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

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ABSTRACT

The application of pig manure to a tillage soil can result in pollution of surface and groundwater bodies. Countries in the European Union (EU) are required to comply with the Water Framework Directive, which states that all EU countries should attain at least 'good status' surface and ground water quality by 2015. Amendment of soil with biochar has previously been shown to reduce nutrient leaching and improve soil properties. The objectives of this laboratory study were to investigate if the application of two types of biochar at a rate of 18 t ha^{-1}: (1) reduced leaching of carbon (C), nitrogen (N) and phosphorus (P) from a low P Index tillage soil amended with pig manure and (2) affected the soil properties before and after pig manure application. Three treatments were examined: (1) non-amended soil (the study control), (2) soil mixed with biochar from the separated solid fraction of anaerobically digested pig manure and (3) of soil mixed with biochar from Sitka Spruce. Columns, filled with sieved soil (<2 mm) and biochar (<2 mm), were incubated for 30 weeks at 10 ^{o}C and 75 % relative humidity and leached with 160 mL distilled water per week. Pig manure, equivalent to 170 kg N ha^{-1} and 36 kg P ha^{-1}, was applied to half of the columns in each treatment after 10 weeks of incubation. Leachate from each soil column was analysed weekly, while soil properties were examined by destructively sampling columns every 10 weeks. Amendment with pig manure biochar increased the Morgan's P content of the soil, while leaching of P and C also increased, indicating the unsuitability of pig manure biochar as an amendment to soils which may be used as pig manure spreadlands. However, the addition of wood biochar increased soil water, C and organic matter contents, while reducing nitrate and organic C leaching. The addition of wood-derived biochar to tillage soil which will receive pig manure may be justifiable, as it reduces nutrient leaching from the soil, sequesters C and may allow for higher application rates of pig manure.

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

1. Introduction

The European Union (EU) Water Framework Directive (WFD) (2000/60/EC; EC, 2000) aims to achieve at least 'good status' of all surface and groundwater by 2015. To meet this objective, Programmes of Measures (POM) must be implemented in all EU member states. In Ireland, POM are enacted by the Nitrates Directive (91/676/EEC; EEC, 1991), which limits the magnitude and timing of inorganic fertilizer and organic manure applications to land. To address the requirements of the WFD, the quantity of livestock manure which can be applied to land cannot exceed 170 kg ha^{-1} $year^{-1}$ for nitrogen (N) and 49 kg ha^{-1} $year^{-1}$ for phosphorus (P). This limit is dependent on soil test phosphorus (STP; based on plant available Morgan's P (Pm)) concentration in the soil. The Soil P Index is used to categorise STP concentrations, with a range from Soil P Index 1 (deficient in STP) to 4 (excessive STP) (Schulte et al., 2010). The amount by which these application limits can be exceeded will be reduced gradually to zero by January 1, 2017. Many grassland soils which have previously been used as spreadlands for pig manure are likely to have become high in STP and, therefore, be unsuitable for this purpose in the future (Hackett, 2007). The implication of this will be that pig farmers may require additional spreadlands than is currently the case, thereby increasing the need for pig slurry export, thus increasing costs. The addition of biochar to soil may provide an answer to this problem. Previous studies have shown that biochar can increase the nutrient retention capacity of soil, reducing leaching, sequestering carbon (C), improving soil properties, and allowing for higher application rates of organic manures (Laird et al., 2010a, 2010b; Singh et al., 2010).

Biochar is produced from the pyrolysis of organic feedstocks such as wood and crop residues, sludge, digestate and manures (Troy et al., 2013a). During the pyrolysis process, the organic portion of the feedstocks is converted to solid (char), liquid (pyrolysis oil) and gaseous fractions. When applied to soil as a soil conditioner, the char is known as biochar. Biochar addition to soil has been shown to influence soil physico-chemical properties, such as pH, porosity, bulk density, pore-size distribution, water holding capacity, soil surface area, drainage and aeration (Glaser et al., 2002; Chan et al., 2007; Downie et al., 2009; Laird et al, 2010b). The response of soils to biochar amendment depends on the biochar properties, soil properties, and on further nutrient addition to soil (Lehmann and Rondon, 2006). The feedstock and pyrolysis conditions used to produce the biochar can also have a significant impact on the effects of the biochar when applied to soils; differences in feedstock nutrient concentrations can persist even after pyrolysis (DeLuca et al., 2009), while the pyrolysis temperature can also affect the concentrations of these nutrients (Chan et al., 2008; Gaskin et al., 2008).

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

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

2. Materials and Methods

2.1. Soil and Biochar

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

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

2.2. Preparation of Soil Columns

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

2.3. Soil Column Incubation and Leaching

The temperature (10 ^{o}C) and relative humidity (75 %) at which the columns were stored were based on climatic conditions in Ireland (Walsh, 2012). All columns were leached with 160 mL of distilled water, applied twice weekly in two 80-mL doses over two hours, each week for 30 weeks. The rate of water addition was designed to simulate a weekly total rainfall of 19 mm per week; 980 mm per year, which is in the mid-range of average yearly precipitation in Ireland (Walsh, 2012). On week 10 of the study, pig manure, collected from an integrated pig farm in Fermoy, Co. Cork, was applied to the surface of four columns of each treatment at a rate equivalent to 170 kg N ha^{-1} and 36 kg P ha^{-1}. The treatments which received pig manure were then known as Control+PM, PM600+PM and W600+PM. The pig manure had a dry matter content of 3 % and total N (TN), ammonium (NH_4-N) and total P (TP) contents of 2.94, 1.74 and 0.62 kg m^{-3}, respectively.

