University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2018

Microstructural and associated chemical changes during the composting of a high temperature biochar: Mechanisms for nitrate, phosphate and other nutrient retention and release

Stephen D. Joseph

University of Wollongong, sjoseph@uow.edu.au

Claudia Kammann

Geisenheim University

Jessica Shepherd

University of Edinburgh

Pellegrino Conte

University of Palermo

Hans-Peter Schmidt

Ithaka Institute for Carbon Strategies

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Microstructural and associated chemical changes during the composting of a high temperature biochar: Mechanisms for nitrate, phosphate and other nutrient retention and release

Abstract

Recent studies have demonstrated the importance of the nutrient status of biochar and soils prior to its inclusion in particular agricultural systems. Pre-treatment of nutrient-reactive biochar, where nutrients are loaded into pores and onto surfaces, gives improved yield outcomes compared to untreated biochar. In this study we have used a wide selection of spectroscopic and microscopic techniques to investigate the mechanisms of nutrient retention in a high temperature wood biochar, which had negative effects on *Chenopodium quinoa* above ground biomass yield when applied to the system without prior nutrient loading, but positive effects when applied after composting. We have compared non-composted biochar (BC) with composted biochar (BCC) to elucidate the differences which may have led to these results. The results of our investigation provide evidence for a complex series of reactions during composting, where dissolved nutrients are first taken up into biochar pores along a concentration gradient and through capillary action, followed by surface sorption and retention processes which block biochar pores and result in deposition of a nutrient-rich organomineral (plaque) layer. The lack of such pretreatment in the BC samples would render it reactive towards nutrients in a soil-fertilizer system, making it a competitor for, rather than provider of, nutrients for plant growth.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Joseph, S., Kammann, C. I., Shepherd, J. G., Conte, P., Schmidt, H., Hagemann, N., Rich, A. J., Marjo, C. E., Allen, J., Munroe, P., Mitchell, D. R. G., Donne, S., Spokas, K. & Graber, E. R. (2018). Microstructural and associated chemical changes during the composting of a high temperature biochar: Mechanisms for nitrate, phosphate and other nutrient retention and release. *Science of the Total Environment*, 618 1210-1223.

Authors

Stephen D. Joseph, Claudia Kammann, Jessica Shepherd, Pellegrino Conte, Hans-Peter Schmidt, Nikolas Hagemann, Anne Rich, Christopher Marjo, Jessica Allen, Paul R. Munroe, David R. G Mitchell, Scott Donne, Kurt Spokas, and Ellen Graber

1 Microstructural and associated chemical changes during the composting of a high
2 temperature biochar: Mechanisms for nitrate, phosphate and other nutrient retention
3 and release

4 *Stephen Joseph^{1,2,3}, Claudia I. Kammann⁴, Jessica G. Shepherd⁵, Pellegrino Conte⁶,*
5 *Hans-Peter Schmidt⁷, Nikolas Hagemann⁸, Anne M. Rich⁹, Christopher E. Marjo⁹,*
6 *Jessica Allan¹, Paul Munroe², David R.G. Mitchell³, Scott Donne¹, Kurt Spokas¹⁰ and*
7 *Ellen R. Graber¹¹*

8 *corresponding author: joey.stephen@gmail.com

9
10 ¹ *Discipline of Chemistry, University of Newcastle, Callaghan, NSW 2308, Australia;*
11 *University of New South Wales, School of Material Science and Engineering, NSW*
12 *2052, Australia. E-mail joey.stephen@gmail.com, scott.donne@newcastle.edu.au,*
13 *j.allen@newcastle.edu.au*

14 ² *School of Materials Science and Engineering, University of NSW., Kensington,*
15 *NSW, Australia 2052. E-mail p.munroe@unsw.edu.au*
16

17 ³ *Electron Microscopy Centre, Australian Institute for Advanced Materials, Innovation*
18 *Campus, University of Wollongong, Squires Way, North Wollongong, NSW 2517,*
19 *Australia. E-mail dmitchel@uow.edu.au*

20 ⁴ *Department of Soil Science and Plant Nutrition, working group Climate Change*
21 *Research for Special Crops, University Geisenheim, Von-Lade Str. 1, D-65366*
22 *Geisenheim, Germany, E-mail Claudia.Kammann@hs-gm.de*

23 ⁵ *School of GeoSciences, University of Edinburgh, Crew Building, Alexander Crum*
24 *Brown Road, EH9 3BZ, Edinburgh, UK*

25 ⁶ *Dipartimento di Scienze Agrarie e Forestali, Università degli Studi di Palermo, viale*
26 *delle Scienze ed. 4 90128 - Palermo (Italy).*

27 ⁷ *Ithaka Institute for Carbon Strategies, Ancienne Eglise 9, 1974 Arbaz, Switzerland*

28 ⁸ *Geomicrobiology, Center for Applied Geoscience, University of Tuebingen,*
29 *Sigwartstrasse 10, 72076 Tuebingen, Germany*

30 ⁹ Solid State and Elemental Analysis Unit, Mark Wainwright Analytical Centre,
31 University of New South Wales, Kensington, NSW, Australia 2052

32 ¹⁰ United States Department of Agriculture – Agricultural Research Service, Soil and
33 Water Management Unit, 1991 Upper Buford Circle, St. Paul, MN USA.

34 ¹¹Institute of Soil, Water and Environmental Sciences, The Volcani Center,
35 Agricultural Research Organization, POB 6, Bet Dagan 50250 Israel

36

37 **Highlights:**

- 38 • Composting substantially increases the concentration of nutrients in biochar
- 39 • Dissolved nutrients are taken into biochar pores during initial composting phase
- 40 • Later composing phases result in pore blocking, deposition of additional
41 nutrients
- 42 • The process limits negative biochar-nutrient interactions in the cropping system

43

44 **Keywords:** Composted biochar; Biochar nutrient interactions; Phosphorus and
45 nitrogen capture; Soil amendments

46

47

50 **Abstract**

51 Recent studies have demonstrated the importance of the nutrient status of biochar and
52 soils prior to its inclusion in particular agricultural systems. Pre-treatment of nutrient-
53 reactive biochar, where nutrients are loaded into pores and onto surfaces, gives
54 improved yield outcomes compared to untreated biochar. In this study we have used a
55 wide selection of spectroscopic and microscopic techniques to investigate the
56 mechanisms of nutrient retention in a high temperature wood biochar, which had
57 negative effects on *Chenopodium quinoa* above ground biomass yield when applied to
58 the system without prior nutrient loading, but positive effects when applied after
59 composting. We have compared non-composted biochar (BC) with composted biochar
60 (BCC) to elucidate the differences which may have led to these results. The results of
61 our investigation provide evidence for a complex series of reactions during composting,
62 where dissolved nutrients are first taken up into biochar pores along a concentration
63 gradient and through capillary action, followed by surface sorption and retention
64 processes which block biochar pores and result in deposition of a nutrient-rich
65 organomineral (plaque) layer. The lack of such pretreatment in the BC samples would
66 render it reactive towards nutrients in a soil-fertiliser system, making it a competitor
67 for, rather than provider of, nutrients for plant growth.

1 Introduction

Many studies have been undertaken to examine how the application of biochar can affect crop yields (i.e. Liu et al., 2013). Recent studies have shown that pyrolysing biomass with minerals, and/or post-treating the biochar through either oxidation (e.g. aerobic composting) and/or through the addition of minerals can significantly increase crop yields (Nielsen et al., 2014; Ogawa and Okimori, 2010; Ye et al., 2016). Khan et al., (2016) found that composting could increase CEC and showed a strong affinity for C, N and S although they also found that under some treatments the biochars could lose B, Mg and S. However, there is currently only a very limited understanding of the underlying processes on a molecular level. In particular, the mechanisms of nitrate and phosphate release from co-composted biochar are generally unknown. In this study, we follow up on the study of Kammann et al., (2015) and perform further spectro(micro)scopic analysis of the co-composted biochar used in their study.

Kammann et al., (2015) observed that high temperature biochar, prepared from scrap wood (of which some was partially covered with soil, rich in oxides of Al, Si, Fe and containing some Mn), applied at a high rate of 2 % (w/w) with low mineral fertilization (28 kg N ha⁻¹ from Wuxal Super NPK liquid fertilizer) in a glasshouse experiment significantly reduced above ground biomass yield of *Chenopodium quinoa* compared with an equally fertilized control with no biochar. They also observed reduced nitrate leaching in biochar-soil leaching experiments. Interestingly, the above ground biomass yield reductions also occurred with high dosage application of the same commercial fertilizer, however, the strongest reduction occurred in the treatment with the lowest nutrient supply. This lead to the hypothesis that reduced nutrient availability was responsible for the growth reduction. The biochar in question also had been used as a compost additive in a windrow-composting with daily turnover (mechanical aeration) during the thermophilic phase (Schmidt et al., 2014). After the compost was mature, biochar pieces were separated from it and used in the quinoa growth study (Kammann et al., 2015). The purpose of the study was to examine whether the changes that the biochar underwent during composting would make a difference to the observed impact on plant above ground biomass yield. Upon adding the separated composted biochar in conjunction with low or high application of N, above ground biomass yields were increased by 305% and 160%, respectively, compared to the no biochar control (Kammann et al., 2015). Electro-ultra filtration

and sequential biochar-particle washing revealed that pre-composted biochar was nutrient-enriched, particularly with the anions nitrate and phosphate. The study also found that the composted biochar retained 2 to 5.3 g NO₃ kg⁻¹ (after sequential washing) compared with nearly no nitrate in the fresh biochar; also, the extractable P content of the biochar was doubled by co-composting. Interestingly, standard extraction protocols, i.e. 1 h shaking with de-ionized water or 2 M KCl solution, underestimated the biochar nitrate content. Similar but smaller differences were found for N_{org} (total organic N) and NH₄⁺. Prost et al., (2013) co-composted biochar in litterbags that were harvested and investigated at different times throughout the composting process. They were the first to document that the biochars used (charcoal and gasifier biochar) were loaded with nutrients assumed to be from the composting; noting that the maturing phase, in particular, was important in this regard. In this earlier study, however, no plant growth experiment was carried out. Moreover, standard (soil) methods of nutrient extraction may have underestimated the total amount of nitrate taken up by the biochar (Kammann et al., 2015). Recently, Haider et al., (2016) demonstrated that sequential extractions are necessary to remove all of the nitrate from biochar particles, and thus current methodologies likely underestimate biochar nitrate capture potential. This entrapment of nitrate may shed new light on results that mostly attribute missing (nitrate-)N to microbial immobilization (e.g. Güereña et al., 2015).

Based on these findings, here we characterized the external and internal biochar surfaces from the Kammann et al., (2015) study. Our goals were to elucidate the mechanisms that explain: (i) the ability of the non-composted biochar to capture and hold N and P compounds and/or ions, (ii) the increased capacity for capture and slower release of N and P from the composted biochar, and (iii) the increase in DOC in the biochar. Emphasis has been placed on examining the changes in the mineral and organic phases on the external and internal surfaces of the composted biochar to determine the mechanisms that may be responsible for nutrient capture and release, causing the contrasting impacts on plant yield of the untreated versus composted biochar.

