup>	0.0021	<0.001
<b><u>C:N ratio</u></b>									
0		8.18 <sup>a</sup>	9.93 <sup>b</sup>	11.84 <sup>c</sup>				0.052	<0.001
10	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>c</sup>				0.338	<0.001
20	0-5	10.34 <sup>a</sup>	11.92 <sup>ab</sup>	11.25 <sup>a</sup>	10.40 <sup>a</sup>	11.72 <sup>ab</sup>	13.13 <sup>b</sup>	0.233	<0.001
	5-10	8.48 <sup>ab</sup>	9.66 <sup>abc</sup>	11.15 <sup>c</sup>	8.43 <sup>a</sup>	10.36 <sup>bc</sup>	10.82 <sup>c</sup>	0.233	<0.001
	10-20	8.71 <sup>a</sup>	10.19 <sup>b</sup>	11.30 <sup>c</sup>	8.58 <sup>a</sup>	10.43 <sup>bc</sup>	10.90 <sup>bc</sup>	0.233	<0.001
30	0-5	8.53 <sup>a</sup>	10.43 <sup>b</sup>	10.91 <sup>b</sup>	8.35 <sup>a</sup>	10.12 <sup>b</sup>	11.24 <sup>b</sup>	0.161	<0.001
	5-10	8.84 <sup>a</sup>	10.06 <sup>ab</sup>	10.96 <sup>bc</sup>	8.93 <sup>a</sup>	10.43 <sup>b</sup>	11.86 <sup>c</sup>	0.161	<0.001
	10-20	8.90 <sup>a</sup>	10.04 <sup>bc</sup>	11.37 <sup>bc</sup>	8.83 <sup>a</sup>	10.11 <sup>ab</sup>	11.61 <sup>c</sup>	0.161	<0.001

<sup>abc</sup> Means were separated using the Tukey-Kramer adjustment for multiple comparisons. Means, in a row, without a common superscript are significantly different (p<0.05).

609 Table 4: Water Extractable Phosphorus (WEP, mg kg<sup>-1</sup>) contents for the soil (Control), the soil  
 610 and pig manure biochar mix (PM600) and the soil and wood biochar mix (W600) at 3 sampling  
 611 depths (cm below surface) over 4 sampling events

Week	Depth	Pig manure added week 10						s.e.	p
		Control	PM600	W600	Control	PM600	W600		
0		0.364 <sup>a</sup>	0.524 <sup>b</sup>	0.391 <sup>a</sup>				0.0167	<0.05
10	0-5	0.500 <sup>a</sup>	1.774 <sup>b</sup>	0.533 <sup>a</sup>				0.1861	<0.01
10	5-10	0.506 <sup>a</sup>	1.532 <sup>b</sup>	0.515 <sup>a</sup>				0.1861	<0.01
10	10-20	0.576 <sup>a</sup>	1.131 <sup>b</sup>	0.525 <sup>a</sup>				0.1861	<0.01
20	0-5	0.403 <sup>a</sup>	1.670 <sup>b</sup>	0.284 <sup>a</sup>	0.965 <sup>ab</sup>	2.923 <sup>c</sup>	0.682 <sup>a</sup>	0.1371	<0.001
20	5-10	0.398 <sup>a</sup>	1.682 <sup>b</sup>	0.263 <sup>a</sup>	0.387 <sup>a</sup>	1.974 <sup>b</sup>	0.425 <sup>a</sup>	0.1371	<0.001
20	10-20	0.413 <sup>a</sup>	1.861 <sup>b</sup>	0.312 <sup>a</sup>	0.440 <sup>a</sup>	1.942 <sup>b</sup>	0.249 <sup>a</sup>	0.1371	<0.001
30	0-5	0.518 <sup>a</sup>	1.106 <sup>b</sup>	0.482 <sup>a</sup>	0.969 <sup>b</sup>	1.921 <sup>c</sup>	0.881 <sup>ab</sup>	0.4708	<0.001
30	5-10	0.473 <sup>a</sup>	1.213 <sup>b</sup>	0.479 <sup>a</sup>	0.525 <sup>a</sup>	1.333 <sup>b</sup>	0.402 <sup>a</sup>	0.4708	<0.001
30	10-20	0.520 <sup>a</sup>	1.276 <sup>b</sup>	0.509 <sup>a</sup>	0.458 <sup>a</sup>	1.299 <sup>b</sup>	0.475 <sup>a</sup>	0.4708	<0.001