2.4. Leachate Analyses

A sample of leached water was collected from the base of each column once per week for analysis. Unfiltered leachate samples were analysed for total organic C (TOC) and TN 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 to remove particulates and analysed colorimetrically for total oxidised N, NH_4, nitrite (NO_2) and dissolved reactive P (DRP) using a nutrient analyser (Konelab 20, Thermo Clinical Labsystems, Finland). Nitrate was calculated by subtracting NO_2 from total oxidised N. Filtered and unfiltered samples were tested for total dissolved P (TDP) and TP using acid persulfate digestion. Particulate P (PP) was calculated by subtracting TDP from TP. Dissolved unreactive P (DUP) was calculated by subtracting DRP from TDP.

2.5. Analysis of Soil and Biochar Properties

Columns (n=4) from each treatment were destructively sampled at time increments of 10, 20 and 30 weeks. 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 organic matter (OM) content of the soil was determined using the loss on ignition test (B.S.1377-3; BSI, 1990). Bulk density (ρ_b) and total porosity (n) were calculated according to Haney and Haney (2010). Water-filled pore space (WFPS) was estimated from WC, bulk density, and total porosity in accordance with Haney and Haney (2010):

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

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

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

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

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

2.6. Statistical Analysis

Soil and leachate data were analyzed using the Statistical Analyses System (SAS Institute, 2004) with each column as the experimental unit. For all analyses, statistical significance was given as $p<0.05$.Water content, OM, Morgan's P, WEP, 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: WC, OM, Morgan's P, WEP, N and C contents, and C:N ratio. For all the above analyses, the fixed effects were: treatment, week, depth and column. Comparison of cumulative leaching of TN, NO_3, NO_2, NH_4, TP, TDP, DRP, DUP, PP and TOC (between both week 1 and 30, and week 11 and 30) was performed using the MIXED procedure in SAS. Total nitrogen, NO_3, NO_2, NH_4, TP, TDP, DRP, DUP, PP and TOC were the dependent variables. Treatment was included as a fixed effect. Total organic C and NO_3 were analysed as repeated measures using the MIXED procedure of SAS with Tukey-Kramer adjustment for multiple comparisons. The dependent variables were: TOC and NO_3. The fixed effects were: treatment, week and column.

3. Results and Discussions

3.1. Water Content and Organic Matter

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

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

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

3.2. Carbon Leaching and Soil Content

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

There was significantly less TOC being leached from W600, compared with the Control ($p<0.001$), on weeks 2-18. This occurred despite the fact that W600 had a higher WSOC content than the Control at the beginning of the experiment (Table 2). The reduction in TOC leaching in this study is likely to be due to enhanced mineralisation in the wood-biochar-amended treatments. Some of the organic C may also be used as an electron donor for denitrification. This reduction in TOC leaching is not seen in the PM600 treatment compared with the Control, due to the high WSOC of this treatment (Table 2). Laird et al. (2010a) also found reduced TOC leaching through the addition of wood-based biochar to soil compared with unamended soil. They suggested that TOC leaching was reduced through the ability of wood biochar to adsorb organic C. However, this was not the case in the current study, as the cation exchange capacity (CEC) of the biochar-amended treatments was similar to that of the Control (Table 2). Pig manure addition did not result in increased TOC leaching ($p>0.05$) in the manure-amended treatments.

The C content of the biochar-amended soils was higher than the Control soil on every sampling week (Table 3). The addition of pig manure did not increase the soil C content ($p>0.05$). In a companion study using the same soil columns, Troy et al. (2013b) found that between 44 and 54 % of the total applied manure C was mineralised to CO_2 in the 28 days after manure application. The soil C:N ratio in the W600 treatment was generally greater than that of the Control on all sampling weeks and depths ($p<0.05$) (Table 3). The soil C:N ratio of the PM600 soil was also greater than that of the Control on the majority of sampling days and depths. The addition of pig manure did not increase the soil C:N ratio in the manure-amended treatments, except for the 0-5 cm depth in W600+PM on week 20 (Table 3).

3.3. Nitrogen Leaching and Soil Content

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

The total amount of N leached from the soil columns over the 30-week experiment is shown in Figure 4. Over 90 % of the total mass of TN leached from the columns over the entire study duration was in the form of NO_3. Following pig manure application, between weeks 10 and 11, there was a significant increase in the total amount of TN leached from the manure-amended columns compared with the other columns ($p<0.001$ for all three treatments). Of the 144 mg of pig TN added as pig manure, 66-70 mg had leached by week 30, with no significant differences between treatments.

The amount of NO_3 and NO_2 in the leachate exiting the soil columns each week is shown in Figure 5 (a) and (b). High concentrations of NO_3 were leached from all treatments for the first number of weeks, peaking at >110 mg L^{-1} for all treatments on week 3. There was a swift decline in the concentration of NO_3 in the leachate after week 4, and by week 9, the concentration of NO_3 in the leachate had decreased to <35 mg L^{-1} for all treatments and remained below this value for all the non-manure-amended columns for the duration of the experiment. Drying and re-wetting of soil during the construction of the columns may have caused a burst in microbial activity and a sharp increase in C and N mineralisation (Van Gestel et al., 1991; Bengtsson et al., 2003; Borken and Matzner, 2009), resulting in surplus available NH_4 and high levels of nitrification. The soil used in this experiment also had a low C:N ratio of 8.2. Soil with C:N ratios below 20 can be characterised as having a surplus of available NH_4 for nitrification (Bengtsson et al., 2003).