In this study we use the term “organomineral layer” to describe the amorphous associations of C, O and mineral elements identified on the surfaces of the composted

biochar. Similar terms have been used in previous studies (e.g. Archanjo et al., 2017), whilst other studies have referred to these layers as “plaques” (e.g. Zheng et al., 2012).

2 Materials and Methods

2.1 Biochar and Compost Production

Biochar was produced from woody chips (80% coniferous, 20% deciduous wood) by Carbon Terra (formerly German Charcoal GmbH, Wallerstein, Germany) in vertical retorts. These chips were derived from tree waste and as such likely contained entrained soil. This would explain the detectable concentrations of Al, Si, Mn, Fe, and O observed in the biochar (Supplementary Table 1 and 2).

The biochar was produced over 36 h at an average pyrolysis highest treatment temperature of approximately 700°C. The highest treatment temperatures of approximately 850 °C were reached for a short final period just before the biochar was quenched with water. This biochar had a carbon content of 75.8%, H/C_{org} ratio of 0.21 and, considering the wood feedstock, a high ash content (16.3% dry basis). The pH was 9.5 and the BET N₂ surface area was 144 m² g⁻¹. More specific details are given in Kammann et al., (2015).

Methods used for composting and separating the composted biochar pieces and the methods of chemical analysis of the samples are given in Schmidt et al., (2014). The compost feedstock consisted of animal manures, straw, stone meal, soil, BC and mature compost, and the composting process was carried out with daily turnover during the thermophilic phase. The properties of the composted biochar were detailed in Kammann et al., (2015).

2.2 Microscopic and spectroscopic characterization of BC and BCC surface properties

Characterization of BC and BCC surfaces to identify P and N binding mechanisms was carried out using a number of spectroscopic and microscopic techniques. Twenty particles were chosen at random from all of the recovered BCC and fresh BC used in the experiment. Samples for organic functional group determination were prepared by crushing a subset of the samples and sieving those crushed particles (0.1 mm). X-ray

photo-electron spectroscopy (XPS) was carried out on the surface of a whole BCC particle and on a crushed particle to determine if there was a difference in concentration of N and P on the surface of the biochar particles and in the interior. The equipment and procedures used for XPS and Fourier-transform infrared spectroscopy (FTIR) have previously been detailed in Joseph et al., (2010, 2013). Raman spectroscopy was carried out using the procedure and equipment detailed in Bian et al., (2014) and Chia et al., (2012a).

To determine the dimensions of the graphitic nanocrystallites at biochar surfaces by Raman spectroscopy, the technique described in Jorio et al., (2010) was used. Deconvolution of the graphite and the defect (D-G) bands in the Raman spectra was performed using a Gaussian-Lorentzian function with the crystallite size (L_a) determined from the G peak full-width at half maximum (T_G) using the formula:

$$L_a \text{ (nm)} = 560/[T_G - 11] \quad (1)$$

Modified Boehm titrations were performed to determine the distribution and content of biochar surface acid groups following the procedure in Tsechansky and Graber, (2014), whereby dried and weighed biochar subsamples were sequentially pre-treated with NaOH and HCl to remove soluble organic acids and minerals that can interfere with the titrations. Total acid group concentration ('total acidity') is given by the result for the NaOH reaction base, carboxylic acid group concentration by the result for the NaHCO_3 reaction base, lactonic acid group concentration by the difference between the results for Na_2CO_3 and NaHCO_3 reaction bases, and phenolic acid group concentration by the difference between results for NaOH and Na_2CO_3 reaction bases. The modified method represents maximal acidic functionality, because the preliminary acid treatment guarantees that all acidic sites are protonated. It also removes all surface adsorbed organic acids as well as acidic minerals, and thereby assumes to provide an assessment of the non-labile solid biochar surface (Tsechansky and Graber, 2014). Mean and standard deviation of two replicates are reported. Means were compared by one-way ANOVA using RealStatistics for Excel (<http://www.real-statistics.com/>).

To investigate surface and near-surface pore characteristics (which may explain the

greater retention of nitrates and phosphates in the composted biochar compared to its initial zero N and low P content before composting), characteristics of the flow of water into and out of the pores of the biochar was studied using fast field cycling nuclear magnetic resonance (FFC NMR) relaxometry (Conte and Alonzo, 2013). One gram each of BC and BCC was suspended in 3 ml of MilliQ-grade water (resistivity 18.2 Ω , Merck-Millipore Simplicity 185, Milan, Italy) and subjected to FFC NMR relaxometry investigation. ^1H NMR dispersion (NMRD) profiles (i.e., relaxation rates R_1 (or $1/T_1$) vs proton Larmor frequencies, ω_L) were acquired on a Stelar Smartracer Fast-Field-Cycling Relaxometer (Stelar s.r.l., Mede, PV–Italy) at a constant temperature (25°C). The proton spins were polarized at a polarization field (B_{POL}) corresponding to a proton Larmor frequency (ω_L) of 8 MHz for a period of polarization (T_{POL}) corresponding to about five times the T_1 estimated at this frequency. After each B_{POL} application, the magnetic field intensity (indicated as B_{RLX}) was systematically changed in the proton Larmor frequency ω_L comprised in the range 0.01–10.0 MHz. The period τ , during which B_{RLX} was applied, was varied on 32 logarithmically spaced time sets. 8 scans were set, and the $T_{1\text{max}}$, T_{POL} and Recycle Delay (RD) were adjusted at every relaxation field in order to optimize the sampling of the decay/recovery curves.

Free induction decays (FIDs) were recorded following a single ^1H 90° pulse applied at an acquisition field (B_{ACQ}) corresponding to the proton Larmor frequency of 7.20 MHz. A time domain of 100 μs sampled with 512 points was applied. Field-switching time was 3 ms, while spectrometer dead time was 15 μs . A non-polarized FFC sequence was applied when the relaxation magnetic fields were in the range of the proton Larmor frequencies (10.0 to 3.6 MHz), whereas a polarized FFC sequence was applied in the proton Larmor frequencies B_{RLX} range (3.0–0.01 MHz) (Kimmich and Anzardo, 2004).

Laser ablation inductive-coupled plasma mass spectrometry (LA ICP-MS) was carried out on a sample of BC and BCC to investigate the relationship between P binding and mineral content of the biochar. The technique was used to determine semi-quantitative concentrations of P, C, Na, Mg, Al, Si, K, Ca, Mn, Fe, Cu and Pb at individual locations (up to 92 locations, spot size 110 μm) for each of 3 (BCC) or

4 (BC) lines (laser beam wavelength of 213 nm, repetition frequency of 10 Hz, laser energy density of 0.48 J cm^{-2} (at 30%), scan speed of $20 \mu\text{m s}^{-1}$) on both biochar samples, as described in (Bian et al., 2014). ICP-MS was performed at R_f power of 1150 W, helium gas flow rate of 0.8 l min^{-1} , argon gas flow rate of 0.6 l min^{-1} , in peak hopping scan mode and with a dwell time of 0.05 s. NIST610 and NIST612 glass standards were used to estimate elemental concentrations. R-Studio was used to determine the correlation between P and C, Na, Mg, Al, Si, K, Ca, Mn, Fe, Cu and Pb for both BC and BCC (RStudio Team, 2015). Pearson's product-moment correlation coefficient was used to determine correlations between P and the other elements analyzed, except where one or more sets of data were not normally distributed, in which case Spearman's rho was used. As no strong relationships between elemental concentrations were elucidated using this analysis for BC, a Principal Component Analysis (PCA) of the data was performed using the prcomp function in R-Studio (R Core Team) with data centering, scaling and a tolerance of 0.2 to limit the number of principal components (PCs) identified, therefore giving those PCs which explain the maximum variability in the dataset.

Microscopic examination of the pores and the external surfaces of the biochars was carried out using a Zeiss Sigma scanning electron microscope (SEM) fitted with a Bruker energy dispersive x-ray (EDS) analyzer as described in Joseph et al. (2013). Both transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) providing detailed microstructural, crystallographic and microchemical analysis were carried out using a JEOL 2100 Transmission Electron Microscope (TEM) fitted with an Oxford EDS, a JEOL ARM200F aberration corrected TEM fitted with an Electron Energy Loss spectrometer (EELS) and EDS detector and a Phillips CM200 TEM fitted with EDS. Selective area electron diffraction (SAED) was carried out using the JOEL 2100TEM and determination of the Fe EELS oxidation state was carried out on the JOEL ARM as per Quin et al. 2015.

To determine the relative redox activity of the BC and BCC, solid state cyclic voltammetry was undertaken. Electrochemical investigations were performed using a custom-built electrochemical cup-cell. The full cycle was repeated three times. A scan

rate of 0.02 mV s^{-1} was used. Further details of the equipment and method of analysis is given in Joseph et al., (2015). The BC or BCC was first combined using a mortar and pestle in a black-mix consisting of graphite 78 wt % (KS6-Timrex Switzerland), 8 wt % biochar and 14 wt % of a neutral electrolyte (0.05 M K_2HPO_4 and 0.05 M KH_2PO_4). 0.2 g of the mix was then pressed under 1200 psi in the bottom of the cup-cell with paper dividers used to prevent it from adhering to the compaction ram. The method started at a potential of 0.1 V vs. Standard Calomel Electrode (SCE) and cycling to a negative potential of -0.5 V before returning to a higher potential than the initial start potential of 0.4 V.

3 Results

3.1 Mineral Composition of BC and BCC

There are substantial chemical differences between BC and BCC which reflect the accumulation of minerals in the pores and on the surfaces of the BCC. The predominant elements in the BC are Ca, Fe and K with small quantities of P, Mg, Mn, Na and Al and smaller amounts of micronutrients (Zn, B, Cu, Mo) and heavy metals (Ni, Cr). There was a statistically significant increase in the quantity of most of the elements after composting (Supplementary Information Table 1). Fe, Mg, P, K, B, Co, Cu, Mo, Ni doubled and there was a 4-fold increase in Al and an 8-fold increase in Na. Cr levels have more than doubled. Further research is required to determine the mechanisms for the significant increase in its capture. Detailed LA-ICPMS, FFC NMR, SEM and TEM examination of the pores and the surfaces of the fresh and aged biochar allowed identification of the minerals and inorganic compounds.