<sup>abc</sup> Means were separated using the Tukey-Kramer adjustment for multiple comparisons. Means, in a row, without a common superscript are significantly different (p<0.05).

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623 Table 5: Morgan's Phosphorus ( $\text{mg L}^{-1}$ ) contents for the soil (Control), the soil and pig manure  
 624 biochar mix (PM600) and the soil and wood biochar mix (W600) at 3 sampling depths (cm  
 625 below surface) over 4 sampling events

Week	Depth	Pig manure added week 10			Control	PM600	W600	s.e.	p
		Control	PM600	W600					
0		4.84 <sup>a</sup>	7.53 <sup>b</sup>	5.04 <sup>a</sup>				0.143	<0.01
10	0-5	5.66 <sup>a</sup>	10.14 <sup>b</sup>	5.06 <sup>a</sup>				0.183	<0.0001
	5-10	5.68 <sup>a</sup>	10.72 <sup>b</sup>	5.28 <sup>a</sup>				0.183	<0.0001
	10-20	5.73 <sup>a</sup>	11.03 <sup>b</sup>	5.44 <sup>a</sup>				0.183	<0.0001
20	0-5	3.88 <sup>a</sup>	29.18 <sup>b</sup>	4.54 <sup>a</sup>	9.03 <sup>a</sup>	36.20 <sup>b</sup>	8.89 <sup>a</sup>	1.445	<0.0001
	5-10	4.28 <sup>a</sup>	32.20 <sup>b</sup>	5.19 <sup>a</sup>	4.36 <sup>a</sup>	35.00 <sup>b</sup>	5.65 <sup>a</sup>	1.445	<0.0001
	10-20	4.67 <sup>a</sup>	32.50 <sup>b</sup>	5.37 <sup>a</sup>	4.24 <sup>a</sup>	36.73 <sup>b</sup>	4.80 <sup>a</sup>	1.445	<0.0001
30	0-5	5.05 <sup>a</sup>	11.63 <sup>b</sup>	5.47 <sup>a</sup>	7.06 <sup>a</sup>	16.05 <sup>c</sup>	8.61 <sup>ab</sup>	0.040	<0.0001
	5-10	5.52 <sup>a</sup>	12.07 <sup>b</sup>	6.08 <sup>a</sup>	5.33 <sup>a</sup>	12.98 <sup>b</sup>	5.89 <sup>a</sup>	0.040	<0.0001
	10-20	5.73 <sup>a</sup>	12.65 <sup>b</sup>	6.38 <sup>a</sup>	5.40 <sup>a</sup>	13.33 <sup>b</sup>	6.16 <sup>a</sup>	0.040	<0.0001

<sup>abc</sup> Means were separated using the Tukey-Kramer adjustment for multiple comparisons. Means, in a row, without a common superscript are significantly different ( $p < 0.05$ ).

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634 **Captions for Figures**

635 Figure 1: Soil water content (WC) at different sampling events and depths. Control = soil only. PM600 =  
636 soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure  
637 between week 10 and 11 are shown with (+PM).

638

639 Figure 2: Soil organic matter (OM) content at different sampling events and depths. Control = soil only.  
640 PM600 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig  
641 manure between week 10 and 11 are shown with (+PM).