Biochar amendment to the soil reduced the amount of NO_3 leached from the columns by 24 and 26 %, respectively, for PM600 and W600, compared with the Control. The reduction in NO_3 leached per week from the biochar-amended soils was only significant ($p<0.05$) in the first 12 weeks of the study. The application of pig manure resulted in a peak in the leaching of NO_3

(Figure 5a), which reached maximum values for all treatments on weeks 17-18. For 4 weeks after pig manure application, PM600+PM and W600+PM leached significantly less NO_3 than the Control+PM. The amount of NO_2 leaching was small when compared with NO_3. The concentration of NO_2 in the leachate was <0.1 mg L^{-1} from week 2-9. This corresponds with the peak in NO_3 leaching (Figure 5a). This low amount of NO_2 leached from all treatment may also be due to the drying and re-wetting effect described earlier. The burst of microbial activity caused by re-wetting may have ensured that almost complete nitrification to NO_3 occurred for the first 9 weeks. The quantity of the NO_2 leached increased significantly from week 9 to week 18 across all treatments, irrespective of whether soil was amended with biochar or pig manure. This temporary build-up of NO_2 in the soil may be due to a time lag between NO_3 reduction and NO_2 reduction during the denitrification process, due to the preference of denitrifiers to NO_3, even when both NO_2 and NO_3 are present (Rivett et al., 2008).

The amount of NH_4 leached was low compared with NO_3. This indicates high nitrification across all treatments and the high CEC of the soil. Throughout the leaching experiment, the quantity of NH_4 leached from each column on most sampling weeks remained between 0.005 and 0.015 mg. There was no significant difference between the amount of NH_4 leached from the columns which received manure and those which did not. There was also no difference between amount of NH_4 leached from the biochar-amended columns and the Control ($p>0.05$).

Many different reasons have been given for reductions in N leaching due to biochar addition to soil, including adsorption of NH_4 or NO_3 onto biochar, and enhanced immobilisation and denitrification of N (Clough et al., 2013). Laird et al. (2010a) attributed significantly reduced NO_3 leaching from pig manure-amended soil + biochar treatments compared with manure-amended soil-only treatments to the adsorption of NH_4 and soluble organic compounds within the soil, thus inhibiting mineralisation of organic N and/or nitrification of NH_4. The reductions in NO_3 leaching were not immediate; only after 23 weeks of biochar weathering was there any reduction in NO_3 leaching (Laird et al., 2010a). Other studies have also shown the ability of biochar to adsorb NH_4 (Dempster et al., 2012; Yao et al., 2012). However, the rationale given for the ability of biochar to enhance NH_4 adsorption in soil is due to its higher CEC (Clough et al., 2013). However, the CEC of the biochar-amended soils in the current study was found to be similar to that of the Control (Table 2), and therefore, a reduction in NO_3 leaching was unlikely, initially at least, to be caused by NH_4 adsorption. The CEC of fresh biochar has previously been shown to be low (Busscher et al., 2010; Clough et al., 2010), with only weathered biochar being shown to have a high CEC due to oxidation and adsorption of other OM in the soil over time (Liang et al., 2006). The CEC of the biochar-amended treatments in the current study may have increased over time. However, biochar oxidation, which results in CEC increases, is temperature dependant (Cheng et al., 2006), and incubation at 10 ^{o}C is unlikely to have caused a dramatic increase in biochar CEC.

The reduction in NO_3 leaching in this study was most likely caused by the impact of biochar on the rates of nitrification and denitrification within the soil due to (1) nitrification inhibitors present on unweathered biochar and (2) denitrification loss of NO_3 due to being stimulated by higher WFPS and organic C contents in the biochar-amended treatments. In an incubation study using freshly made biochar, Clough et al. (2010) measured higher soil NH_4 concentrations in biochar-amended soil after the application of urine, compared with soil amended with urine only. This increase was attributed to nitrification inhibitors which slowed the rate of NH_4 depletion. Unweathered biochar has been shown to contain microbially toxic compounds (e.g. polyaromatic hydrocarbons), some of which may inhibit the *Nitrosomonas* bacteria responsible for nitrification (Kim et al., 2003; Clough and Condron, 2010). This inhibition of nitrification, due to toxic compounds is likely to be short-term: Clough et al. (2010) found that signs of nitrification inhibition had stopped 55 days after soil incubation, as weathering of the biochar decreased its ability to inhibit nitrification.