3.2 SEM and TEM/STEM Characterization of the Fresh Biochar

BC had a considerable amount of mineral matter on its surface (Figure 1A) and inside the pores (Figure 1B). The EDS spectrum of this mineral layer is consistent with interaction of soil minerals that can include clay, oxides of Al, Si, Fe, Mn and possibly CaCO_3 with the wood feedstock during pyrolysis (Joseph et al., 2013; Rawal et al., 2016). Figure 1D provides a higher magnification image of this mineral layer and Figure 1C is an EDS analysis of the mineral content. There is a considerable concentration of Si, K, Fe, Mn, Al, Ca and S, suggestive of soil contamination in the biochar feedstock. Supplementary Figure 1 details the mineral structure in one small area of this biochar. There are a series of Si nodules which appear to have formed,

with which P is associated. Fe and Mn compounds appear to have formed on the carbon matrix. There is an area high in S and another high in P where Fe/P and Fe/S mineral phases may have formed. Potassium, Ca and Mg are associated with the phase identified which was high in Fe and Mn (Figure 1).

Analysis of over 20 particles of BC by high resolution Transmission Electron Microscope (HTREM) supports the observation that soil was entrained on the wood before pyrolysis resulting in the formation of submicron inorganic/mineral phases on the surfaces of the biochar. Figure 2 shows snapshots of some of the different structures observed on the surface of the carbon matrix. Porous heterogeneous inorganic phases can be seen to have formed on the surfaces. Figure 2A, 2B and 2C indicate that there is considerable porosity between a range of different mineral particles which have dimensions ranging from 50 nm to less than 10 nm. Similarly the pore shapes and dimensions are heterogeneous. Figure 2D shows another area where the inorganic phases are physically larger and appear to have fused together, potentially during pyrolysis. Supplementary Figure 2A shows graphitic planes formed around a 5 nm particle rich in Fe. The amorphous phase between the Fe and the outer graphitic planes has a high C content with a small concentration of Ca (Supplementary Figure 2B). The structure observed in Supplementary Figure 2C is probably hollow carbon shells formed during the pyrolysis process as previously observed by McDonald-Wharry et al., (2015). Zhang et al., (2012) proposed that dissolved phosphate and nitrates can be adsorbed into these voids. The structure in Supplementary Figure 2D is a porous amorphous C matrix with a range of sub-5 nm mineral phases containing Al, Si, Fe, Ca, P, and K detected by EDS (data not shown).

3.3 SEM and TEM Characterisation of the Composted Biochar (BCC)

3.3.1 SEM Characterisation

SEM imaging shows that sections of the external surfaces of the biochar and many of the internal macro- and micropores of BCC are coated with a layer (rich in C and inorganic/mineral matter) with some evidence of fungi growth (Figure 3A and 3D) (Vanek and Lehmann, 2015). The morphology of the surface of the composted sample is different to that observed in Figure 1 and Supplementary Figure 1. The surface coating of the BCC has a high concentration of C, Si and O and detectable concentrations of N, P, Fe, Al, Mg, Ca, Cl, and S (Figure 3B) when compared to BC.

There are detectable differences on the samples examined between the intensity of peaks in the EDS spectra some of the elements (Al, Ca, Si, K, P and N) in the BCC compared with the BC. Figure 3F is a high resolution map of the compounds containing N on the surface of BCC surface. Other detected elements in the area included C, O, Al, Si, Fe, K, P, Na, and Mg, and once again a low-concentration of Cl. Some of the pores in the carbon matrix have a very thin layer of the inorganic/mineral phases on their surfaces, while other pores appear to have been coated, resulting in a potential decrease in the pore volume (Figure 3C). The remnants of the vascular structure from the original feedstock can be seen in the surface of BCC in Figure S3A. It appears to be rounded and in some cases broken or fragmented when compared with the sharp inner vascular structure noted in Supplementary Figure 3B. The spectro-microscopic evidence indicates that complex chemical and physical processes are taking place on the external and internal pores of the biochar as redox, pH and temperature varies through the composting process and physical turning occurs. It is also possible that some micro-fracturing of biochar has occurred as suggested by Spokas et al., (2014).

3.3.2 STEM and TEM characterisation of the surfaces of the BCC

Figure 4 and Supplementary Figures 4, 5 and 6 are STEM images and EDS analyses of the the organomineral layers on the BCC surfaces. Supplementary Figure 6 A and B is a high-resolution image of one of the micro-agglomerates formed on the biochar surface. The EDS analysis indicates binding of < 10 nm minerals/inorganic compounds comprising mainly O, Ca, P, Al, Si, Fe and Mg bound together again by C compounds. Figure S7 is a phase map which indicates that the agglomerates have quite different compositions. The phase map shows where a specific group of minerals and/or inorganic compounds are localised in a specific region of the organomineral layer. The green phase at the bottom of the Supplementary Figure S7C has a high concentration of C, O, Ca, P, Fe, Al and Si. The blue phase mainly consists of Fe, O, C, Ca and the red phase has a high content of C, Ca and O and smaller amounts of K, P, Si and Al. A similar complex pattern is noted in the line scan of elements across a thin section of the area imaged (Supplementary Figure 4B). This analysis indicates the formation of a porous micro-agglomerate associations bound together by C compounds on some of the surfaces of the biochar. The interface

between each of the micro-agglomerates is very porous and there appears to be only a few regions bound to the biochar or to each other.

Figure 5A illustrates the formation of a poorly ordered graphitic structure around an Fe/O nanoparticle (evidenced by TEM-EDS, data not shown) inside the carbon matrix of the co-composted biochar. Figure 5B is a TEM field image of a thin layer of amorphous C material that has formed around a Fe/O nanoparticle on the organomineral surface layer on the biochar. Figure S3 is a high-resolution image of a Fe/O particle. The EDS and SAED patterns (Figure S7B and S7D) identify the iron phase as magnetite (Chen et al., 2011). These structures could have formed due to adsorption of organic molecules on the magnetite as proposed by (Kleber et al., 2007) for the interaction of iron oxides present in soil and soil organic matter. It could also be due to abiotic and/or biotic reactions on the nanoparticle surfaces (Bauer and Knoelker, 2015; Harvie et al., 1984; Lee et al., 2008).

EDS and SAED analysis indicates that minerals and inorganic compounds in these micro-agglomerates could consist of Al_2O_3 , SiO_2 , Fe_3O_4 , Fe_2O_3 , FePO_4 , CaCO_3 , CaPO_4 , KCl, clay, and possibly gypsum, MgCO_3 , FeS, FeSO_4 . Further detailed analysis is required to positively identify the specific compounds and minerals.

3.3.3 High resolution imaging of the pore structure

Figure 4 illustrates the pore structure of the organomineral layer (lower left, Figure 4A) that formed on the surface of the biochar (upper right, Figure 4A) during composting. Figure 4B is a micrograph of the interface between the biochar and the organomineral phase showing the range of pore sizes. EDS analysis (data not shown) reveals that the bright areas are minerals or inorganic compounds high in Si and Fe and the light grey areas are thin layers or potentially organic compounds. Supplementary Figures 4C and 5C indicate that there are still < 50 nm pores in the biochar carbon matrix after composting that do not appear to have inorganic or organic compounds attached to their walls. Due to sample preparation, we cannot assign these pores to their original position in the biochar particle (outer surface vs. core of the particle). Figure 5D is a STEM SE image of a very porous layer that could have formed inside a larger pore of the biochar during composting.

Supplementary Figure 5A shows that the pore structure is very different in an expanded Al/Si/O (probably clay) mineral compared with pores in the carbon matrix (Supplementary Figure 5C). Supplementary Figure 5B is a slice through a section of the organomineral layer on the surface of the wood biochar. The dark areas are mineral and the white areas pores. The grey areas are the carbon structure. It can be seen that the pore size, shape and composition is heterogeneous with some pore surfaces composed of a carbon matrix with a small number of mineral nanoparticles that occupy part of the pore surface.

3.3.4 Summary of STEM and TEM characterisation

To summarize the examination of the internal and external surfaces of the fresh biochar (BC), TEM and SEM indicate that:

- a. There are very large macropores (diameter $>1\ \mu\text{m}$) that have formed when the phloem and xylem in the wood have been pyrolysed (Figure 3); however, these structures also exist in the original feedstocks. There are also a substantial number of smaller macropores (diameter $< 100\ \text{nm}$) and mesopores (2-50 nm) of varying sizes that could connect the macropores (Supplementary Figure 5). Micropores ($< 2\ \text{nm}$) cannot be imaged by means of even state-of-art STEM or SEM, although they must have contributed to the specific surface area according to BET measurements.
- b. Mixed mineral phases, probably originating from soil that was on the surface of the wood before pyrolysis, have dimensions of less than 50 nm. These phases are on the biochar surface and are either sintered together or bound with the carbon. Pore diameters in this layer vary from < 5 to 50 nm (Supplementary Figure 4).
- c. Some of the mesopores are associated with the formation of graphitic carbon nanotubes near to Fe/O nanoparticles with a total diameter $< 10\ \text{nm}$.
- d. There are micropores and mesopores (diameter $< 50\ \text{nm}$) existing in the carbon matrix that do not appear to be interconnected (i.e., dead-ended pore).

To summarize the examination of the internal and external surfaces of the composted biochar (BCC), TEM and SEM indicate that:

- a. Porous micro-agglomerates have formed on the external and internal surfaces of the biochar. These micro agglomerates are composed of minerals and

inorganic compounds bound together with C compounds (Figure 4, Supplementary Figures 4 and 5).

- b. Most of the inorganic compounds and minerals have dimensions < 20 nm. Some of these minerals/inorganic compounds have a facet that sits on the surface of a pore and are surrounded by C compounds.
- c. Some of these aggregates have coalesced to form porous organomineral associations (Figure 4B and Supplementary Figure 6)
- d. The organic compounds of the micro-agglomerates probably contain both P, N and Ca, as well as other inorganic elements
- e. There are < 50 nm biochar pores that do not have these organomineral associations at their surfaces (Supplementary Figure 6).
- f. There are a range of pore shapes and sizes in the organomineral associations that exist on the surfaces of the biochar. Figure 5 shows these can vary from < 1 to > 50 nm.

3.5 Characterization of the surface functional groups of the fresh and composted biochar

3.5.1 Boehm Titration.

Total acidity and acid group concentrations are given in Table 1 for the fresh and composted biochar after removal of surface adsorbed organic acids as well as acidic minerals by washing in diluted base. Interestingly, there are no significant differences in acid groups between the original and composted biochars at a level of $p < 0.05$. This suggests that the composting process did not alter the biochar C structure and distribution of surface functional groups when all adhering C compounds from the composting process were removed prior to titration. It is important to note that the previous spectroscopic results were obtained without initial washing in a base.