642

643 Figure 3: Weekly total of TOC leached from soil columns. Control = soil only. PM600 = soil + pig  
644 manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure between week  
645 10 and 11 are shown with (+PM).

646

647 Figure 4: Total amount of nitrogen leached over the 30-week experiment. Control = soil only. PM600 =  
648 soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure  
649 between week 10 and 11 are shown with (+PM).

650

651 Figure 5: Weekly total of NO<sub>3</sub> (a) and NO<sub>2</sub> (b) leached from soil columns. Control = soil only. PM600 =  
652 soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure  
653 between week 10 and 11 are shown with (+PM).

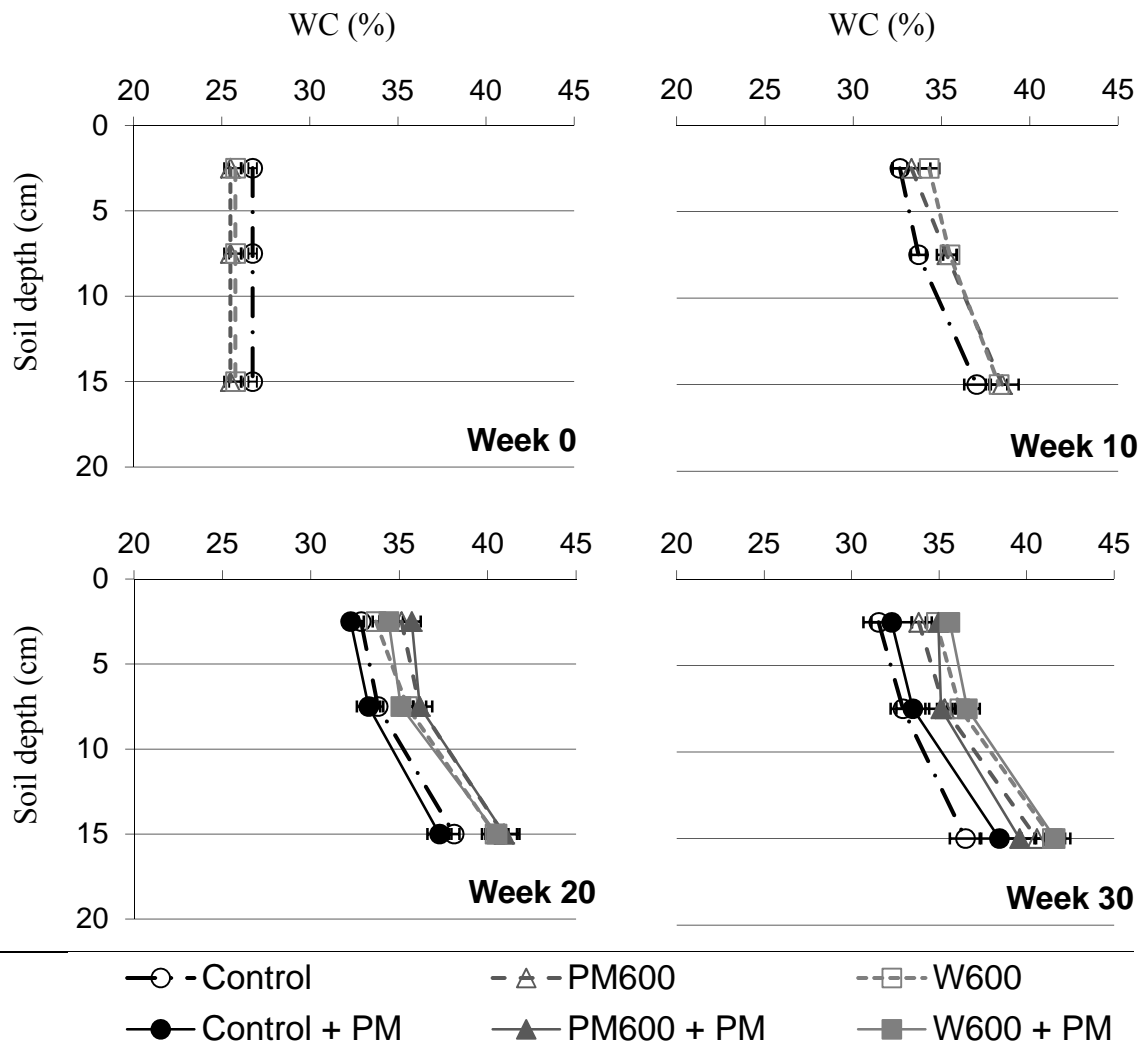
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655 Figure 6: Cumulative amounts of dissolved reactive phosphorus (DRP), dissolved unreactive phosphorus  
656 (DUP) and particulate phosphorus (PP) leached over the 30-week experiment. Control = soil only. PM600  
657 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure  
658 between week 10 and 11 are shown with (+PM).