In general, the presence of anaerobic conditions and organic C as an electron donor facilitates denitrification (Rivett et al., 2008). In a companion study using the same soil columns, Troy et al. (2013b) found that nitrous oxide (N_2O) emissions over a 28-period following manure addition were 79 and 68 % higher from PM600+PM and W600+PM, respectively, when compared with Control+PM. The increased WFPS in the biochar-amended columns may have caused the development of anaerobic zones within the soil, reducing nitrification and increasing denitrification. The WFPS measured at the 10-20 cm depth on weeks 20 and 30 was 69-72 % for the Control. The WFPS was 78 % and 77-79 %, respectively, for PM600 and W600. Increasing the WFPS beyond 60 % causes anaerobic conditions, resulting in reduced aerobic microbial activity and nitrification, and increased denitrification (Dobbie and Smith, 2001; Porporato et al., 2003; Bateman and Baggs, 2005; Yanai et al., 2007; Troy et al., 2013b). In an incubation study, using arable soil fertilised with ammonium nitrate, Dobbie and Smith (2001) found a 30-fold increase in N_2O emissions by increasing the WFPS from 60 to 80 %, due to denitrification attributed to the development of anaerobic zones within the soil. In addition to a higher WFPS, the WSOC content of the biochar-amended treatments was higher than that of the Control (Table 2), indicating higher organic C availability for denitrification. In a study measuring N_2O losses through denitrification from intact soil cores fertilised with NO_3, Jahangir et al. (2012) found N_2O emissions were significantly increased with the addition of dissolved organic C to the soil.

They suggested that adding C sources to the subsoil could increase NO_3 depletion via denitrification (Jahangir et al., 2012). Despite the increased WSOC of the biochar amended soils in the current study, leaching of TOC was lower in the W600 treatment than the Control, an indication that the organic C may have been used as an electron donor for denitrification.

3.4. Phosphorus Leaching and Soil Content

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

The pig manure biochar had no capacity to adsorb P, and it had a higher WEP than the wood biochar (Table 1). Over the 30-week study period, there was significantly more TP ($p<0.001$) and TDP ($p<0.001$) leached from PM600 than the Control or W600. The increase in P leaching from PM600 was primarily due to increased DRP leaching ($p<0.001$). This was a result of higher WEP in the PM600 treatments when compared with the Control and W600 treatments on all sampling weeks and depths ($p<0.001$) (Table 4). The PM600 treatments also had significantly higher Morgan's P values when compared with the Control and W600 treatments on all sampling weeks and depths ($p<0.05$) (Table 5). The addition of PM600 caused the soil to change from a P Index 2 soil (low in STP) to a P index 4 (high STP) soil by week 10. This indicates the unsuitability of this pig manure-derived biochar as an amendment of soil in receipt of animal manure. By increasing the P Index of the soil, the addition of pig manure-derived biochar has reduced the amount of manure which can be applied to the soil, thereby further increasing the costs of pig manure application. The amount of DRP leached from PM600 was between 0.004 mg and 0.01 mg per column from week 5 to 30. In contrast, the amount of DRP leached from both the Control and W600 peaked at between 0.002 and 0.004 mg per column per week between weeks 4 and 14. From week 14 until the end of the experiment, less than 0.002 mg was leached from the Control and W600 on most sampling weeks.

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

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

4. Conclusions

The addition of both pig manure biochar and wood biochar to the low P Index tillage soil had significant effects on soil properties and nutrient leaching. Biochar addition increased the soil WFPS, OM and C contents, while reducing NO_3 leaching, compared with unamended soil. Amendment with pig manure biochar increased Morgan's P and WEP contents in the soil due to the higher concentration of easily extractable P in the manure-derived biochar. Leaching of P and C increased with the addition of pig manure biochar due to the higher concentrations of water soluble P and C in the pig manure biochar. Leaching of organic C was reduced in the wood biochar-amended treatments compared with the unamended soil.

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

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Table 1: Characteristics of the biochars used in the column experiment (mean ± SD)

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

WEP, water extractable phosphorus

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

	Control	PM600	W600
Water Content (%)	26.8 ± 0.24	25.5 ± 0.58	25.8 ± 0.36
Organic Matter (%)	4.62 ± 0.013	5.44 ± 0.194	5.40 ± 0.210
Bulk Density (g cm^{-3})	1.10 ± 0.010	1.11 ± 0.009	1.11 ± 0.017
Total N (%)	0.21 ± 0.008	0.22 ± 0.002	0.21 ± 0.013
Total C (%)	1.75 ± 0.049	2.18 ± 0.001	2.48 ± 0.170
WEP (mg kg^{-1})	0.36 ± 0.037	0.52 ± 0.008	0.39 ± 0016
Morgan's P (mg L^{-1})	4.84 ± 0.269	7.53 ± 0.137	5.04 ± 0.184
WSOC (mg kg^{-1})	120 ± 1.9	196 ± 11.8	163 ± 9.4
K (cmol L^{-1})	0.36 ± 0.003	0.39 ± 0.000	0.33 ± 0.018
Ca (cmol L^{-1})	7.14 ± 0.105	6.74 ± 0.010	7.22 ± 0.154
Mg (cmol L^{-1})	0.30 ± 0.004	0.31 ± 0.004	0.31 ± 0.004
Na (cmol L^{-1})	0.23 ± 0.006	0.14 ± 0.075	0.11 ± 0.048
CEC (cmol L^{-1})	8.03 ± 0.111	7.58 ± 0.079	7.97 ± 0.084
pH	6.9 ± 0.20	6.9 ± 0.18	6.8 ± 0.04

WEP, water extractable phosphorus; WSOC, water soluble organic carbon; CEC, cation exchange capacity.