3.5.2 Analysis of surface functional groups using XPS, FTIR Raman and Cyclic Voltammetry.

XPS analysis of the surface (whole biochar particle, Table 2) indicates an alteration in the chemical composition of the surface moieties as well as alterations in the abundance of C and N functional groups on the outermost 10 nm of the external surfaces of the BCC compared to the BC. The BCC had a higher relative

concentration of carboxyl groups and slightly higher C-O (alcoholic, phenolic, hydroxyl, and/or ether) moieties, but lower amounts of C-C, C-H as well as a lower total C content. XPS showed an almost 3 times higher content of carboxylic groups in BCC compared to BC, while the Boehm titration revealed an increase of ~38%. This is because the modified Boehm methodology removes most of organomineral surface layer during the base/acid pretreatment. From the comparison of the results from XPS and Boehm Titration we find that oxidation of the original surface biochar carbon matrix is only a minor contribution to the overall content of C functional groups in BCC. This strongly suggests that the observed increase in the O and N functional groups is due to the formation of the organomineral coating (potentially the above described micro-aggregates) on the internal and external surfaces of the biochar.

The deconvoluted region spectrum for BCC shows a detectable concentration of quinones at 283.47 eV (Ramesh and Sampath, 2001). These functional groups have been associated with the potential storage and release of electrons from biochar (Klöpfer et al., 2014). The concentrations of highly aromatic C (indicated by the shakeup peaks at 290.62 eV and 290.96 eV) is greater in the BC than the BCC. It also appears that there are O heteroatoms in BC and BCC. These data along with the SEM imaging and analysis confirm that the BCC has been covered by a layer of C that has a lower concentration of condensed aromatic rings than the BC. However, we can not determine conclusively if this C is biochar derived or from an exogenous source.

The BC had a significant concentration of pyrrolic groups at its surfaces whereas there were no pyrrolic groups detected for the BCC indicating that nitrogen detected on the surface was not bound to the carbon matrix of the initial biochar (Amonette and Joseph, 2009; José and Knicker, 2011). The main groups identified on the top 10 nm of the surface of the BCC are NH_2 /amino N, $\text{N}-\text{C}=\text{O}$ and $-\text{NH}_3^+$ /oxidised N/chemisorbed NH_4 groups and these could be mainly associated with the organomineral phase as indicated from the SEM analysis and would have been adsorbed or formed during the composting. The P content on the surface was measured at 0.3 atomic wt % in BCC. To determine if there is a greater concentration of N and P in the BCC particles where crushed and passed through a 100 μm sieve. When the BCC particle was crushed nitrates were measured at a concentration of 0.51 atomic wt % at 407.3 eV (Supplementary Figure 8), and probably an amino group at a

concentration of 5.72% at 400.03 eV. Some of these nitrogen anions could be attached to positively charged nano-hotspots, especially FeO minerals (Tsai and Chen, 2013; Unsoy et al., 2012) as observed in Supplementary Figure 6. However, to our knowledge, it is not possible to confirm this hypothesis here, as the surface charge of these hotspots cannot be specifically measured with any spectroscopic technique. The concentration of surface P was measured at 0.78 atomic wt %. This would suggest that a substantial amount of the N and the P is contained inside the biochar, which might not be immediately available to the water outside of the particle. This could partially explain why some of the N and P is released very quickly when extracted, while a greater percentage of the N is released with each subsequent extraction cycle (Haider et al., 2016; Kammann et al., 2015).

The concentration of K on the surface of the BBC was three times higher than that of BC. It is probable that this K was from salts present in the compost pile, as observed by Prost et al., (2013). The SEM and TEM EDS analyses indicate that K salts have precipitated out or been adsorbed through cation exchange with the functional groups either in the organomineral layer and/or the biochar. Except for Fe, concentrations of all mineral elements were higher on the outer surface of the BCC than in the crushed whole sample analyses (Table 3) indicating adsorption/precipitation/agglomeration onto the biochar during composting.

The baseline-corrected ATR-FTIR spectrum (Figure 6) of the BC is unusual for a high temperature biochar. Most high temperature biochars have little functionality and thus their spectrum contains few intense peaks (Liu et al., 2015). However this biochar has a spectrum very similar to that of an activated carbon that has been treated by ester hydrolysis in an alkaline environment to produce hydrophilic surfaces that bind water by hydrogen bonding (Yao et al., 2014). It has peaks associated with C=O, C-O, COO⁻, OH and Carbonates as well as aromatic C. The baseline-corrected ATR-FTIR spectrum (Figure 6) of the BCC shows as in the BC a number of broad overlapped peaks between 1800 and 650 cm⁻¹, indicative of mineral and organic matter (Guan et al., 2007). The band at 3369 cm⁻¹ band is coincident with the ν(OH) bands of water, carboxylic acids, and hydrated clay minerals. The peak at ~3200 cm⁻¹ is characteristic of aromatic C-H stretching [ν(CH)]. A small shoulder at 1712 cm⁻¹ can be assigned to functional groups containing C=O groups and the stronger peak

at 1581 cm^{-1} can be assigned to the C=C vibration found in aromatic ring deformation modes (Chia et al., 2012a). These aromatic peaks are considerably stronger in the fresh biochar.

Representative peaks for the adsorption of nitrate on minerals have been noted in Rubasinghe and Grassian (2013) at around 3390 cm^{-1} , 1433 cm^{-1} and 1339-1380 cm^{-1} . The peak at 1581 cm^{-1} in the BC sample is not observed in the BCC sample. Another notable difference is the increase in peak intensity of the BCC at 1433-1375 cm^{-1} possibly indicating adsorption of nitrates in the organomineral layer and a broad peak around 1064 cm^{-1} , which is usually associated with C-O stretching of organic polysaccharides (Cheng et al., 2006). On the other hand, this peak is also characteristic of inorganic carbonates, but interpretation is often complicated due to the overlap with mineral Si-O stretching frequencies and shifting in the frequency as a function of the interaction of the carbonate-oxygen atoms with surface complexation (Jolivet et al., 2011; Wijnja and Schulthess, 1999). Nevertheless, if we look at the entire BCC spectra, the $\nu_{1\text{-stretch}}$ and $\nu_{3\text{-stretch}}$ of CO_3^{2-} could be assigned to the dominant peaks in the BCC, with the peak at 872 cm^{-1} attributed to the ν_2 in-plane bend of $-\text{CO}_3$ (872 cm^{-1}) (Wijnja and Schulthess, 1999). In addition, the presence of peaks at 872 cm^{-1} , 820 cm^{-1} and 755 cm^{-1} indicate calcite and silica in the BCC, which agree with the XPS elemental analysis. These compounds were observed in the SEM and TEM. The D-G bands in the Raman spectra (Figure 7) of the BC sample showed an optimum fit to five mixed Gaussian-Lorentzian functions, then the cross-sectional particle size for a bimodal distribution calculated using a G1 peak at 1607 cm^{-1} , FWHM (Full width half maximum) 49 cm^{-1} = 15 nm, G2 1583 cm^{-1} , FWHM 77 cm^{-1} = 9 nm (Jorio et. al. 2012). Similarly, the D-G bands in the Raman spectra of the BCC were fitted to five mixed Gaussian-Lorentzian functions, then the cross sectional particle size for a bimodal distribution calculated using a G1 peak at 1598 cm^{-1} , FWHM 63 cm^{-1} = 11 nm, G2 1542 cm^{-1} , FWHM 226 cm^{-1} = 3 nm (Jorio and Cançado, 2012). The crystallite size range of the BC of 9-15 nm is typical of charcoals (7 – 11 nm) (Ribeiro-Soares et al., 2013) whereas the BCC 3-11 nm is more typical of biochars and black carbon that have a significant coating of organomineral micro aggregates as found in Terra Preta soil particles (2 – 8 nm) (Chia et al., 2012b; Ribeiro-Soares et al., 2013).

Cyclic Voltammetry is a technique that determines whether there are compounds/molecules that can be readily oxidized at the potential that exists in soils (Joseph et al 2015). Figure 8 clearly shows that the BC does not undergo oxidation at normal voltages that are measured in soils (0.4 V vs. Standard Calomel Electrode (SCE)), even after cycling three times. However, after cycling three times the BCC starts to oxidise at a voltage of 0.08 V, indicating that some redox activity does occur, such as oxidation of labile organic molecules or elements that can have different oxidation states (Fe, Mn). This behavior was also observed by Ramesh and Sampath, (2001) on exfoliated graphite that was coated with different types of quinones. Oxidation has also been attributed to the change in oxidation state of Fe/O nanoparticles and the oxidation and/or reduction of N, S, P and C compounds (Joseph et al., 2015).

3.5.3 (FFC) NMR Relaxometry

Figure 9 reports the nuclear magnetic resonance dispersion (NMRD) profiles (i.e. $R1 = 1/T1$ values vs ω_L) of the water-saturated composted and original biochar samples. BCC reveals shorter proton longitudinal relaxation rates in the whole range of the proton Larmor frequencies investigated here (i.e., 0.01-10 MHz) as compared to BC. The fitting procedure applied to the experimental results reported in Figure 9 allowed calculation of the average correlation times (τ_C ; Figure 10). This is the time needed for a molecule of water to rotate by one radian or by a distance corresponding to its length (Conte and Alonzo, 2013). It can be seen that the relaxation time needed by the BC is much greater than the BCC indicating that water is more tightly held in the pores of the biochar.

3.5.4 LA ICP-MS

LA ICP-MS provides spatially resolved data on the elemental composition of the uppermost 5 nm of the sample. Correlation of P concentration with other elements for the LA ICP-MS data for the BC showed statistically significant, but not strong correlations with all elements except C and Si (Supplementary Table 2). Observation of element covariation in plots of the whole data set was not possible due to the presence of high P outliers (Supplementary Figure 9), so the sampled locations where P concentration was $< 100 \text{ mg kg}^{-1}$ were analyzed separately (Supplementary Table 2,

Supplementary Figure 10). Correlation results of these high-P locations were similar, with the exception of that with Na, which was no longer significant. The plots of these data show the mostly random relationships between the analyzed elements and P.

To further characterize the relationships between elements on the surface of BC, a PCA was performed on the whole dataset (Supplementary Figure 9). The loadings indicate that the first principal component (PC), which accounted for 64% of variation in the data, was associated with increasing concentrations of Si, Al, Na, Mg and P and decreasing concentrations of K (Supplementary Table 3). The second PC accounted for 14% of data variation, and was associated with higher Fe and less Na, and strongly associated with lower Pb. The third PC was very strongly associated with higher concentrations of C, and accounted for 10% of total variation. Examining the plot of the first 2 PCs (Supplementary Figure 10), as also indicated by the loadings, Si, Al, Na, Mg and P were all strongly covariant. Fe and K were strongly covariant, whilst Mn and Cu were strongly covariant and both covariant (but less strongly) with Pb and C. These data indicate that the phases of BC biochar containing the most P also contained Si, Al, Na, and Mg.

