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Science of the Total Environment

Driving forces and barriers in the removal of phosphorus from water using crop residue, wood and sewage sludge derived biochars

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Abstract

The removal of phosphorus (P) from sewage effluents is necessary to control eutrophication in receiving waters. Biochar has been proposed and is investigated for the capture and reuse of P, however the forces driving and limiting P adsorption are still largely unclear. To identify the forces governing P uptake by biochar, biochars with markedly different physicochemical characteristics derived from a variety of biomass (oilseed rape straw, wheat straw, miscanthus straw, rice husk, soft wood and sewage sludge residue), pyrolysed at various temperatures, were investigated. The biochar samples were characterised in terms of pH, electrical conductivity, total acidity, carbon chemistry, metal composition, surface area, and porosity, and the uptake and release of P was compared to the biochar properties using multivariate analysis. Uptake of P by the biochars as such was low (< 0.71 mg P/ g biochar with feed solutions of 50 mg P/ L) and, among the variables studied, the biochars' Ca and Mg content was key in P removal and found to be pH dependant. Enhancement of biochar surface area and porosity was carried out by activation with CO₂ at 800°C and the uptake significantly improved ($p < 0.05$) (i.e. an increased surface area from < 20 m²/ g up to 781 m²/ g gave a limited improvement in P removal to < 1.2 mg P/ g biochar at feed level of 50 mg P/ L). These results confirm that the potential to use these unmodified biochars derived from a variety of biomass for P sorption is low, but that the material provides properties that may be modified or enhanced to increase sorption capacity. This study indicates that biochar/biochar feedstock with greater content of Ca and Mg will be more advantageous for P capture.

1 Introduction

Geological sources of phosphorus (P) are relied upon globally to maintain agricultural productivity through the application of P fertiliser. The finite nature of P-rock reserves (Edixhoven et al., 2014) and the eutrophication of water bodies (Stoddard et al., 2016) are obvious signs that the dependence on and use of inorganic P is unsustainable. The development of technologies capable of capturing P from water and wastewater, enabling its reuse in agriculture, is therefore important. There are many approaches to remove P from wastewater, typically precipitation processes using salts of Fe, Al or Ca and biological techniques. Recovery of P can be achieved through various approaches, namely the precipitation of struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) from digested biological sludge streams, or the thermochemical treatment of sewage sludge residues (Egle et al., 2015). The requirement for wastewater treatment plants (WWTPs) to increasingly achieve lower P discharge consents (<1 mg P/L) and the introduction of some P recovery requirements is driving the development of new technological options to enable effective recovery of P (Melia et al., 2017). A popular approach is to adsorb P using suitable materials that can subsequently be applied to land once saturated, as a recovered P fertiliser (Novais et al., 2018a; Wan et al., 2017).

Commonly tested materials for capturing P have included natural and modified minerals, including zeolites (Choi et al., 2012; Xinggang Wang et al., 2014); mining, metallurgical and industrial by-products (Xinjun Wang et al., 2014) and synthetic metal (hydr)oxides (Long et al., 2011; Tu and You, 2014; Xie et al., 2014) often in composite forms. Adsorption of P using these inorganic substrates can be high, however for some materials P bioavailability can be low (for example Fe and Al oxide-containing materials) (Wendling et al., 2013), or in the case of Al-containing minerals, present potential contamination concerns (Poschenrieder et al., 2008). Granular carbon materials are attractive adsorbent materials due to their high surface area,

porosity, and functionality, and are often of a suitable particle size to be applied in column or flow through applications – granular activated carbon (GAC) for example is widely applied commercially to remove organic contaminants from industrial and municipal wastewaters. Biochar is derived from the pyrolysis of organic materials, which are often abundant or considered a waste, and is produced as a by-product from the production of bio-oil and syngas or specifically for environmental applications: namely soil amelioration (Saifullah et al., 2018), carbon sequestration (Crombie et al., 2015) and the removal or immobilisation of contaminants from water (Wang et al., 2015) or soil (Xu et al., 2016) respectively.

Biochar is being investigated for P capture from water (Li et al., 2016; Yao et al., 2011) and can be an attractive material due to its relative low cost. The combined benefits from a soil amendment perspective, of a P-enriched material (after P adsorption) with the inherent soil ameliorant properties of biochar, are overall attractive. Unmodified agricultural waste-derived biochar has been found to have low uptake of P and therefore recent works have often opted towards modifying biochar for the aim of P adsorption (Novais et al., 2018b). A thorough investigation into the role that various biochar properties play, both individually and synergistically, in enabling uptake of P is needed to fully understand the mechanisms driving P uptake, and so optimise P removal. A recent investigation by Shepherd et al. (2017) assessed the underlying mechanisms of P adsorption onto anaerobically digested sewage sludge/ochre derived biochar, which is compositionally very different to the biochars studied here, and found that interactions with Fe minerals in the biochars tested were important for enabling P uptake. The study however was limited in its comparison of various sewage sludge/ochre derived biochars which were produced at temperatures $<550^{\circ}\text{C}$ – surface area, porosity and carbon functionality was not assessed. The objective of this study therefore is to evaluate the P uptake ability of a variety of mainly agriculturally-derived biochars with distinct and varying surface area, metal content, porosity and surface chemistry, and to identify the critical enabling and

disabling characteristics controlling the uptake of P. To date, a comprehensive assessment of this type has not been carried out with biochar from a variety of feedstocks. These results have important relevance for the use of biochars for both the recovery of P in water and wastewater but also for the application of biochar to soil. The findings are likely to help select or modify biochar feedstock for better P capture.

2 Materials and methods

2.1 Materials

The chemicals used for the characterisation of the biochar samples and the study of P uptake were Na_2HPO_4 , potassium hydrogen phthalate (99.95%), NaOH (98.5%) and 37% HCl. All were of analytical grade and supplied from Fisher Scientific. HNO_3 ($\geq 69\%$) and H_2O_2 ($\geq 30\%$) were of trace metal analysis quality and were used for that purpose, and a certified P standard solution (100 mg/L) was used for the analysis of P and were from Sigma Aldrich. Ultrapure water ($15 \text{ M}\Omega\cdot\text{cm}$) was obtained with an ELGA Purelab system and used in all experiments.