Table 3: Carbon, nitrogen (%) and C:N ratio for the soil (Control), the soil and pig manure biochar mix (PM600) and the soil and wood biochar mix (W600) at 3 depths (cm below surface) over 4 events

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

^{abc} 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).

Table 4: Water Extractable Phosphorus (WEP, mg kg^{-1}) contents for the soil (Control), the soil and pig manure biochar mix (PM600) and the soil and wood biochar mix (W600) at 3 sampling depths (cm below surface) over 4 sampling events

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

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

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

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

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

Captions for Figures

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

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

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

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

Figure 5: Weekly total of NO_3 (a) and NO_2 (b) leached from soil columns. Control = soil only. PM600 = soil + pig manure biochar. W600 = soil + wood biochar. Treatments amended with the pig manure between week 10 and 11 are shown with (+PM).

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

Figure 1

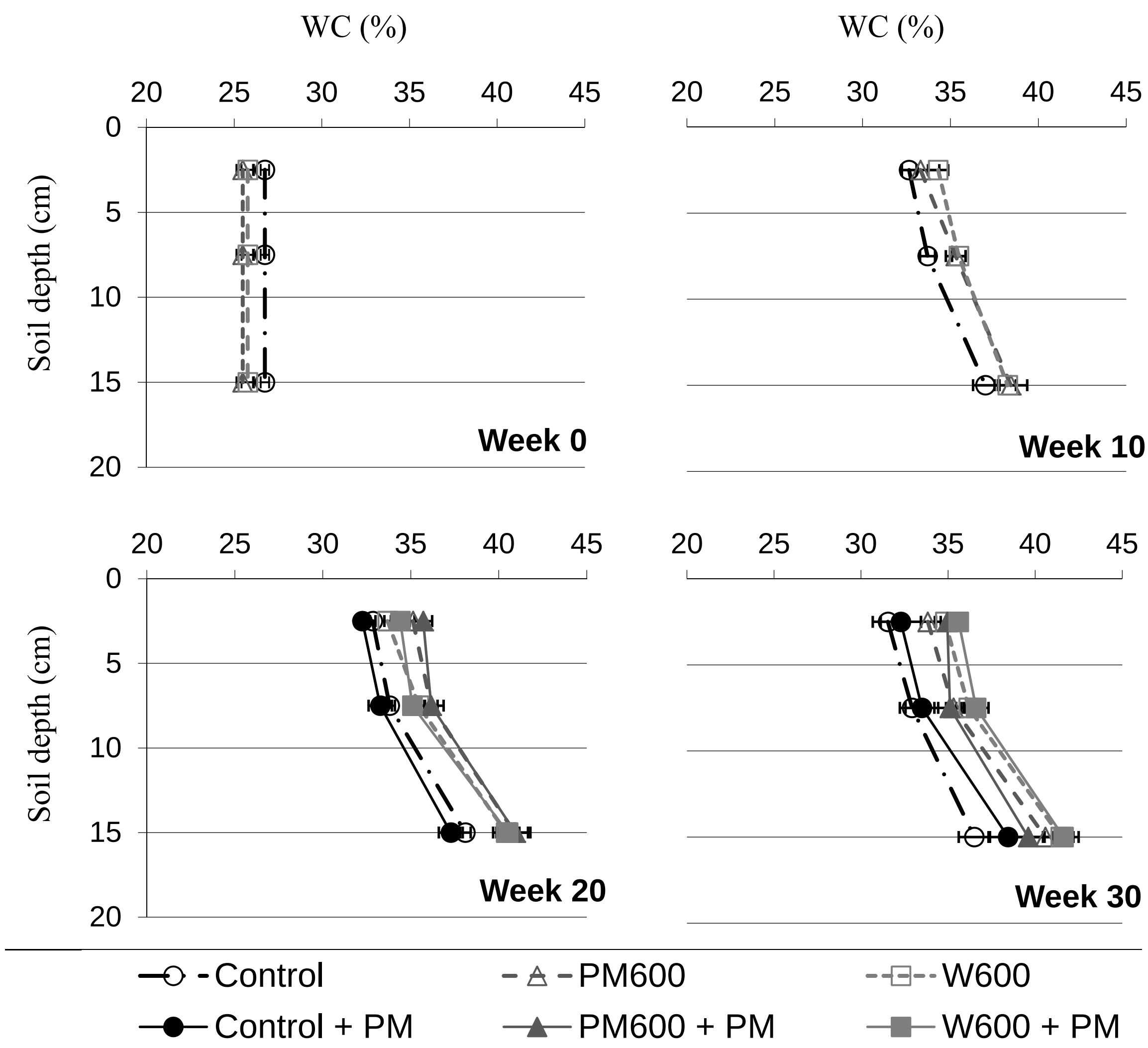

WC (%)
WC (%)
20 25 30 35 40 45
0 5 10 15 20
Soil depth (cm)
Week 0
Week 10
Week 20
Week 30
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM

Figure 2

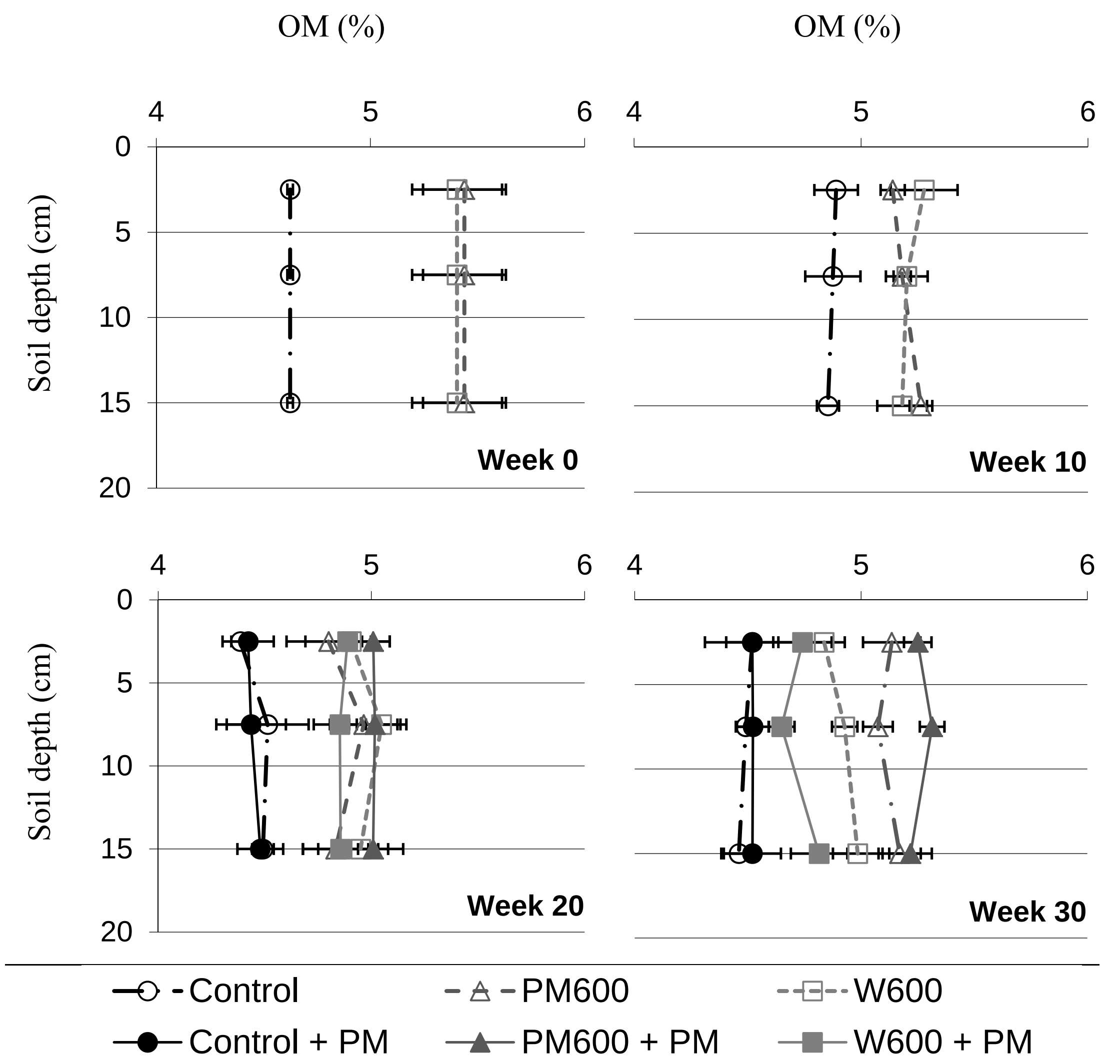

OM (%)
OM (%)
Soil depth (cm)
Soil depth (cm)
Week 0
Week 10
Week 20
Week 30
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM

Figure 3

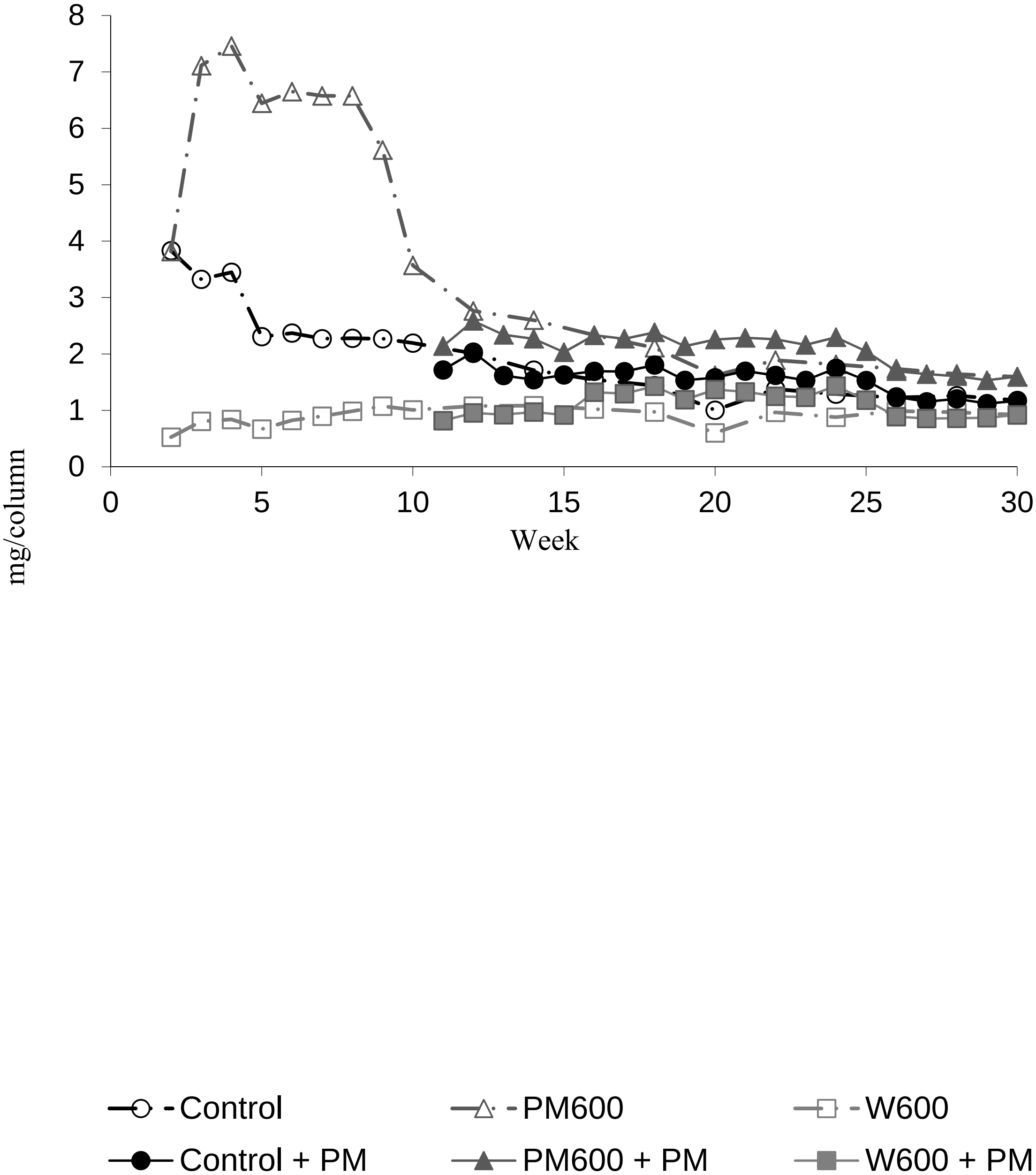

8
7
6
5
4
3
2
1
0
mg/column
0
5
10
15
20
25
30
Week
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM

Figure 4

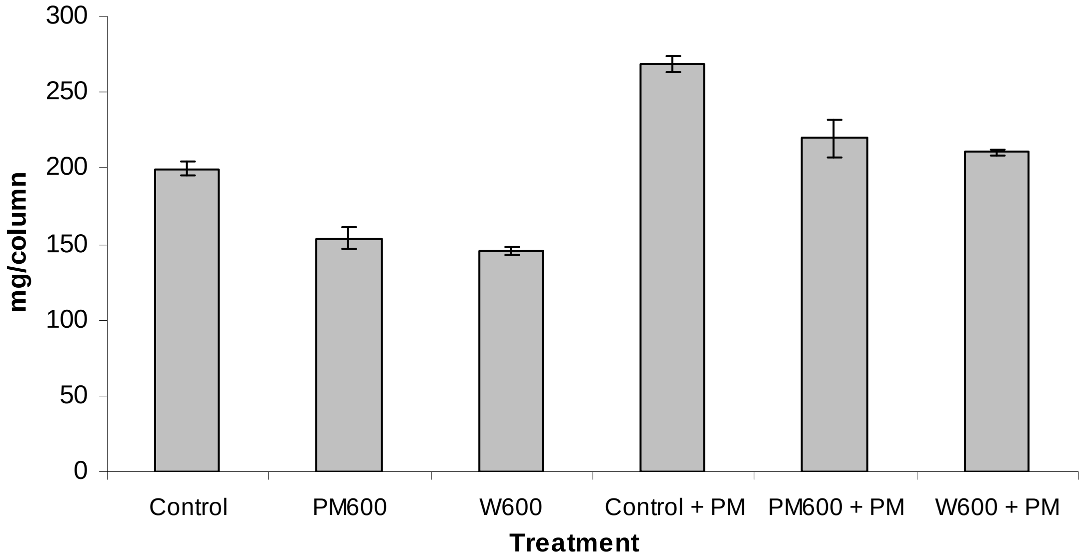
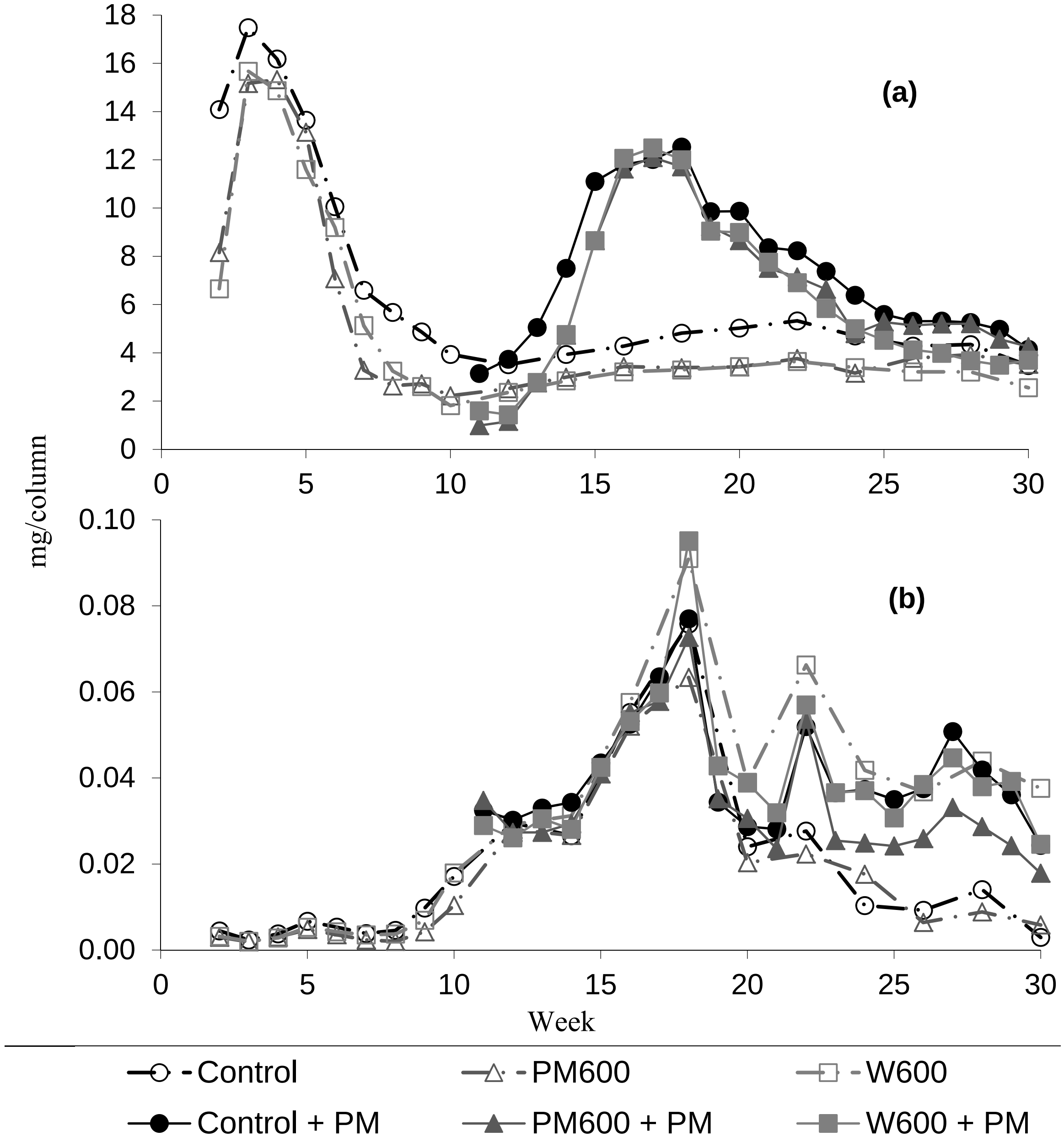
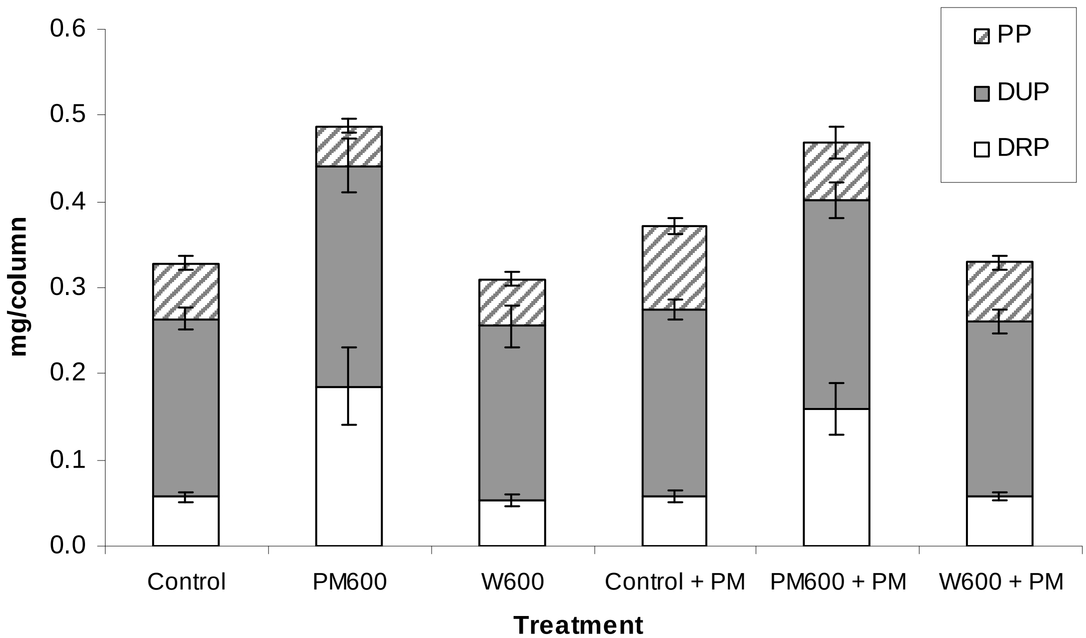

mg/column
300
250
200
150
100
50
0
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM
Treatment

Figure 5



(a)
(b)
mg/column
Week
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM

Figure 6


PP
DUP
DRP
mg/column
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Control
PM600
W600
Control + PM
PM600 + PM
W600 + PM
Treatment