There was a strong and significant correlation between the concentrations of C, Na, Mg, Al, Si, K, Ca, and Fe with P for the composted biochar (BCC) (Supplementary Table 2). Visual inspection of the plots in Supplementary Figure 12 show that the strongly significant correlations are influenced by the large number of sampled locations with low concentrations of P. Sampled locations where the concentration of P was higher than 1000 mg kg⁻¹ were much fewer in number, and showed different covariance characteristics than the statistical analysis of the whole dataset indicated. At higher concentrations of P, only C and Ca appeared to be strongly covariant with P. For the other elements, there were multiple sampled locations which were not strongly covariant with P, indicating that these high P sample locations could be sites of Ca-mediated P precipitation, associated with organic matter. At lower concentrations (< 1000 mg kg⁻¹), P is most strongly correlated with Mg, Ca and K, but these correlations are associated with lower Spearman's ρ values than for the whole dataset (Supplementary Table 2), suggesting these associations might be more strongly associated with higher P concentrations. Conversely, the correlations between P and Fe, Al and Si are stronger for the lower P data than those for the whole

dataset. Like the results of the PCA for BC, the variation of P concentration at sampled locations $< 1000 \text{ mg kg}^{-1}$ is related to the variation of Si and Al (although the concentrations are one order of magnitude lower), so these may be related to the original biochar surface, whilst the higher concentration locations may be the result of composting processes.

4 Discussion

In this study, we used spectroscopic and microscopic methods to identify alterations in surface structure, surface elemental content and carbon speciation of a co-composted biochar (BCC) compared to non-composted, original biochar (BC). Here, we found evidence for potential mechanisms underlying this phenomenon of “nitrate and phosphate capture”, i.e. nitrate and phosphate that is not retained only by conventional anion exchange capacity.

Our results indicate this process begins with the capture of nutrient-rich water into the pores of BC, followed by partial clogging of meso- and micropores with a nutrient-rich organomineral layer from the composting process. The clogging of the internal pores could induce other chemical changes as well as changing the suction forces (capillary) that would allow the diffusion of anion rich water into the interior of the biochar. This is underlined by the close-correlation ($R^2 > 0.99$) observed between the release of dissolved organic carbon (DOC), and nitrate and phosphates, from the BCC particles during electro-ultra-filtration (EUF) (Kammann et al., 2015). Barrow, (2015) noted that sorption (of phosphate) onto a substrate will take place when there is a negative concentration gradient within the soil. This transfer of nutrients will cease only when all of the sorption sites are taken up. Here, we put forward the hypothesis that the dissolved anions, which become concentrated in the solution (in the soil/biomass/mineral mixture in the compost) during drying, could be drawn into small biochar pores. The rate of this reaction would be directly correlated to the concentration gradient between the pore and the outside water solution, accelerating transport of the nitrate and phosphate solution inside the pore. This pore water becomes trap, but would not be released as the soil/compost mixture rehydrates due to the stronger capillary forces of these micropores (with the added osmotic potential, in addition).

We outline the evidence for the different processes below. It should be noted that nitrates are highly soluble, do not easily form precipitates and do not easily bind to activated carbon/biochar in aqueous solution (Gai et al., 2014) unless the surface has been acidified so that it has a significant concentration of positive functional groups (Bhatnagar and Sillanpää, 2011). Among the anions commonly present in water, chloride competes with nitrate sorption to the greatest extent, and phosphate the least (Bhatnagar and Sillanpää, 2011). On the other hand, phosphates can react either weakly or strongly with Al, Fe and Ca surfaces (depending on pH), and also exist in organic forms in compost. The behavior of phosphate in soil is dominated by pH and it is most plant available (or soluble) at pH 6-7. The biochar itself has a pH of 9.5, the soil has a pH of approximately 7.5 and the compost has a pH of 7.2 (Kammann et al., 2015). In a review of nitrate capture by different adsorbents, Loganathan et al., (2013) note that nitrate adsorption is most effective when substrate (including biochar) is impregnated with a metal oxide, treated with an acid, grafted with an amine group, has heat treated minerals and/or a surfactant added to its surface.

Spectro(micro)scopy and microscopy revealed a number of important features of the original high temperature wood biochar used in this experiment. It has a high content of porous inorganic μm and sub- μm sized phases that are rich in nano-sized particles comprised of Mn/O, Fe/O, Fe/S, Al_2O_3 , SiO_2 , K/Na/Ca compounds and clay, (Supplementary Figure 1, 2 and 3, Supplementary Table 1 and 2) as well as hollow graphitic shell structures. Some of these inorganic particles are crystalline as evidenced by TEM SAED, whilst others are amorphous. Some of the inorganic nano-hotspots are surrounded by amorphous carbon and some by graphitic domains (Figure 2) and some of the mineral phases have an expanded structure (Supplementary Figure 5). The pores within the BC are heterogeneous and have a range of inorganic compounds and minerals on their surfaces (Fig. 2). Heating of minerals (as occurs during pyrolysis) can result in an increase in surface area and porosity and this increases the ability to adsorb nitrates (Soías-Viciano et al., 2008). FTIR spectrum indicates that there is a significant content of amine groups and esters/-COO- groups in the biochar matrix and XPS also indicates that C=O and COOH bonds exist on both the surfaces within the biochar. Modified Boehm titration results suggest that the fresh and the composted biochar surfaces have similar contents of acidic functional groups indicating little oxidation of the biochar carbon matrix during composting.

In the initial phase of the composting when the macro pores are not clogged, water containing dissolved nutrients and organic compounds will diffuse initially into the smaller pores due to capillary forces. The nuclear magnetic resonance dispersion (NMRD) profiles (i.e. $R_1 = 1/T_1$ values vs ω_L) reported in Figure 9 indicate that when water enters the internal pores of BC it becomes constrained and that cations and anions will be tightly held. Innes et al. (2015) noted that salt solutions can be tightly held in nanopores depending on the surface charge and the type and concentration of functional groups on the pore surface. XPS results indicated that nitrates and phosphates were detected in BCC after crushing (which allows analysis of the inner surfaces of the particle). This would lead to the conclusion that the nitrates and phosphates are thus entrapped with water in these micropores, which are not readily available to plants or microbes.

Previous research into the adsorption of natural organic matter anions and cations by activated carbon has shown that the internal sub-50 nm biochar pores could contain both organic compounds as well as dissolved oxygen and CO_2 , cations, anions and colloids (Shao et al., 2014; Velten et al., 2011). Research on mineral/activated carbon (especially those impregnated with Fe/O) composites have shown increased adsorption of natural organic compounds and anions (Koduru et al., 2016). A complex series of reactions can take place in these pores, which could result in the formation of porous organomineral layers, altering pore distribution profiles. Given the complexities of this system, based on the results from Kammann et al (2015) and the detailed examination of the biochars' from their experiments we put forward the following working hypotheses.

1. Within the pore system, oxygen can be consumed through biotic and abiotic oxidation of organic matter on the surfaces of the carbon matrix and Fe^{2+} and Mn^{2+} sitting on the surfaces of the pores. This will result in both a change of pH and Eh as has been measured for submerged soils (Kirk, 2004). Biochar has been repeatedly suggested to rapidly form anoxic microsites (Hagemann et al., 2016; Van Zwieten et al., 2009).
2. Once this oxygen has been consumed further reactions can take place between the oxidized species of Fe and Mn and organic matter in the water resulting on the formation of CO_2 . Dissolved CO_2 could react with Ca^{2+} and Fe^{2+} to form carbonates (Joseph et al., 2010).

- 745 3. Dissolved soil organic matter can also be adsorbed on the functionalized
746 surfaces in the pores, especially on the positively charged Fe/O and Mn/O.
747 This process would be accelerated if the biochar was hydrophilic (Hyung and
748 Kim, 2008). Evidence from this is seen from the FTIR spectrum and from the
749 EDS analysis of the elemental composition of the internal pores.
- 750 4. Reducing or eliminating O_2 will lower the Eh of the nutrient rich water and the
751 Pourbaix diagram (Quin et al 2015) for N shows that it would be present as
752 both nitrates and nitrites, and possibly NH_4^+ .
- 753 5. In this environment, dissolved organic nitrogen can mineralize to NH_4^+ , which
754 in turn can complex with acidic functional group on the surface of the carbon
755 matrix (Le Leuch and Bandosz, 2007). As the temperature in the compost
756 increases, so the rate of these complex reactions should increase. This could
757 partly explain the results of the EUF where the majority of the organic
758 nitrogen and the NH_4^+ was extracted after 45 to 60 minutes. Very little NH_4^+
759 was extracted in the first 30 minutes and only approximately $\frac{1}{4}$ of the
760 dissolved organic nitrogen was extracted in this time.
- 761 6. Since magnetite containing both Fe^{2+} and Fe^{3+} was detected in the biochar,
762 further redox reactions can take place resulting in the oxidation of the
763 ammonia to nitrate (Kirk, 2004; Li et al., 2012).
- 764 7. Extraction of DOC by EUF mainly occurred after 40 minutes, indicating that
765 that the inner pores also contained a substantial amount of these organic
766 molecules that could have both positively and negatively charged sites and act
767 as surfactants, thus binding nitrate and NH_4^+ .
- 768 8. Nitrates could be held via water to the mineral surfaces by hydrogen bonds
769 (Bhatnagar and Sillanpää, 2011) or could be directly bonded to the positive
770 sites of the different minerals in different modes including monodentate,
771 bidentate and bridging as measured by (Rubasinghege and Grassian, 2013).
772 Given the complexity, ligand exchange electrostatic bonding with the anions
773 could also take place (Loganathan et al., 2013).

774
775 Further detailed research is required to determine the range of potential reactions that
776 can take place in the oxygen deprived pores of the biochar both in the initial stages of
777 composting and after these pores have been partially blocked to determine the validity
778 of our hypotheses.

779

780 We hypothesize that once the internal meso and micropores are blocked, the
781 mechanism for capture of anions would be more complex. It is important to note that
782 after an initial low temperature phase of composting, temperatures of 60-70°C are
783 reached and drying starts to occur (Bernal et al., 2009). The compost pile is then
784 wetted and this changes physical and chemical properties and the microbiology of the
785 reacting biomass, which in turn will affect the processes occurring on the surfaces of
786 the biochar.

787

788 EUF has shown that a significant percentage of the nitrates and DOC are not held
789 tightly in the composted biochar. The NMRD curve for the BCC sample is flatter than
790 that acquired for BC, thereby indicating that the molecular mechanisms of water
791 motions in contact with the surface of BC and BCC are also not the same. BCC
792 surfaces have a lower concentration of polycondensed aromatic carbons than BC. This
793 leads to the proposition that the paramagnetic effect is more effective in BC than in
794 BCC, thus resulting in the BC NMRD curve at longest T_1 values compared to the
795 BCC NMRD profile (Figure 9). Yet, the amount of potentially paramagnetic Fe is
796 larger in BCC than in BC. Notwithstanding the larger BCC Fe content, the flattened
797 BCC NMRD profile is placed at the highest T_1 values along the whole range of proton
798 Larmor frequencies investigated here. However, paramagnetism has an effect on
799 NMRD profiles only for short distances, i.e. up to 10 nm (Conte et al., 2004) and
800 could thus be hidden by organomineral layers coated on biochar pore surfaces
801 containing paramagnetic species. This would be in accordance with the results from
802 the XPS, FTIR and SEM/TEM examination that the BCC is covered by a thin
803 organomineral layer which very likely influences the short range paramagnetic effect
804 on pore water.