Biochar materials were obtained from the pyrolysis at 550 and 700 °C of biomass: sewage sludge (SS550 and SS700); pelleted oilseed rape straw (OSR550 and OSR700); pelleted wheat straw (WSP550 and WSP700); pelleted miscanthus straw (MSP550 and MSP700); rice husk (RH550 and RH700) and pelleted soft wood (SWP550 and SWP700). The conditions of their production have been earlier described (Mašek et al., 2018). Biochar samples were purged with nitrogen and stored in sealed 1L containers at room temperature and atmospheric pressure before further treatment and analysis.

2.2 Pre-treatment of the biochar for P uptake studies and analysis

Biochar samples of particle size 0.5–1 mm were prepared from the pellets of the biochar materials by crushing with a pestle and mortar before sieving, between mesh sizes of 1mm and 500 microns. The sized biochar samples were then washed (throughflow with ultrapure water, 200 bed volumes) to remove residual ash and readily soluble P. The biochar particles were subsequently dried at 40°C under vacuum and stored in air-tight containers before analysis.

2.3 Adsorption studies

Adsorption tests were carried out in batch mode under equilibrium conditions using an orbital shaker at 90 rpm, 25°C for 48h. Analysis of P concentrations at initial and equilibrium conditions was carried out using Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES) model ULTIMA 2C (Horiba Jobin Yvon), after filtering using 0.22µm syringe-driven PES filters (Merck Millipore, Ireland). To assess the performance of biochars that showed very low adsorptive capacity it was necessary to use high initial P concentrations and high adsorbent to adsorbate doses, as such an initial P concentration of 50 mg P/L and a biochar dose of 50 g/L was used.

The adsorptive capacity (q_{eq} , mg P/g biochar) was obtained from the mass of P removed from solution by the biochar, as expressed in equation 1, where C_0 and C_{eq} are the initial and final concentrations in solution respectively. V (L) is the volume of solution and w (g) is the amount of sorbent used.

$$q_{eq} = (C_0 - C_{eq}) \frac{V}{w} \quad (1)$$

Due to release of soluble P from washed biochar samples a net P removal capacity was also calculated (q_{net} , mg P/g biochar). This was calculated as q_{eq} (equation 1) added to P release

assessed using control samples consisting of biochar suspended in ultrapure water under the same conditions.

2.4 Porosimetry

The structure of the biochars and activated carbons was determined via N₂ adsorption-desorption isotherms at 77 K. All isotherms were carried out with a BELSORP-miniII porosimeter (MicrotracBEL, Japan). The samples were degassed for 24h at 150°C prior to analysis. The specific surface area (S_{BET}) was calculated using the standard BET (Brunauer-Emmett-Teller) model (Gregg and Sing, 1995), the BJH (Barrett-Joyner-Halenda) model was used for pore characterisation. Total pore volume, V_p , was estimated at $P/P_0 \sim 0.99$, where P and P_0 denote equilibrium pressure and saturation pressure of N₂ at 77 K respectively.

2.5 Metal composition

The concentration of metals within the biochar samples was quantified following the EPA method 3052 (U.S. EPA, 1996) in triplicate. Briefly, 200 mg of biochar was added to a microwave vessel with 2 mL of concentrated HNO₃, 0.5 mL of H₂O₂ and 0.5 mL of ultrapure water. Digestion took place within a microwave digestion unit (Mars 5, CEM), held at 250 psi for 30 min. After dilution to <5% HNO₃, trace elemental concentrations were determined using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) (7700 Series, Agilent Technologies, UK), with some major elemental concentrations (Ca, Fe, K, P, S), which were poorly resolved due to polyatomic interferences, quantified using ICP- Atomic Emission Spectroscopy (AES) (model ULTIMA 2C, Horiba Jobin Yvon).

2.6 Scanning electron microscopy and X-ray diffraction

Biochar was mounted on specimen stubs fitted with adhesive carbon pads, sputter coated with gold-palladium and examined using a Zeiss Evo50 (Oxford Instruments, Cambridge, UK) scanning electron microscope (SEM) – micrographs were obtained at an accelerating voltage of 20 kV. X-ray diffraction (XRD) analysis was carried out (model X'Pert³ Powder, PANalytical) across a 5–70 2θ range.

2.7 Total acidity, pH, electric conductivity and FT-IR analysis

pH and electrical conductivity measurements were carried out using the International Biochar Initiative recommended method (Rajkovich et al., 2012). Briefly, 1g of washed biochar was equilibrated with 20 mL of ultrapure water for 1.5h on an orbital shaker (90 rpm). After equilibration, pH and electrical conductivity were determined using pre-calibrated pH and conductivity meters. Total acidity was assessed using a Boehm titration method (Boehm, 2002), however as reactive ash and organic compounds can be gradually released from within biochar, this can lead to inaccurate results (Fidel et al., 2013). Therefore a modified Boehm titration method involving further washing steps was adopted (Tsechansky and Graber, 2014). Carried out in triplicate, using ~0.8 g biochar and 40 mL of wash or reactant solution.

FT-IR spectra were collected using a Nicolet iS5 spectrometer with an iD1 transmission attachment (Thermo Scientific, UK). The biochar samples were diluted to 1% weight with KBr and pressed into a disc before analysis, which consisted of 20 scans with a resolution of 1 cm^{-1} .

2.8 Data treatment

Minitab 16 was used for all statistical analysis; significance was deemed for values of $p < 0.05$. For multiple component analyses, the data were scaled to between -1 and 1 in each series of experimental values to correct for differences between units of measurement.

3 Results and discussion

The selection of biochar for environmental applications involving the uptake and release of P is currently ambiguous. The extent of P uptake by biochar can be affected by a range of chemical and structural characteristics that may exert a synergistic effect. The driving forces and performance of biochar for the removal of P from water was investigated with a range of biochars (Table 1) with differentiated characteristics from various biomass produced under reproducible conditions. The P removal rate attained was used as the response to assess the different physicochemical properties in biochar affecting its removal efficiency. Experiments did not use buffer solutions to control pH, to avoid any competition effects between the anions from the buffer salts and P species.