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660 Figure 1



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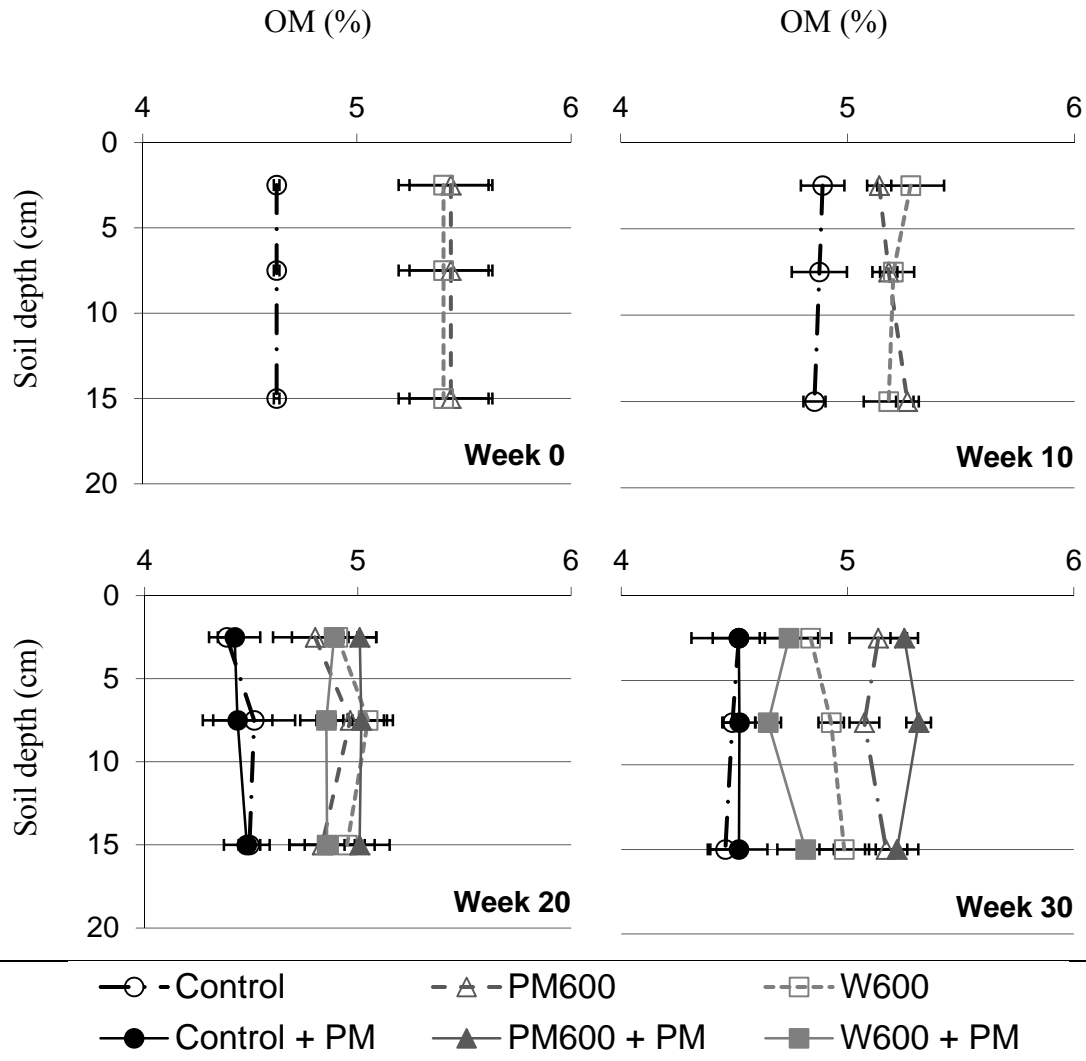
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668 Figure 2