805

806 The above examination of this layer indicates that the interaction of biochar surfaces
807 with organic carbon molecules of different sizes, and with minerals/inorganic
808 compounds have modified pore structures (especially those larger pores resulting
809 from the carbonization of the phloem and xylem of the feedstock) inside the biochar
810 particles. The examination of the outer surfaces of the BCC also revealed a coating
811 with a range of different pore sizes and shapes, as seen in Figure 3 and 4. The Raman,
812 FTIR spectroscopy and XPS all indicate that that this layer has a range of highly

functionalized organic molecules that are similar to those found in aged biochar and black carbon in Terra Preta-like soils (Singh et al., 2014; Wiedner and Glaser, 2009). The spectroscopy and the results of the EUF shows that nitrates, ammonium and organic N compounds all exist in this layer. The presence of quinones, minerals with both Fe^{2+} and Fe^{3+} and the measurement of redox active surfaces indicate that a complex set of both biotic and abiotic redox reactions has taken place during the formation of this organomineral layer during the fluctuating redox conditions over the composting period. The above would indicate that:

1. The anions may bond directly with the positively charged minerals (especially Fe and Mn oxides) and amines on the surface of the carbon matrix or indirectly with positive sites on any surfactants that are in the DOC. Given the heterogeneity of the compounds on the surfaces of the biochar it is likely that both hydrogen, ligand exchange and electrostatic bonding with anions takes place (Loganathan et al., 2013).
2. Large macromolecules (humic like substances) can act as surfactants and bind nitrates on their positive sites through electrostatic attraction (Quagliotto et al., 2005).
3. Conte et al., (2013) has attributed bonding of water in these pore to unconventional H-bonds, thereby resulting in weak ^1H - ^1H dipolar interactions which in turn may result in some of the nitrates to be weakly held as outer-sphere complexes.
4. TEM analysis of the nanostructure and LA-ICPMS of the surface of this organomineral layer indicates that phosphates could form inner sphere complexes with the positively charged minerals on biochar surfaces and in the pores that have a diameter > 1 nm (especially the Fe and Al in a soil pH of 6.5, but also Si) or could form precipitates (with Mg and Ca) during the initial contact with soil moisture.

Since composting involves complex biotic and abiotic reactions in a fluctuating redox environment (Khalil et al., 2008), the detection of quinones, iron compounds with both Fe^{2+} and Fe^{3+} and the redox active nature of the surfaces of the composted biochar as revealed by cyclic voltammetry, confirms that a series of oxidation and reduction reactions have taken place. These redox reactions could involve both nitrification and denitrification as well as oxidation of organic matter (Klöpfer et al.,

2014; Prévotau et al., 2016; Quin et al., 2015). These reactions could result in an increase in the concentration of nitrates on the surfaces of organomineral layer which could, in turn, be weakly or strongly held in the pores in the organomineral layer. Further research using ^{15}N labeled nitrogen is required to determine if these potential redox reactions on the surface and in the pores of the biochar are resulting in the formation and bonding of nitrates. The data from the extractions in Kammann et al., (2015) and from the LA-ICPMS shows that the phosphates on the other hand are still tightly bound in the organomineral layer indicating that inner sphere complexes or precipitates have formed.

When composted biochar has already had all of the potentially nutrient reactive sites loaded via composting and is then put into a fertilised soil system, the system is either at equilibrium in relation to nutrients, or the biochar may leach (or provide to plants) nutrients if the external nutrient concentration is low enough. Plants can create a depletion zone and hence invoke a gradient to access the nutrients either from the biochar or the compost. If one puts non-composted biochar with potentially nutrient reactive sites into compost (or, fertilized soil), the equilibrium will be in the direction of the nutrients binding of the biochar, because it is nutrient-poor (and reactive towards nutrients). Thereby, there is now a competitor for nutrients in the system. However, if nutrient-loaded biochar is put into a low nutrient soil, the nutrients should in part desorb into the soil system. This was indeed observed in an initial leaching carried out in the study of Kammann et al., (2015, Figure 1). Whether or not they are available to plants depends on the soil conditions (e.g. water content, soil type, pH etc.), pore arrangement, soil- or substrate-organic carbon and mineral coating of the biochar.

5 Conclusions

Our results clearly show that the woody biochar underwent significant changes with co-composting which were detectable by XPS, NMR, FFC NMR, LA-ICPMS, FTIR, Cyclic Voltammetry, Raman spectroscopy, TEM, SEM. The observed changes are in line with earlier results and support its improved functionality as nutrient-providing soil additive for promoting plant growth. Particularly, breaking up the particles revealed, as expected, the nitrate and phosphate was at least partly captured inside the biochar particles. Boehm titration results revealed that the biochar surfaces were most

likely not oxidized themselves during composting, but were rather coated by organic substances derived from the compost material, combined with clay-mineral complexes. The findings further suggest that the biochar pore size distribution is altered by DOC, organomineral coatings and precipitates, and these alterations could be involved in capturing mobile anions such as nitrate and phosphate. These smaller pores would substantiate the delayed release along a gradient towards the nutrient-poor soil-plant-root interface. We hypothesize that the nitrate loading occurs by a combination of physico-chemical mechanisms that may involve alternating soil/substrate moisture cycles resulting in changes in Eh, pore-clogging, and electrostatic as well as H-bonding forces as we have shown. However, it is unclear how to promote desired properties, i.e. to reach a trade-off between anion protection against leaching and release for plant consumption along a (plant-root generated) concentration gradient; and how environmental conditions (e.g. soil moisture) or biochar properties (e.g. modified by pyrolysis, feedstock or post-treatments such as composting) will impact these desired functions of biochar. More research is clearly needed to improve the anion-retaining and -plant-providing functionality of designer biochars.

Acknowledgments

We acknowledge the help of the Electron Microscope and X-ray unit of University of Newcastle, the Electron Microscope Unit of the University of NSW and University of Wollongong and Dr B Gong and Rabeya Akter of the Solid State and Elemental Analysis Unit. This work was supported by the grant LP120200418 of the ARC, Renewed Carbon Pty Ltd. and the DAFF Carbon Farming Futures Filling the Research Gap (RG134978).

References

- Amonette, J.E., Joseph, S., 2009. Characteristics of biochar: Microchemical properties, in: Lehmann, J., Joseph, S. (Eds.), *Biochar for Environmental Management: Science and Technology*. Earthscan, London, pp. 33–52.
- Archanjo, B.S., Mendoza, M.E., Albu, M., Mitchell, D.R.G., Hagemann, N., Mayrhofer, C., Mai, T.L.A., Weng, Z., Kappler, A., Behrens, S., Munroe, P., Achete, C.A., Donne, S., Araujo, J.R., van Zwieten, L., Horvat, J., Enders, A., Joseph, S., 2017. Nanoscale Analyses of the Surface Structure and Composition

915 of Biochars Extracted After Composting and from Field Trials Using Advanced
 916 Analytical Electron Microscopy. *Geoderma* 294, 70-79.

917 Barrow, N.J., 2015. Soil phosphate chemistry and the P-sparing effect of previous
 918 phosphate applications. *Plant Soil* 397, 401–409. doi:10.1007/s11104-015-2514-
 919 5

920 Bauer, I., Knoelker, H.-J., 2015. Iron Catalysis in Organic Synthesis. *Chem. Rev.*
 921 (Washington, DC, United States) 115, 3170–3387. doi:10.1021/cr500425u

922 Bernal, M.P., Albuquerque, J.A., Moral, R., 2009. Composting of animal manures
 923 and chemical criteria for compost maturity assessment. A review. *Bioresour.*
 924 *Technol.* 100, 5444–5453.

925 Bhatnagar, A., Sillanpää, M., 2011. A review of emerging adsorbents for nitrate
 926 removal from water. *Chem. Eng. J.* doi:10.1016/j.cej.2011.01.103

927 Bian, R., Joseph, S., Cui, L., Pan, G., Li, L., Liu, X., Zhang, A., Rutledge, H., Wong,
 928 S., Chia, C., Marjo, C., Gong, B., Munroe, P., Donne, S., 2014. A three-year
 929 experiment confirms continuous immobilization of cadmium and lead in
 930 contaminated paddy field with biochar amendment. *J. Hazard. Mater.* 272, 121–
 931 128. doi:10.1016/j.jhazmat.2014.03.017

932 Chen, B., Chen, Z., Lv, S., 2011. A novel magnetic biochar efficiently sorbs organic
 933 pollutants and phosphate. *Bioresour. Technol.* 102, 716–723.
 934 doi:10.1016/j.biortech.2010.08.067

935 Cheng, C.H., Lehmann, J., Thies, J.E., Burton, S.D., Engelhard, M.H., 2006.
 936 Oxidation of black carbon by biotic and abiotic processes. *Org. Geochem.* 37,
 937 1477–1488. doi:10.1016/j.orggeochem.2006.06.022

938 Chia, C.H., Gong, B., Joseph, S.D., Marjo, C.E., Munroe, P., Rich, A., 2012a.
 939 Imaging of mineral-enriched biochar by FTIR, Raman and SEM-EDX. *Vib.*
 940 *Spectrosc.* 62, 248–257. doi:10.1016/j.vibspec.2012.06.006

941 Chia, C.H., Munroe, P., Joseph, S.D., Lin, Y., Lehmann, J., Muller, D.A., Xin, H.L.,
 942 Neves, E., 2012b. Analytical electron microscopy of black carbon and
 943 microaggregated mineral matter in Amazonian dark Earth. *J. Microsc.* 245, 129–
 944 139.

945 Conte, P., Alonzo, G., 2013. Environmental NMR: Fast-field-cycling Relaxometry.
 946 *eMagRes* 2, 389–398. doi:10.1002/9780470034590.emrstm1330

947 Conte, P., Marsala, V., De Pasquale, C., Bubici, S., Valagussa, M., Pozzi, A., Alonzo,
 948 G., 2013. Nature of water-biochar interface interactions. *GCB Bioenergy* 5, 116–

949 121. doi:10.1111/gcbb.12009

950 Conte, P., Spaccini, R., Piccolo, A., 2004. State of the art of CPMAS ^{13}C -NMR
 951 spectroscopy applied to natural organic matter. *Prog. Nucl. Magn. Reson.*
 952 *Spectrosc.* 44, 215–223.

953 Gai, X., Wang, H., Liu, J., Zhai, L., Liu, S., Ren, T., Liu, H., 2014. Effects of
 954 feedstock and pyrolysis temperature on biochar adsorption of ammonium and
 955 nitrate. *PLoS One* 9, e113888.

956 Guan, X.H., CHEN, G.H., Shang, C., 2007. ATR-FTIR and XPS study on the
 957 structure of complexes formed upon the adsorption of simple organic acids on
 958 aluminum hydroxide. *J. Environ. Sci.* 19, 438–443.