Biochar derived from sewage sludge showed the highest net uptake of P, 0.71 mg P/g SS550, and it is among the samples with lower P release (0.007 and 0.02 mg P release/g for SS550 and SS700, respectively). In contrast, the agriculturally derived biochars were characterised by relatively high releases of P, up to 0.44 mg P/g, despite their pre-treatment with 200 bed volumes of water (see section 2.2). Biochar derived from rice husk and soft wood pellet showed no net uptake of P – soft wood pellet biochars produced at both pyrolysis temperatures (550 and 700°C) showed no release or uptake of P whereas rice husk biochars showed the highest amount of P release but no uptake of P. Hence, rice husk biochar (and presumably biochars pyrolysed from biologically similar feedstocks) may serve the purpose of P recycling, regardless of their null capacity for P adsorption. The markedly different performance of the biochars will serve to identify the factors driving the capacity of some biochars to uptake P.

3.1 Effect of structural characteristics on biochar affinity for P

Structural characteristics that may have relevance to the uptake of P are the pore size distribution, S_{BET} , and particle size, although the latter was constant in our study and has limited

contribution in batch studies carried out at equilibrium. The differences in structure are derived from differences in the original feedstocks' cellular structure and pyrolysis conditions. Based on qualitative microscopy assessment, the biochars with more developed macroporosity (>50 nm) were the samples derived from straw feedstocks, in contrast, biochars derived from sewage sludge showed limited ordered macroporosity (but also porosity <50nm based on the porosimetry analysis). SEM micrographs (Figure 2) illustrate examples of macroporosity in two of the biochar samples studied.

Macroporosity facilitates the transport and access of substances to key sites involved in the uptake of P, and it is not a main contributor to S_{BET} . Mesopores (2-50nm) and micropores (<2 nm), the latter with potential higher involvement in the uptake of P due to the capacity to provide interaction in 3D with phosphate species, are not evident from the SEM micrographs or from gas adsorption isotherms. The isotherms showed that surface area amongst the biochar samples was generally low, <50 m²/g, when compared to granular activated carbon (GAC) materials which are commonly used commercially within the water industry, for example 552 m²/g (Busquets et al., 2014). The specific surface area and total pore volumes for the study samples are summarised in Table 1. The low surface area and pore volumes of these biochars may limit the amount and availability of key functional groups and adsorptive sites available to interact with P. Interestingly however, S_{BET} and V_p values do not show significant correlation with the uptake of P ($p > 0.05$).

To further assess the influence of surface area and porosity over the uptake of P, biochars pyrolysed at 550°C were further activated with CO₂ at 800°C. S_{BET} and porosimetry data show that activation increases the materials' surface areas with a larger amount of pore volume and micro- and mesoporosity as evident in isotherm and BJH plots (data provided in supplementary information), compared with the respective biochar pyrolysed at 550°C. Hence the conditions applied did not cause collapse of the pores. The activation enabled higher net uptake of P

(Figure 3) in all cases, however correlation of S_{BET} and P uptake was still not found ($p > 0.05$). Increased concentration of and accessibility to metal cations due to loss of volatiles after activation may be more dominant in controlling uptake of P (see below). Other changes in biochar characteristics caused by activation may be changes in the surface chemistry and composition of the carbon – these warrant further investigation. Activation as a modification approach however may be costly, energy intensive and, on a larger scale, may not represent a practical approach to increase P retention by biochar.

3.2 Effect of surface chemistry on the uptake of P

The activation of the biochar samples pyrolysed at 550 °C resulted in a marked increase in the uptake of P (Figure 3). In contrast carrying out the pyrolysis at 700°C (as opposed to at 550°C) did not improve the uptake of P. Changes that may have occurred on the surface of the biochars under the conditions of pyrolysis contributing to this outcome can be the loss of oxidised groups (e.g. carboxylic acids or lactones as CO_2) (Figueiredo et al., 1999). The total acidity found in the biochars from vegetal origin (SS samples excluded) was greater for those which had been pyrolysed at 550 °C than at 700 °C (Table 1). The greater acidity indicates a higher proportion of oxidised functional groups (e.g. carboxylic acids, phenols and hydroxyls), which, at the pH of the media (>10 for OSR and WSP samples as indicated in Table 1) will be mainly deprotonated and hence negatively charged and solvated in solution. Indeed, Figure 4 shows that all the biochars pyrolysed at 700°C had a lower proportion of carbonyl groups (band at 1600 cm^{-1}) but also a lower proportion of secondary amines (band at 3500 cm^{-1}) for example, compared with the same feedstock pyrolysed at 550°C. For these study biochars, decreases in carbonyl groups at the surface have not provided an improvement in P uptake, and indicate that

other surface groups may be controlling these changes or that metal speciation has a larger importance.

At a pH closer to neutrality (e.g. for SS, RH and SWP biochars in water), acidic and basic groups would be present with a higher proportion of protonation and have the effect of an overall lower negative charge. A basic pH will favour a higher abundance of $\text{HPO}_4^{2-}/\text{PO}_4^{3-}$ species as opposed to $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ at neutral pH – the species with greater charge would be expected to be more difficult to extract from solution given their greater stability solvated in aqueous media. However, the conditions that led to a lower proportion of charged oxygen functional groups, i.e. pyrolysis at 700°C and neutral pH favouring P in a single-charged anion (for example adsorption using RH and SWP biochars), have been found the least favourable for the net uptake of P. SS biochars have lower pH and showed the best performance in the uptake of P (Figure 1), however the removal of P by SS biochars could be different because these have a lower amount of organic matter and changes in their organic surface chemistry may have less net effect than the changes taking place in their inorganic composition. As significant positive correlation was found between net P uptake and total acidity ($p < 0.05$) the effect of total acidity needs to be examined in a wider context in multivariate analysis (Section 3.4). EC in the washed biochars was measured to monitor the release of ions and assess if it interfered in the uptake of P. The net uptake of P has not been affected by the release of ions from biochar in our study; for instance, RH and SWP presented the highest and lowest EC, respectively, and their net P uptake was null for both. In contrast, SS presented an intermediate conductivity among the washed biochars (Table 1) and presented the greatest net uptake.

3.3 Bulk metal composition and P uptake

The raw materials used to produce biochar have metals/metalloids dispersed within their bulk structure and on exposed surfaces, and pyrolysis and activation exposes these at the material surface and makes them available to react. Concentrations of various major metals and nutrients, and potentially toxic elements, have been determined in the study biochars and are shown in Table 3. Potentially toxic elements were included in the study to identify their involvement in the uptake of P, and the consequent limitations of the use of biochar as a soil amendment.