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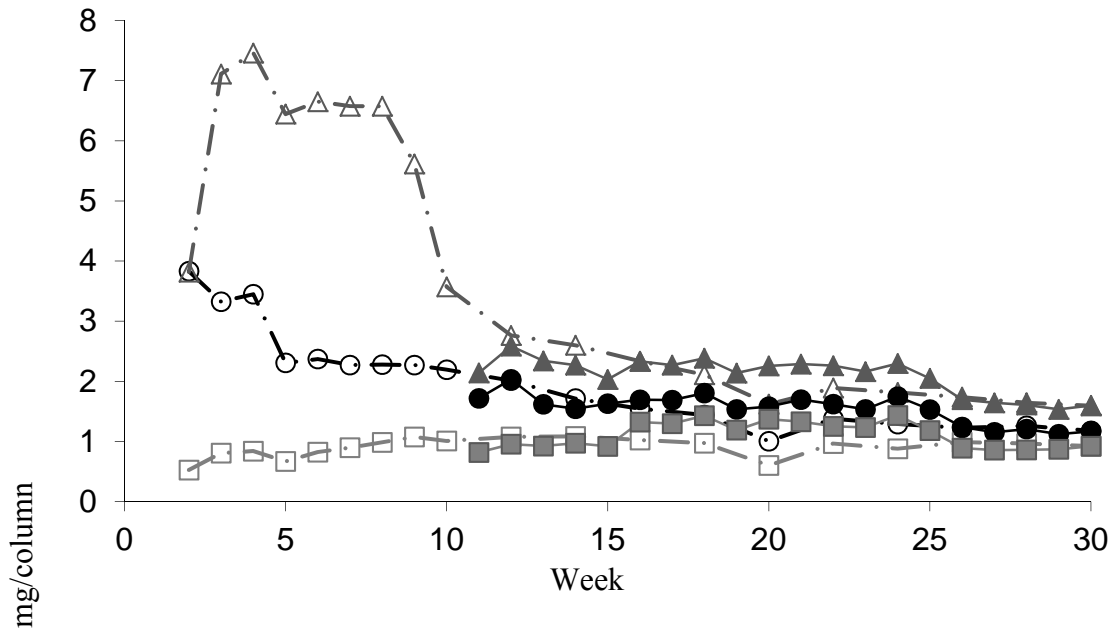
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676 Figure 3



○ - Control                      △ - PM600                      □ - W600  
● Control + PM                  ▲ PM600 + PM                ■ W600 + PM