959 Güereña, D.T., Lehmann, J., Thies, J.E., Enders, A., Karanja, N., Neufeldt, H., 2015.
 960 Partitioning the contributions of biochar properties to enhanced biological
 961 nitrogen fixation in common bean (*Phaseolus vulgaris*). *Biol. Fertil. Soils* 51.

962 Hagemann, N., Harter, J., Behrens, S., 2016. Elucidating the Impacts of Biochar
 963 Applications on Nitrogen Cycling Microbial Communities, in: Ralebitso-Senior,
 964 T.K., Orr, C.H. (Eds.), *Biochar Application*. Elsevier, Amsterdam, pp. 163–198.

965 Haider, G., Steffens, D., Müller, C., Kammann, C.I., 2016. Standard extraction
 966 methods may underestimate nitrate stocks captured by field-aged biochar. *J.*
 967 *Environ. Qual.* 45, 1196–1204.

968 Halle, B., Jóhannesson, H., Venu, K., 1998. Model-free analysis of stretched
 969 relaxation dispersions. *J. Magn. Reson.* 135, 1–13. doi:10.1006/jmre.1998.1534

970 Harvie, C.E., Møller, N., Weare, J.H., 1984. The prediction of mineral solubilities in
 971 natural waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system
 972 to high ionic strengths at 25 C. *Geochim. Cosmochim. Acta* 48, 723–751.

973 Hyung, H., Kim, J.H., 2008. Natural organic matter (NOM) adsorption to multi-
 974 walled carbon nanotubes: effect of NOM characteristics and water quality
 975 parameters. *Environ. Sci. Technol.* 42, 4416–4421.

976 Jolivet, J.-P., Chanéac, C., Chiche, D., Cassaignon, S., Durupthy, O., Hernandez, J.,
 977 2011. Basic concepts of the crystallization from aqueous solutions: The example
 978 of aluminum oxy(hydroxi)des and aluminosilicates. *Comptes Rendus Geosci.*
 979 343, 113–122. doi:10.1016/j.crte.2010.12.006

980 Jorio, A., Cançado, L.G., 2012. Perspectives on Raman spectroscopy of graphene-
 981 based systems: from the perfect two-dimensional surface to charcoal. *Phys.*
 982 *Chem. Chem. Phys.* 14, 15246. doi:10.1039/c2cp42621h

983 Jorio, A., Lucchese, M.M., Stavale, F., Ferreira, E.H.M., Moutinho, M.V.O., Capaz,
 984 R.B., Achete, C. a, 2010. Raman study of ion-induced defects in N-layer
 985 graphene. *J. Phys. Condens. Matter* 22, 334204/1-334204/5. doi:10.1088/0953-
 986 8984/22/33/334204
 987 José, M., Knicker, H., 2011. Bioavailability of N released from N-rich pyrogenic
 988 organic matter: an incubation study. *Soil Biol. Biochem.* 43, 2368–2373.
 989 Joseph, S., Graber, E.R., Chia, C., Munroe, P., Donne, S., Thomas, T., Nielsen, S.,
 990 Marjo, C., Rutledge, H., Pan, G., Li, L., Taylor, P., Rawal, A., Hook, J., 2013.
 991 Shifting paradigms: development of high-efficiency biochar fertilizers based on
 992 nano-structures and soluble components. *Carbon Manag.* 4, 323–343.
 993 doi:10.4155/cmt.13.23
 994 Joseph, S., Husson, O., Graber, E., van Zwieten, L., Taherymoosavi, S., Thomas, T.,
 995 Nielsen, S., Ye, J., Pan, G., Chia, C., Munroe, P., Allen, J., Lin, Y., Fan, X.,
 996 Donne, S., 2015. The Electrochemical Properties of Biochars and How They
 997 Affect Soil Redox Properties and Processes. *Agronomy* 5, 322–340.
 998 doi:10.3390/agronomy5030322
 999 Joseph, S.D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C.H., Hook, J., Van
 1000 Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J., Foidl, N.,
 1001 Smernik, R.J., Amonette, J.E., 2010. An investigation into the reactions of
 1002 biochar in soil, in: *Australian Journal of Soil Research*. pp. 501–515.
 1003 doi:10.1071/SR10009
 1004 Kammann, C.I., Schmidt, H.-P., Messerschmidt, N., Linsel, S., Steffens, D., Müller,
 1005 C., Koyro, H.-W., Conte, P., Stephen, J., 2015. Plant growth improvement
 1006 mediated by nitrate capture in co-composted biochar. *Sci. Rep.* 5, 11080.
 1007 doi:10.1038/srep11080
 1008 Khalil, A., Domeizel, M., Prudent, P., 2008. Monitoring of green waste composting
 1009 process based on redox potential. *Bioresour. Technol.*
 1010 doi:10.1016/j.biortech.2007.11.043
 1011 Kimmich, R., Anoardo, E., 2004. Field-cycling NMR relaxometry. *Prog. Nucl. Magn.*
 1012 *Reson. Spectrosc.* 44, 257–320. doi:10.1016/j.pnmrs.2004.03.002
 1013 Kirk, G., 2004. *The biogeochemistry of submerged soils*. John Wiley & Sons,
 1014 Chinchester, UK.
 1015 Khan N., Clark I., Sánchez-Monedero M. A, Shea S., Meier f S. Qi F., Kookana

1016 R. S., Bolan N. (2016) Physical and chemical properties of biochars co-
 1017 composted with biowastes and incubated with a chicken litter compost
 1018 Chemosphere 142 14–23

1019 Kleber, M., Sollins, P., Sutton, R., 2007. A conceptual model of organo-mineral
 1020 interactions in soils: Self-assembly of organic molecular fragments into zonal
 1021 structures on mineral surfaces. Biogeochemistry 85, 9–24. doi:10.1007/s10533-
 1022 007-9103-5

1023 Klüpfel, L., Keiluweit, M., Kleber, M., Sander, M., Klüpfel, L., Keiluweit, M.,
 1024 Kleber, M., Sander, M., 2014. Redox properties of plant biomass-derived black
 1025 carbon (biochar). Environ. Sci. Technol. 48, 5601–5611. doi:10.1021/es500906d

1026 Koduru, J.R., Lingamdinne, L.P., Singh, J., Choo, K.H., 2016. Effective removal of
 1027 bisphenol A (BPA) from water using a goethite/activated carbon composite.
 1028 Process Saf. Environ. Prot. 103, 87–96.

1029 Le Leuch, L.M., Bandosz, T., 2007. The role of water and surface acidity on the
 1030 reactive adsorption of ammonia on modified activated carbons. Carbon N. Y. 45,
 1031 568–578.

1032 Lee, S.C., Chae, H.J., Lee, S.J., Choi, B.Y., Yi, C.K., Lee, J.B., Ryu, C.K., Kim, J.C.,
 1033 2008. Development of regenerable MgO-based sorbent promoted with K₂CO₃
 1034 for CO₂ capture at low temperatures. Environ. Sci. Technol. 42, 2736–2741.

1035 Li, Y., Yu, S., Strong, J., Wang, H., 2012. Are the biogeochemical cycles of carbon,
 1036 nitrogen, sulfur, and phosphorus driven by the “FeIII–FeII redox wheel” in
 1037 dynamic redox environments?. J. Soils Sediments 12, 683–693.

1038 Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., Pan, G., Paz-Ferreiro, J., 2013.
 1039 Biochar’s effect on crop productivity and the dependence on experimental
 1040 conditions-a meta-analysis of literature data. Plant Soil 373, 583–594.
 1041 doi:10.1007/s11104-013-1806-x

1042 Liu, Y., He, Z., Uchimiya, M., 2015. Comparison of biochar formation from various
 1043 agricultural by-products using FTIR spectroscopy. Mod. Appl. Sci. 9, 246.

1044 Loganathan, P., Vigneswaran, S., Kandasamy, J., 2013. Enhanced removal of nitrate
 1045 from water using surface modification of adsorbents - A review. J. Environ.
 1046 Manage. doi:10.1016/j.jenvman.2013.09.034

1047 McDonald-Wharry, J., Marilyn Manley-Harris, Pickering, K., 2015. A comparison of
 1048 the charring and carbonisation of oxygen-rich precursors with the thermal
 1049 reduction of graphene oxide. Philos. Mag. 95, 4054–4077.

1050 Nielsen, S., Minchin, T., Kimber, S., van Zwieten, L., Gilbert, J., Munroe, P., Joseph,
 1051 S., Thomas, T., 2014. Comparative analysis of the microbial communities in
 1052 agricultural soil amended with enhanced biochars or traditional fertilisers. *Agric.*
 1053 *Ecosyst. Environ.* 191, 73–82. doi:10.1016/j.agee.2014.04.006
 1054 Ogawa, M., Okimori, Y., 2010. Pioneering works in biochar research, Japan, in:
 1055 *Australian Journal of Soil Research*. pp. 489–500. doi:10.1071/SR10006
 1056 PrévotEAU, A., Ronsse, F., Cid, I., Boeckx, P., Rabaey, K., 2016. The electron
 1057 donating capacity of biochar is dramatically underestimated. *Sci. Rep.* 6, 32870.
 1058 doi:10.1038/srep32870
 1059 Prost, K., Borchard, N., Siemens, J., Kautz, T., Séquaris, J.M., Möller, A., Amelung,
 1060 W., 2013. Biochar affected by composting with farmyard manure. *J. Environ.*
 1061 *Qual.* 42, 164–172.
 1062 Quagliotto, P., Viscardi, G., Montoneri, E., Goberro, R., Adani, F., 2005. Compost
 1063 humic acid-like matter as surfactant. *Geophys. Res. Abstr.* 7, 10555.
 1064 Quin, P., Joseph, S., Husson, O., Donne, S., Mitchell, D., Munroe, P., Phelan, D.,
 1065 Cowie, A., Van Zwieten, L., 2015. Lowering N₂O emissions from soils using
 1066 eucalypt biochar: the importance of redox reactions. *Sci Rep* 5, 16773.
 1067 doi:10.1038/srep16773
 1068 Ramesh, P., Sampath, S., 2001. Electrochemical and spectroscopic characterization of
 1069 quinone functionalized exfoliated graphite. *Analyst* 126, 1872–1877.
 1070 doi:10.1039/b106199m
 1071 Rawal, A., Joseph, S.D., Hook, J.M., Chia, C.H., Munroe, P.R., Donne, S.W., Lin, Y.,
 1072 Phelan, D., Richard, D., Mitchell, G., Pace, B., Horvat, J., Beau, J., Webber, W.,
 1073 2016. Mineral-Biochar Composites: Molecular Structure and Porosity. *Environ.*
 1074 *Sci. Technol.* 50, 7706–7714. doi:10.1021/acs.est.6b00685
 1075 Ribeiro-Soares, J., Cançado, L.G., Falcão, N.P.S., Martins Ferreira, E.H., Achete,
 1076 C.A., Jorio, A., 2013. The use of Raman spectroscopy to characterize the carbon
 1077 materials found in Amazonian anthrosoils. *J. Raman Spectrosc.* 44, 283–289.
 1078 RStudio Team, 2015. RStudio: Integrated Development for R.
 1079 Rubasinghege, G., Grassian, V.H., 2013. Role (s) of adsorbed water in the surface
 1080 chemistry of environmental interfaces. *Chem. Commun.* 49, 3071–3094.
 1081 Schmidt, H.P., Kammann, C., Niggli, C., Evangelou, M.W.H., Mackie, K.A., Abiven,
 1082 S., 2014. Biochar and biochar-compost as soil amendments to a vineyard soil:
 1083 Influences on plant growth, nutrient uptake, plant health and grape quality.