The sewage sludge-derived biochar samples are characterised by higher concentrations of metals compared with the biochars derived from agricultural materials, especially Fe, Al, trace and potentially toxic elements (Table 3). Metals, especially Ca, are found in relatively high concentrations in the straw derived samples compared with the rice husk and soft wood samples (Table 3). Higher metal content is generally found in materials produced at higher pyrolysis temperatures due to the loss of volatile compounds. Figure 5 shows that the content of Ca and Mg in biochar significantly ($p < 0.05$) correlate with net P uptake in unmodified biochars (R^2 values 0.8736 and 0.8479, for Mg and Ca respectively, $p < 0.05$). Splitting the data into groups representing biochars pyrolysed at 550 and 700°C (C and D, Figure 5, respectively) shows two distinct and stronger correlations between biochar produced at 550°C and 700°C and Ca and Mg content, with R^2 values of 0.9898 and 0.9725 for Ca, and R^2 values of 0.9728 and 0.9639 for Mg, respectively. This confirms the greater efficiency of the pyrolysis at lower temperature and the role of Ca and Mg species play in the uptake of P. Ca and Mg will preferably uptake P under basic conditions, which are precisely the pH conditions resulting from the organic composition of the biochar and from the abundant alkali earth metals exposed on biochar surfaces.

The biochars pyrolysed at 700°C possess a lower ability to uptake P, in contrast, these biochars have higher concentration of metals: this indicates that characteristics other than bulk metal

content are important for the uptake of P with biochars; and the speciation of metals in the biochar structure, i.e. as hydroxides or oxides could play a role in P uptake. This relationship between the type of metal and pyrolysis temperature is interesting and warrants further investigation as higher S_{BET} , V_p and cationic content is generally thought to provide better properties for the uptake of anions. Redox reduction of Fe species present within biochar and decrease in microporosity have been cited as possible causes of reduced P uptake in higher pyrolysis temperature sewage sludge biochar (Shepherd et al., 2017). This could be a reason for differences seen here especially with the sewage sludge biochars which possess considerable concentrations of Fe, agriculturally derived biochars however do not contain a considerable Fe content.

3.4 Multivariate examination of the effect of physicochemical biochar properties on the uptake of P

The examination of the effect of biochar variables on P uptake has led to partial information on the behaviour and mechanisms involved. Multivariate analysis can provide a broader overview of the variables that are related with the recovery of P and the ones that have limited or no effect. Principal component analysis (PCA) was carried out to elucidate synergistic biochar characteristics enabling P uptake and to reveal possible mechanisms driving the sorption of P. Figure 6 shows PCA plots of the unmodified biochar samples' physicochemical characteristics that were analysed for their potential role in the removal of P. Sewage sludge derived biochar samples are not included in the plots shown as they present significantly different characteristics compared with the agriculturally derived materials and have a large control over the data.

The multivariate analysis showed that only 89% of the variability in the data is accounted for by 4 principal components, where 1st to 4th PCs accounted for 45%, 23%, 12% and 9%, respectively, evidencing the multiple forces involved in explaining the net P uptake by the biochars. For clarity, we have carried out 2 types of analysis, which are displayed in Figure 6: A and B correspond to the scores and loading plots from the main factors assessed in relation to the net P uptake, according to a preliminary PCA analysis considering all the variables; and C and D are the equivalent plots focused in screening the effect of metal/metalloids on the uptake of P species from solution. The scores plot (Figure 6B) shows that the biochars distributed across PC1, from high to low PC magnitude, correspond to the sorbents with high to lower P uptake. This indicates that most of the variability related with the uptake of P is explained by PC1 (Figure 6B). The distribution of biochars in the score plot focused on metal composition (Figure 6D) shows that these with net P uptake are in two quartiles, whereas RH and SWP, are in the opposite quartile. This distribution indicates that RH and SWP have an overall metal composition that does not favour P uptake, therefore, metal composition is a defining characteristic, although not the only one for P uptake. The metal composition that has been found to be relevant for P uptake in the biochars that showed better performance is defined by high concentrations of Al, Ca, Fe, Mg and Ni, in the case of OSR (Figure 6 C, D and Table 3).

Correlations between Ca, Mg, pH of the solution and S were found with P uptake and are main contributors to PC1 (Figure 6 A). The presence of S was indeed higher in OSR and WSP, which are the biochars with higher uptake of P. P and S are elements with relatively similar properties, located in neighbouring groups and the same period of the periodic table, and their anions would have similar charge and volume. We could speculate that sites in the biochar hosting sulphates could host phosphate, however this fact was not investigated further. Other minor

elements correlated with the uptake of P, were Mo and Pb. It could be that these elements are present in minerals containing relevant species such as Ca (calcium hydrogen carbonate cations, calcium hydroxide, calcium hydrogen phosphate (Shepherd et al., 2016)) and S and thus were indirectly related with P uptake only but this remains a speculation as XRD carried out on the biochar samples did not have enough sensitivity to inform on the speciation of minor elements. The concentrations of Al and Fe were found to be in the higher range in rice husk (Table 3), however the performance of that sample and the multivariate plot indicate that these elements are not main factors in the removal of P, or it may be that they are not accessible.

4 Conclusions:

The screening of 12 biochars from different sources found the net removal of P to be between 0–0.71 mg P /g biochar from a relatively high initial P concentration of 50 mg P/L. Oilseed rape straw and wheat straw have been found to be the best agriculturally derived biochars for the uptake of P among the materials studied – the presence of potentially toxic trace elements in sewage sludge biochars, and its variable composition inherent to the feedstock material, may limit the applicability of this biochar for the recovery of P. Rice husk biochars could present beneficial properties for soil amendment, despite their null P uptake, due to their inherent high P content and high P release. Activation, carried out at 800°C under a CO₂ atmosphere, led to large increases in surface area and porosity and equated to higher uptake of P. However, correlation with P uptake was not found to be significant.

The concentration of Ca and Mg in the study biochars pyrolysed at 550°C and 700°C was significantly correlated to net P uptake. However, biochars pyrolysed at higher temperature had a lower capacity to uptake P despite having higher concentrations of Ca, Mg, Fe and Al, and a larger surface area, when compared to the respective biochar pyrolysed at lower

temperature. This clearly indicates that there are other characteristics influencing the interaction of P with biochar. The multivariate analysis showing the relation between typical structural and compositional factors of agriculturally derived biochars with P uptake revealed that content (and possibly its speciation) of Ca, Mg, S and pH are important properties driving the P uptake. The findings suggest that for effective P retention, the best approach is to use a low pyrolysis temperature and to increase the Ca and Mg concentrations of biochar.