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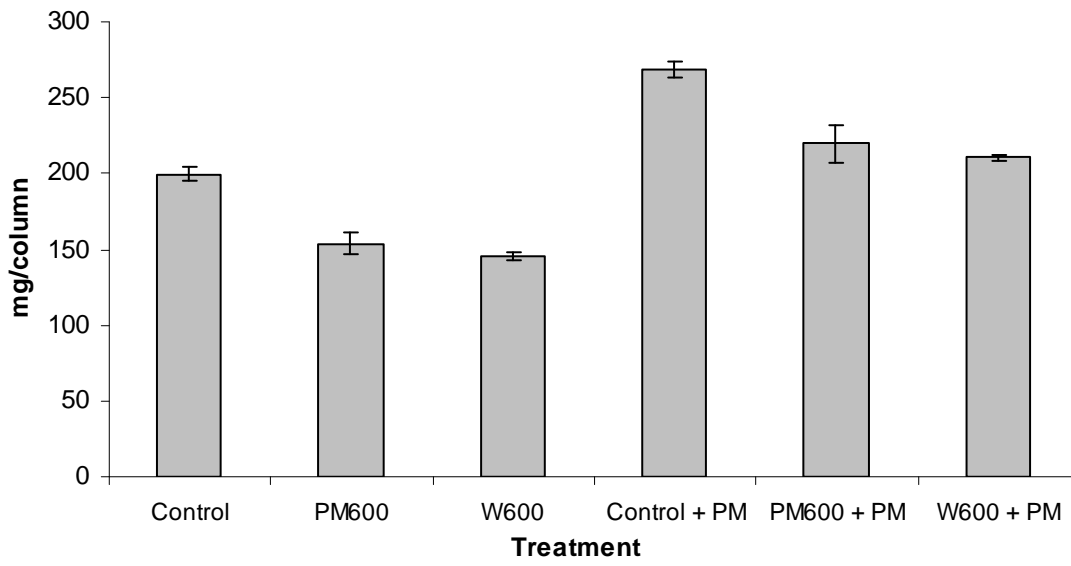
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682 Figure 4

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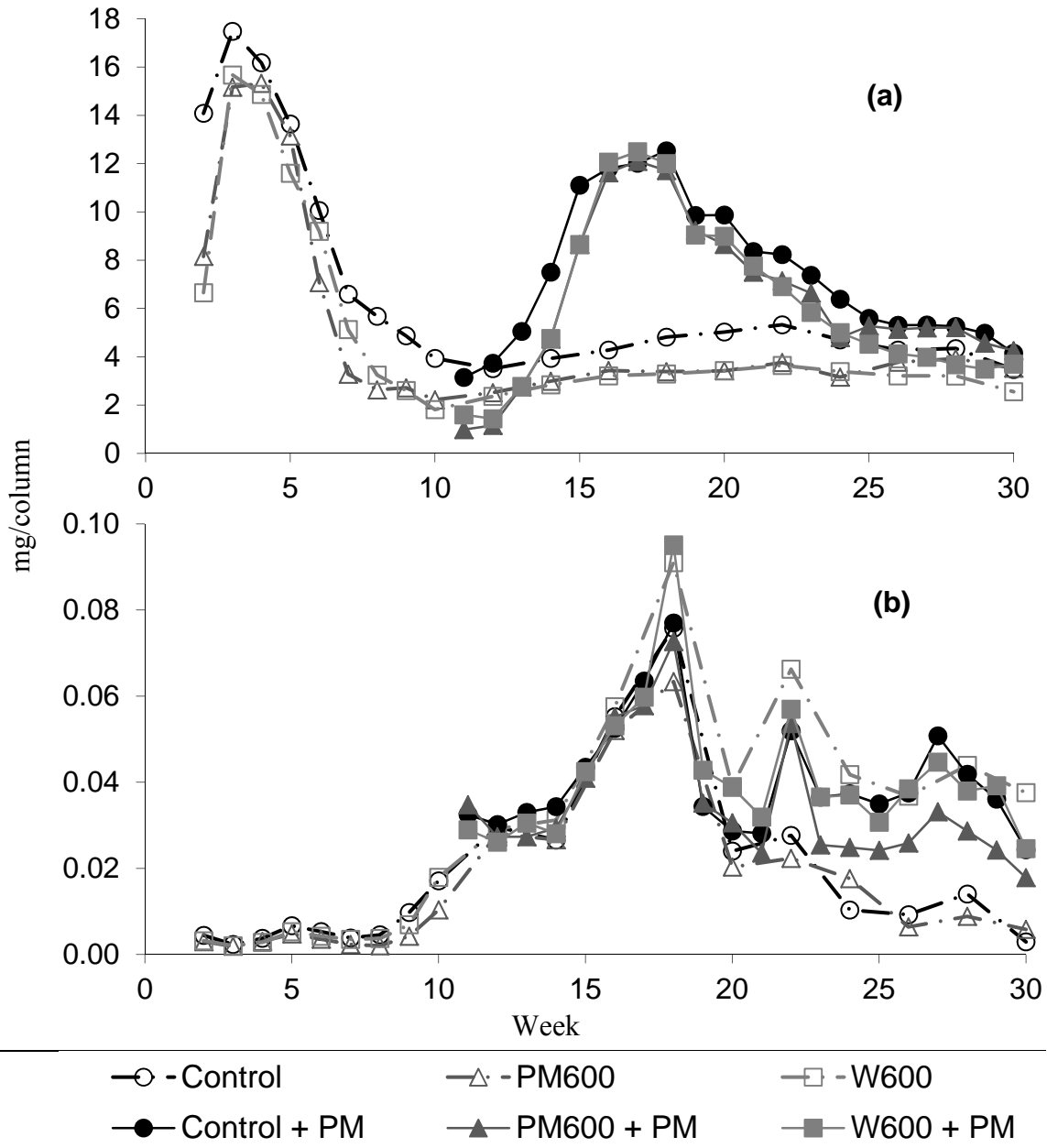
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697 Figure 5