1084 Agric. Ecosyst. Environ. 191, 117–123. doi:10.1016/j.agee.2014.04.001
 1085 Shao, S., Qu, F., Liang, H., Chang, H., Yu, H., Li, G., 2014. Characterization of
 1086 membrane foulants in a pilot-scale powdered activated carbon–membrane
 1087 bioreactor for drinking water treatment. *Process Biochem.* 49, 1741–1746.
 1088 Singh, B., Fang, Y., Cowie, B.C., Thomsen, L., 2014. NEXAFS and XPS
 1089 characterisation of carbon functional groups of fresh and aged biochars. *Org.*
 1090 *Geochem.* 77, 1–10.
 1091 Soías-Vicianá, M.M., Ureña-Amate, M.D., González-Pradas, E., García-Cortéz, M.J.,
 1092 López-Teruel, C., 2008. Nitrate removal by calcined Hydrotalcite-type
 1093 compounds. *Clays Clay Miner.* 56, 2–9. doi:10.1346/CCMN.2008.0560101
 1094 Spokas, K.A., Novak, J.M., Masiello, C.A., Johnson, M.G., Colosky, E.C., Ippolito,
 1095 J.A., Trigo, C., 2014. Physical Disintegration of Biochar: An Overlooked
 1096 Process. *Environ. Sci. Technol. Lett.* 1, 326–332. doi:10.1021/ez500199t
 1097 Tsai, C.S., Chen, H.Y., 2013. Study on the Spectral Analysis of Reduced Dextran-
 1098 Coated Fe₃O₄ Magnetic Nano-Particles. 19, 2220–2224.
 1099 Tsechansky, L., Graber, E.R., 2014. Methodological limitations to determining acidic
 1100 groups at biochar surfaces via the Boehm titration. *Carbon N. Y.* 66, 730–733.
 1101 doi:10.1016/j.carbon.2013.09.044
 1102 Unsoy, G., Yalcin, S., Khodadust, R., Gunduz, G., Gunduz, U., 2012. Synthesis
 1103 optimization and characterization of chitosan-coated iron oxide nanoparticles
 1104 produced for biomedical applications. *J. Nanoparticle Res.* 14, 964.
 1105 Van Zwieten, L., Singh, B., Joseph, S., Kimber, S., Cowie, A., Chan, K.Y., 2009.
 1106 Biochar and emissions of non-CO₂ greenhouse gases from soil, in: Lehmann, J.,
 1107 Joseph, S. (Eds.), *Biochar for Environmental Management: Science and*
 1108 *Technology*. Earthscan, London, UK, pp. 227–250.
 1109 Vanek, S.J., Lehmann, J., 2015. Phosphorus availability to beans via interactions
 1110 between mycorrhizas and biochar. *Plant Soil* 395, 105–123. doi:10.1007/s11104-
 1111 014-2246-y
 1112 Velten, S., Knappe, D.R., Traber, J., Kaiser, H.P., Von Gunten, U., Boller, M.,
 1113 Meylan, S., 2011. Characterization of natural organic matter adsorption in
 1114 granular activated carbon adsorbers. *Water Res.* 45, 3951–3959.
 1115 Wiedner, K., Glaser, B., 2009. Traditional use of biochar. *Biochar Environ. Manag. -*
 1116 *Sci. Technol.* 15–38.
 1117 Wijnja, H., Schulthess, C.P., 1999. ATR–FTIR and DRIFT spectroscopy of carbonate

1118 species at the aged γ -Al₂O₃/water interface. *Spectrochim. Acta Part A Mol.*
1119 *Biomol. Spectrosc.* 55, 861–872.

1120 Yao, X., Li, L., Li, H., He, S., 2014. A new method for preparing hydrophilic-
1121 activated carbon through ester hydrolysis in an alkaline environment. *J. Mater.*
1122 *Sci.* 49, 4807–4815. doi:10.1007/s10853-014-8180-9

1123 Ye, J., Zhang, R., Nielsen, S., Joseph, S.D., Huang, D., Thomas, T., 2016. A
1124 combination of biochar-mineral complexes and compost improves soil bacterial
1125 processes, soil quality, and plant properties. *Front. Microbiol.* 7.
1126 doi:10.3389/fmicb.2016.00372

1127 Zhang, M., Gao, B., Yao, Y., Xue, Y., Inyang, M., 2012. Synthesis, characterization,
1128 and environmental implications of graphene-coated biochar. *Sci. Total Environ.*
1129 435–436, 567–572. doi:10.1016/j.scitotenv.2012.07.038

1130 Zheng, R.L., Cai, C., Liang, J.H., Huang, Q., Chen, Z., Huang, Y.Z., Arp, H.P.H.,
1131 Sun, G.X., 2012. The effects of biochars from rice residue on the formation of
1132 iron plaque and the accumulation of Cd, Zn, Pb, As in rice (*Oryza sativa* L.)
1133 seedlings. *Chemosphere* 89, 856–862.

1134
1135
1136

Tables

Table 1: Acidic functional groups on non-composted and co-composted biochar as determined by Boehm titration. Data presented as average $\pm$ Standard error (SE).

Sample	Carboxylic acid groups (mmol g ⁻¹)	Lactonic acid groups (mmol g ⁻¹)	Phenolic groups (mmol g ⁻¹)
BC (n=2)	0.08 $\pm$ 0.029	0.13 $\pm$ 0.034	0.04 $\pm$ 0.018
BCC (n=4)	0.11 $\pm$ 0.009	0.13 $\pm$ 0.014	n.d.

1143 Table 2: Measurement of C/O/N functional groups on the surface of BC and BCC

	BC			BCC		
Name	Groups	Peak BE (eV)	At. %	Groups	Peak BE (eV)	At. %
C 1s	C-C/C-H	285.02	64.7	C-C/C-H	284.96	53.3
C 1s	C-O/C-OC	286.52	11.3	C-O/C-OC	286.46	12.9
C 1s	C=O	288.02	3.4	C=O	287.96	3.2
C 1s	O=C-O	289.22	1.6	O=C-O	289.16	4.4
C 1s	Shake up peak	290.62	6.2	Shake up peaks	290.96	4.0
C 1s				Quinone	283.47	0.8
O 1s		532.35	11.4		531.99	17.1
				NH ₂ /amino type nitrogen	399.11	0.2
N 1s	pyrrolic	400.68	1.4	amine/NH ₃	400.96	0.3
				-NH ₃ ⁺ /Oxidised N chemisorbed NH ₄	403.08	0.1
K 2p ₃			n.d.		293.75	2.1

1144

1145

1146 Table 3: XPS Survey scan of the major elements on the surface of BC and BCC
 1147 biochar (whole particle)

	BC		BCC	
Name	Peak BE	At. %	Peak BE	At. %
C 1s	285.19	83.5	284.81	71.9
O 1s	532.55	10.6	531.73	19.2
N 1s	400.7	1.4	399.45	0.3
Mg 1s	1304.91	0.4	1304.14	0.9
Fe 2p	713.02	0.2	712.44	0.2
Ca 2p	348.12	0.9	347.65	0.9
K 2s	378.45	0.6	378.42	1.9
Si 2p	103.39	1.2	102.64	3.1
Al 2p	74.97	1.0	74.65	1.3
P 2p	134.15	0.2	134.06	0.3

1148

1149

Figure 1: A) Fresh biochar with areas of high mineral content. B) Side view showing the mineral matter in the pores of the BC. C) EDS spectrum of area shown in D), which is a subsection of B covered in minerals.

Figure 2: A) High-angle annular dark field (HAADF) and B) bright field (BF) image of a piece of fresh biochar covered in minerals/inorganic compounds (dark phase in B) that have dimensions less than 50 nm and are porous. C) High resolution HAADF image of a cluster on the surface of the biochar, and D) A secondary electron image of another mineral cluster.

Figure 3: A) Secondary electron image of the composted surface with fungal hyphae;

B) EDS spectrum of this area; C) and D) pore structures on the surface; E) higher

resolution image of organomineral layer; F) a map of N concentration (light areas are

detectable concentrations) on the internal surface of a pore that is coated with a range of minerals.

Figure 4: A) STEM secondary electron (SE) image of interface of a BCC biochar particle (right of the image) and the porous organomineral layer most likely formed during composting. B) HAADF micrograph showing that there is porous interfaces between different micro-agglomerates (dark spots = low density of material/pore). The lighter phases are inorganic compounds or minerals and are surrounded by organic compounds C) STEM BF images of the same area (zoomed out) show that there are very few pores (the white areas) greater than 10 nm in the biochar but significant numbers in the organomineral layer (left). The circle in C indicates that the smallest pores exist at the interface and these pores are less than 5 nm in diameter. The bright 10 nm particle in B is iron oxide (EDS data not shown). D) STEM Secondary Electron (SE) image of a very porous layer that appears to have formed in a larger pore in the biochar during composting.

1197

1198

1199 Figure 5: A) TEM BF image of poorly ordered graphitic planes around an Fe/O
 1200 particle (dark region) in the carbon lattice of the co-composted biochar (BCC) and B)
 1201 amorphous carbon around the Fe/O particle (evidenced by TEM-EDS, data not
 1202 shown) in the organomineral layer of BCC.
 1203

1204

1205 Figure 6: ATR FTIR spectra of the composted (BCC) and uncomposted (BC) biochar
 1206

1207

1208

1209

Figure 7: Raman spectra for BC and BCC

Figure 8: Cyclic voltammetry of the BCC and BC at of 0.02 mV s^{-1} , scan direction indicated in both figures

Figure 9: Nuclear magnetic resonance dispersion (NMRD) profiles (i.e. variations of longitudinal relaxation rates vs proton Larmor frequency) obtained by FFC NMR relaxometry of BCC (squared dots) and BC (circled dots) samples. The black lines are the fitting curves obtained by application of the free model analysis (Halle et al., 1998).

Figure 10: FFC NMR relaxometry: correlation time (τ_c) values as obtained by the application of the free model analysis reported in Section 2.2

1257

1258

1259

1260

1261

1262

1263

1264