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Figure captions

Figure 1 Comparison of the uptake of P by a range of biochars. The net P uptake was measured at equilibria (2g biochar in 40 ml of 50 mg P/L). Their water-soluble P release (measured in ultrapure water), and P release/uptake at equilibrium (biochar (2g) was incubated with 50 mg P/L (40 ml)) are also included in the figure. Determinations were carried out in triplicate, RSD<5%. SS: sewage sludge; OSR: oilseed rape straw, WSP: wheat straw; MSP: miscanthus straw; RH rice husk; SWP: soft wood – 550 and 700 indicate the pyrolysis temperature (in °C).

Figure 2 Scanning electron microscope micrographs of rice husk and wheat straw samples obtained under 550°C pyrolysis conditions.

Figure 3 Net P uptake capacities of biochar samples and samples activated at 800 °C under CO₂ atmosphere. P uptake from an initial concentration of 50 mg P/L without control over pH. Analysis n=3, RSD<5%.

Figure 4 FT-IR spectra of the 12 unmodified biochar samples, after dilution to 1% weight with KBr.

Figure 5 Correlations between net P uptake and Mg and Ca for all 12 unmodified biochars (A), and between Fe and Al for all of the unmodified biochars excluding the SS samples (B). Correlation between net P uptake and Ca for all 12 biochars pyrolysed at 550°C and 700°C (C) and between net P uptake and Mg for all 12 biochars pyrolysed at 550°C and 700°C (D).

Figure 6 Loading and score plots of Principal Component Analysis of: net P uptake, P release, major element concentrations, total acidity, pH and electrical conductivity (EC) (left, A and B) and; elemental concentrations and net P uptake (right, C and D). Both for the unmodified biochars, excluding the SS-derived samples.

Table Captions

Table 1 Physicochemical characteristics of biochar samples. S_{BET} and V_p measurements derived from BET analysis of N₂ isotherms at 77 K. pH and EC values are from singular measurements following the method recommended by the IBI (Rajkovich et al., 2012), using 1g biochar in 20mL water.

Table 2 Weight loss and conditions of activation. Activation carried out on the respective biochar pyrolysed at 550°C, weight loss represents the difference in weight between the respective biochar and activated carbon.

Table 3 Major element and nutrient (g/kg biochar), and trace elements (mg/kg biochar) within biochar samples. Results expressed as average \pm standard deviation, n=3. LOD values for As, Cd, Mo and Pb are 0.085, 0.028, 0.389, 0.102 mg/kg respectively.

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Table 1 Physicochemical characteristics of biochar samples. S_{BET} and V_p measurements derived from BET analysis of N_2 isotherms at 77 K. pH and EC values are from singular measurements following the method recommended by the IBI (Rajkovich et al., 2012), using 1g biochar in 20mL water.

Sample	S_{BET} (m^2 / g)	Pore volume (cm^3 / g)	pH (water)	Total acidity (mmol / g) ¹	EC mS m^{-1}
SS550	18.5	0.058	6.9	1.20 ± 0.07	133
SS700	37.1	0.071	7.8	1.42 ± 0.05	108
OSR550	3.43	0.009	10.2	0.53 ± 0.07	363
OSR700	28.7	0.029	10.4	0.41 ± 0.06	264
WSP550	2.94	0.009	10.6	0.53 ± 0.07	359
WSP700	1.13	0.007	10.1	0.43 ± 0.07	247
MSP550	n.d. ²	n.d. ²	10.4	0.52 ± 0.07	319
MSP700	n.d. ²	n.d. ²	10.4	0.42 ± 0.02	473
RH550	44.8	0.035	6.2	0.48 ± 0.05	682
RH700	17.0	0.017	9.7	0.36 ± 0.04	372
SWP550	n.d. ²	n.d. ²	7.7	0.34 ± 0.02	42.0
SWP700	n.d. ²	n.d. ²	7.6	0.19 ± 0.02	32.6

¹Total acidity is presented as mmol of oxygen containing functional groups present per gram of biochar \pm confidence interval at p 0.05 (n=3).

²n.d corresponds to non detected. The estimated limit of detection of S_{BET} in our system is 0.01 m^2 / g however, due to sample cell limitations and sample density differences, the value may differ due to differences in sample weight (i.e. total surface area assessed).

³Values reported for S_{BET} and pore volume; pH and EC; and total acidity are based on sample sizes and mass of n=1 (0.3g); n=1 (1g); and n=3 (0.8g).

Table 2 Weight loss and conditions of activation. Activation carried out on the respective biochar pyrolysed at 550°C, weight loss represents the difference in weight between the respective biochar and activated carbon.

Sample	Original feedstock	Activation conditions	Weight loss (%)	SBET (m ² /g)		Pore volume (cm ³ /g)	
				550°C	800°C	550°C	800°C
A-SS	Sewage sludge	800 °C, 20 min under CO ₂ atmosphere.	40.3	18.5	109.0	0.058	0.085
A-OSR	Oilseed rape straw		36.3	3.43	451.2	0.009	0.246
A-WSP	Wheat straw pellet		33.9	2.94	425.0	0.009	0.253
A-MSP	Miscanthus straw pellet		24.8	n.d.	478.5	n.d.	0.254
A-RH	Rice husk		20.0	44.8	260.6	0.035	0.147
A-SWP	Soft wood pellet		56.0	n.d.	781.3	n.d.	0.459

Table 3 Major element and nutrient (g/kg biochar), and trace elements (mg/kg biochar) within biochar samples. Results expressed as average \pm standard deviation, n=3. LOD values for As, Cd, Mo and Pb are 0.085, 0.028, 0.389, 0.102 mg/kg respectively.