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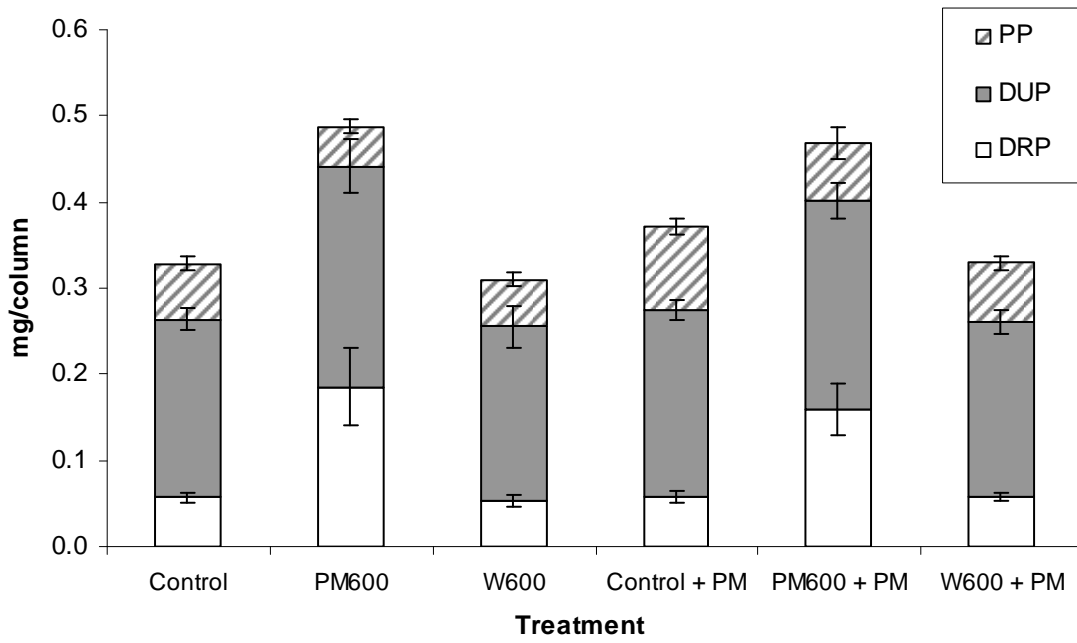
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703 Figure 6



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