Major elements and nutrients (g / kg biochar)																		
	Al		Ca		Fe		Mg		K		Mn		Na		P		S	
SS550	35.5	±	19.8	±	37.7	±	9.09	±	5.25	±	0.98	±	1.47	±	17.0	±	4.22	±
	1.03		0.09		6.38		0.02		0.46		0.02		0.15		3.10		0.52	
SS700	42.2	±	22.2	±	39.6	±	9.75	±	6.58	±	1.10	±	1.89	±	17.8	±	4.32	±
	0.61		0.21		14.7		0.07		0.13		0.004		0.02		7.61		1.12	
OSR550	0.70	±	8.67	±	0.78	±	3.19	±	15.5	±	0.03	±	0.28	±	2.26	±	0.82	±
	0.008		0.32		0.02		0.13		0.76		0.004		0.08		0.05		0.02	
OSR700	1.29	±	10.5	±	1.50	±	3.81	±	13.9	±	0.03	±	0.25	±	2.92	±	1.01	±
	0.03		0.64		0.16		0.35		0.10		0.001		0.06		0.05		0.01	
WSP550	0.42	±	8.06	±	0.54	±	1.58	±	11.8	±	0.12	±	0.37	±	1.77	±	1.11	±
	0.03		0.60		0.23		0.10		0.50		0.007		0.13		0.10		0.07	
WSP700	0.48	±	11.1	±	0.78	±	2.45	±	13.9	±	0.09	±	0.40	±	4.65	±	1.29	±
	0.02		0.54		0.04		0.10		0.52		0.002		0.06		0.17		0.05	
MSP550	0.16	±	5.06	±	0.41	±	1.74	±	9.52	±	0.12	±	0.45	±	2.81	±	0.71	±
	0.007		0.15		0.05		0.06		0.38		0.003		0.07		0.07		0.02	
MSP700	0.45	±	6.10	±	0.28	±	1.77	±	11.9	±	0.09	±	0.42	±	3.00	±	1.06	±
	0.26		0.44		0.03		0.02		0.31		0.001		0.05		0.11		0.04	
RH550	0.61	±	2.99	±	0.65	±	1.18	±	7.18	±	0.54	±	0.29	±	1.44	±	0.29	±
	0.05		0.17		0.08		0.05		0.40		0.11		0.02		0.13		0.01	
RH700	0.78	±	1.92	±	0.85	±	1.24	±	8.29	±	0.66	±	0.56	±	1.63	±	0.35	±
	0.06		0.11		0.10		0.05		0.46		0.13		0.04		0.15		0.02	
SWP550	0.12	±	2.50	±	0.31	±	0.54	±	2.41	±	0.31	±	0.35	±	0.23	±	0.11	±
	0.01		0.04		0.10		0.03		0.27		0.005		0.10		0.003		0.004	
SWP700	0.13	±	3.22	±	0.15	±	0.90	±	1.58	±	0.25	±	0.36	±	0.19	±	0.12	±
	0.008		0.08		0.06		0.02		0.13		0.001		0.08		0.001		0.01	

Trace and potentially toxic elements (PTE) (mg / kg biochar, *g / kg biochar)																				
	As		B		Cd		Co		Cr		Cu		Mo		Ni		Pb		Zn	
SS550	7.17	±	24.8	±	1.47	±	12.6	±	294	±	334	±	11.9	±	52.9	±	0.22	±	*1.06	±
	0.50		0.84		0.05		0.32		5.90		9.61		1.16		0.82		0.02		0.02	
SS700	7.53	±	26.5	±	0.92	±	14.1	±	325	±	351	±	13.1	±	60.7	±	0.29	±	*1.16	±
	0.92		0.90		0.02		0.14		4.42		21.5		1.38		0.31		0.29		0.009	
OSR550	<LOD		6.81	±	<LOD		0.20	±	2.23	±	367	±	2.39	±	2.86	±	<LOD		22.0	±
			0.52				0.05		0.33		24.8		0.15		0.77				0.68	
OSR700	<LOD		6.56	±	<LOD		0.33	±	4.39	±	381	±	2.73	±	5.35	±	0.20	±	26.2	±
			0.03				0.03		0.08		5.08		0.10		0.18		0.10		7.91	
WSP550	<LOD		7.96	±	<LOD		0.13	±	0.79	±	262	±	1.83	±	0.35	±	<LOD		30.2	±
			0.42				0.006		0.09		210		0.12		0.03				7.74	
WSP700	<LOD		15.7	±	<LOD		0.15	±	1.66	±	139	±	11.7	±	0.60	±	<LOD		35.1	±
			0.99				0.02		0.17		209		0.62		0.09				0.96	
MSP550	<LOD		7.86	±	<LOD		0.06	±	0.83	±	16.1	±	1.56	±	0.39	±	0.12	±	33.5	±
			1.08				0.01		0.11		3.45		0.39		0.02		0.24		2.86	
MSP700	<LOD		11.3	±	<LOD		0.05	±	0.72	±	14.7	±	3.09	±	0.23	±	0.32	±	32.1	±
			0.43				0.01		0.14		2.19		0.04		0.07		0.14		3.39	
RH550	<LOD		6.13	±	<LOD		0.45	±	0.89	±	14.7	±	0.88	±	0.90	±	<LOD		30.6	±
			0.72				0.14		0.32		2.11		0.08		0.29				0.85	
RH700	<LOD		6.18	±	<LOD		0.68	±	1.63	±	15.3	±	0.82	±	1.16	±	<LOD		30.3	±
			0.73				0.21		0.59		1.10		0.08		0.38				1.05	
SWP550	<LOD		7.39	±	<LOD		0.13	±	0.52	±	12.8	±	<LOD		0.24	±	<LOD		41.5	±
			0.87				0.01		0.20		4.73				0.03				18.9	

SWP700	<LOD	8.57 ± 1.28	<LOD	0.06 ± 0.003	0.26 ± 0.23	11.7 ± 3.69	<LOD	0.12 ± 0.10	<LOD	51.5 ± 19.0
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Highlights

- Biochars from different sources had low uptake of P from water (<1 mg P/ g biochar)
- Rice husk biochar presents high P release which could have importance for P reuse
- No correlation is found between surface area and P removal even after activation
- In many cases biochar pyrolysed at 700°C had lower P uptake than at 550°C
- Concentrations of Ca, Mg and S, in addition to total acidity, correlated with P uptake

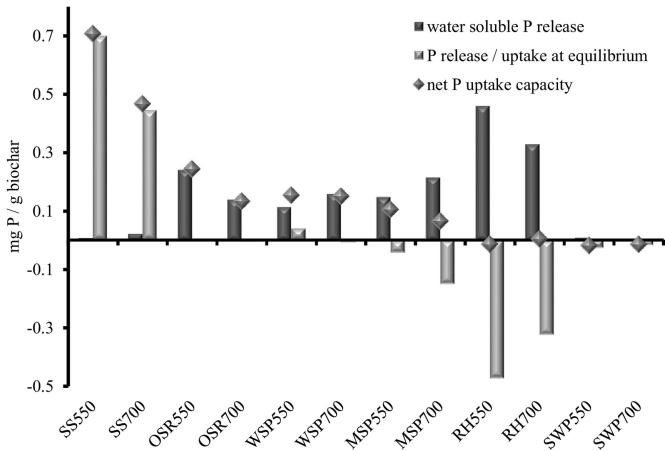


Figure 1

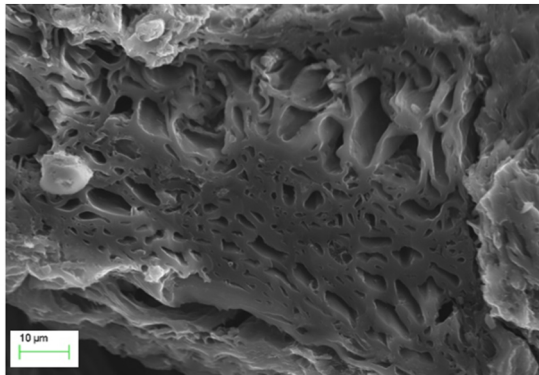
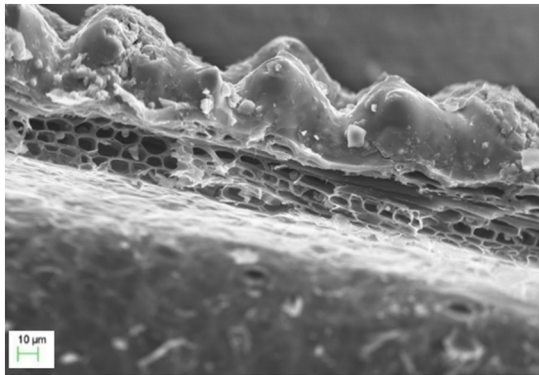


Figure 2

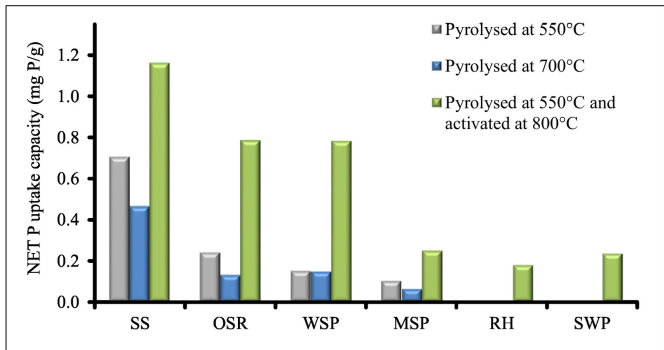


Figure 3

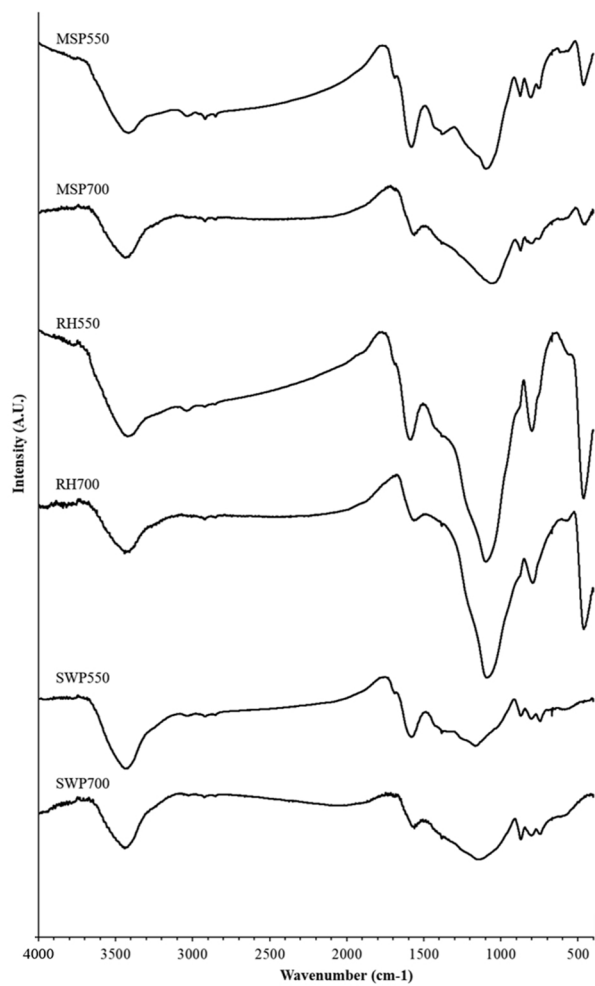
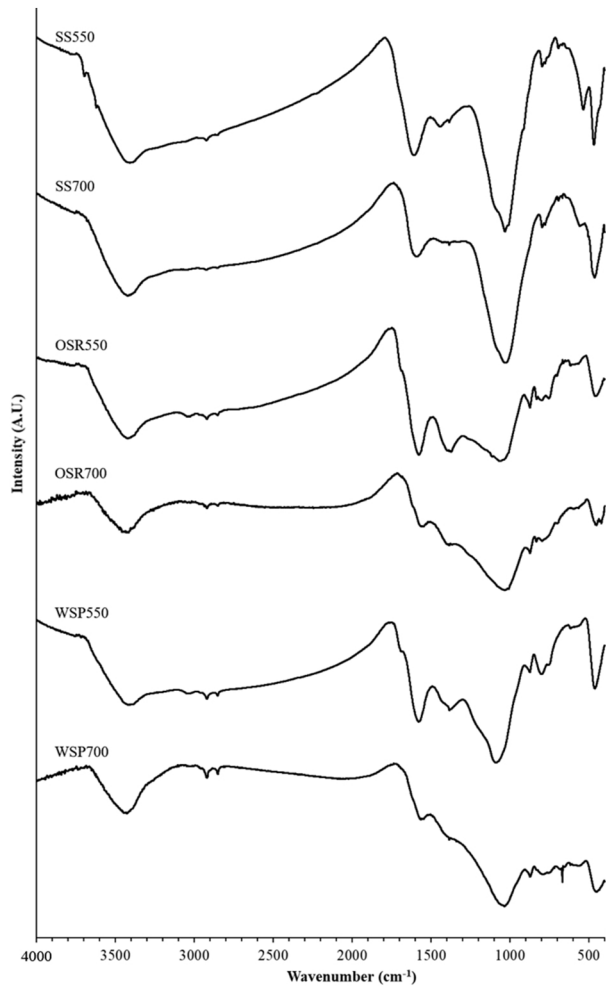


Figure 4

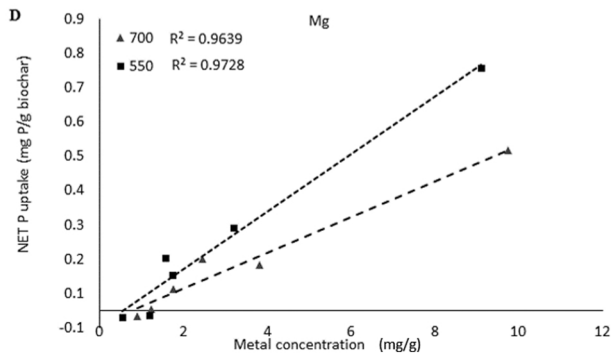
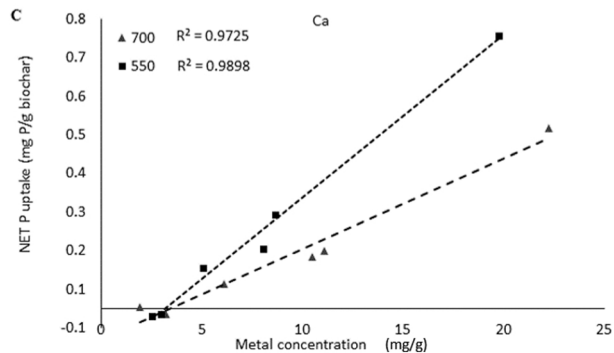
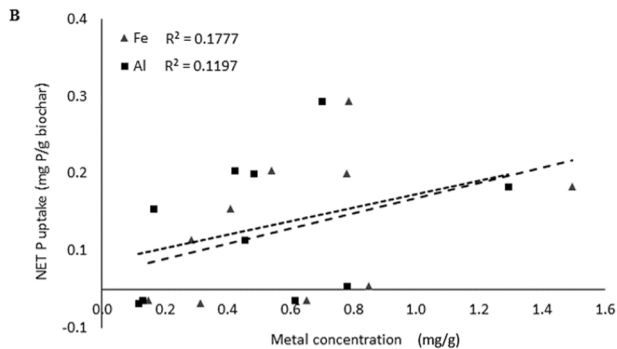
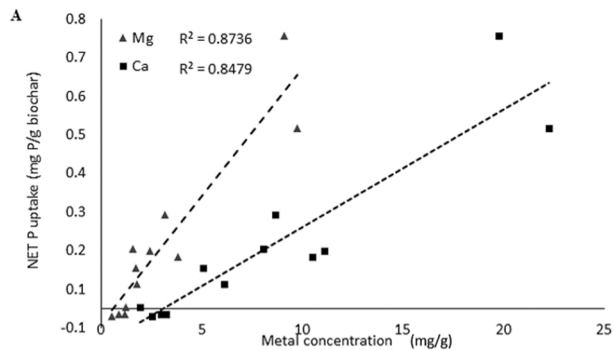


Figure 5

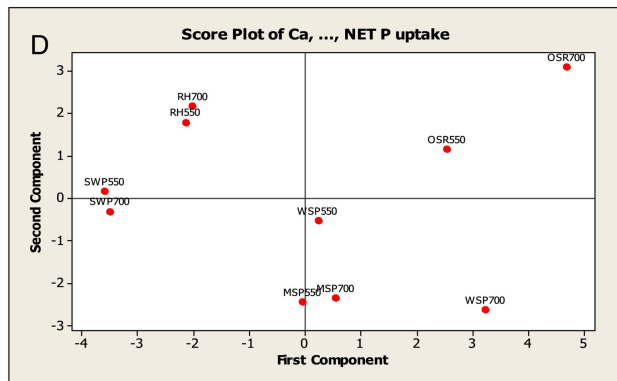
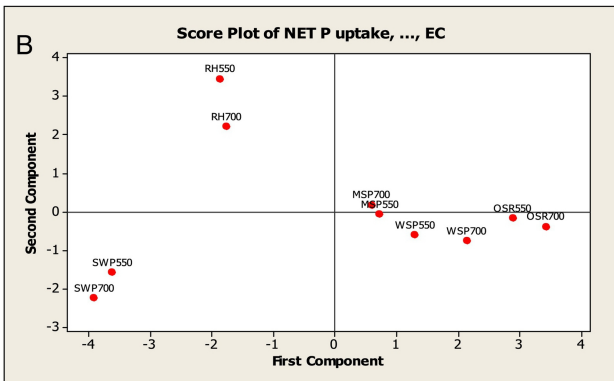
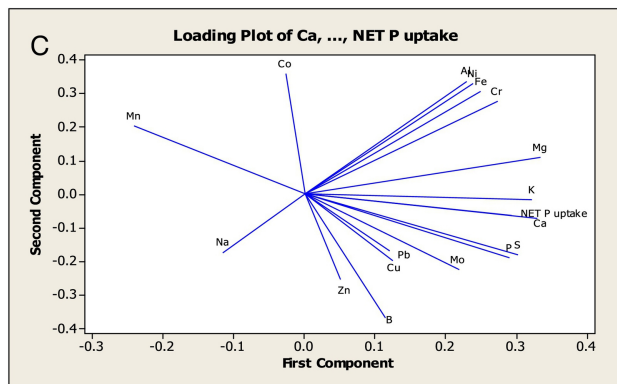
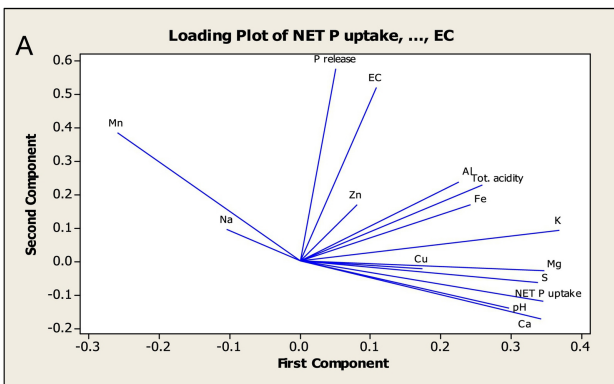


Figure 6