Agriculture, Ecosystems and Environment 236 (2017) 21–29

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Research paper

Short-lived effects of walnut shell biochar on soils and crop yields in a long-term field experiment

Deirdre E. Griffin*, Daoyuan Wang, Sanjai J. Parikh, Kate M. Scow

Department of Land, Air and Water Resources, University of California, Davis, One Shields Avenue, Davis, CA 95616, United States

ARTICLE INFO

Article history:
Received 27 July 2016
Received in revised form 2 November 2016
Accepted 4 November 2016
Available online xxx

Keywords:
Biochar
Nitrogen transformations
Long-term field experiment
Plant-available nutrients
Plant productivity

ABSTRACT

Many field studies exploring biochars' effects on plant productivity and soil quality have been limited to just one or two seasons, particularly in temperate agroecosystems, and have not shown how such impacts change as biochars age in the soil. Therefore, we investigated the lasting effects of a walnut shell (WS) biochar on crop yields and soil nutrient cycling and availability over four years in a field experiment. Long-term plots of a tomato-corn rotation were established in a 2×2 factorial design of treatments i) with or without WS biochar amendment and ii) fertilized with mineral fertilizer (MF) or composted poultry manure (CP). Biochar was applied once in 2012 (Year 1) at a rate of $10\,t\,ha^{-1}$. Crop yields were measured over four seasons, and soil samples were analyzed for ammonium (NH_4^+-N) and nitrate (NO_3^--N) concentrations and for other nutrient parameters, including exchangeable K^+, Ca^{2+}, PO_4-P, SO_4-S, each year. Walnut shell biochar had an effect only in Year 2 when it increased corn yields by ~8% in both MF and CP fertilizer systems and increased exchangeable K^+, PO_4-P, and Ca^{2+} in soil through direct additions of these nutrients. These impacts were not observed until a year after application and faded in subsequent years. Inorganic N pools were not significantly affected by the biochar in any season. The WS biochar has a delayed yet short-lived effect on plant-available nutrient concentrations and crop productivity but does not significantly alter nutrient transformations.

1. Introduction

The short-term effects of biochar applications on soil nutrient availability and plant productivity have been well studied across a variety of cropping systems and environmental conditions. However, reviews on this topic (*e.g.* Gul et al., 2015; Lone et al., 2015; Jeffery et al., 2011; Spokas et al., 2012; Huang et al., 2013; Quilliam et al., 2012) continually note the lack of field experiments investigating the effects of biochar over multiple seasons and call for more long-term field trials. One meta-analysis of 371 independent experiments reported that the average study length was 113 days and the longest spanned 3 years (Biederman and Harpole, 2013). The amendment of biochar to a soil is an irreversible decision, and it is therefore critical to evaluate the potential impacts of biochars on crops and soil quality beyond the typical one or two-season experiment cycle. This is especially important given that biochar is not typically intended for annual application, and the logistics of handling and applying it are challenging. Biochar in the soil can persist decades and even centuries beyond non-pyrogenic organic matter (OM) (Wiedner and Glaser, 2015; Gul et al., 2015; Lehmann et al., 2015), but it is also aging over time, altering its interactions with and potential effects on plants and the soil environment. Agricultural management and environmental conditions will affect biochar aging (Verheijen et al., 2010; Jeffery et al., 2011). Therefore, field experiments incorporating realistic farming operations are valuable in determining the changing effects of biochar over time.

The main proposed mechanisms for increased plant productivity involve biochar-induced increases in plant-available nutrients. Changes to nutrient availability can be both direct, such as added potassium (K) weathering from high ash biochars (Major et al., 2010), and indirect, such as changing nutrient solubility by altering soil pH (Gul et al., 2015; Lone et al., 2015). Most biochars have an alkaline pH and contain negatively charged functional groups that bind protons to raise soil solution pH (Gul et al., 2015). Biochars can also increase nutrient retention as these functional groups act as exchange sites for nutrient ions in solution (Major et al., 2010; Gul et al., 2015). This increase in cation exchange capacity (CEC) can reduce leaching and provide a slow-release source for nutrients, particularly in coarse-textured or highly weathered soils containing low activity clay minerals with naturally lower CEC. Effects from direct nutrient additions are likely to quickly diminish as

* Corresponding author.
E-mail address: degriffin@ucdavis.edu (D.E. Griffin).

http://dx.doi.org/10.1016/j.agee.2016.11.002
0167-8809/

these ions are taken up by plants or leached from the root zone (Major et al., 2010). Indirect mechanisms also vary over time; however, the direction and magnitude of these changes is more unpredictable as they depend on the unique properties of the biochar and the soil to which it is added, as well as climatic conditions of the soil environment. Nutrient retention capacity can increase over time as biochar surfaces become increasingly oxidized (Pignatello et al., 2015), but biochar particles can also become masked by native soil OM, reducing CEC and nutrient retention (Gul et al., 2015). Similarly, the effects of biochar on soil pH tend to decrease over time as charged sites become saturated with H^+ and other ions (Gul et al., 2015; Nelissen et al., 2015).

Many studies have focused on the impacts of biochars and other pyrogenic carbon (C) products on nitrogen (N) transformations as a potential explanation for changes in plant productivity. Biochars have the potential to interact with and alter the N cycle at several points due to their chemical properties, influencing C availability and pH, and physical characteristics, such as surface area and aromaticity (DeLuca et al., 2015). Several studies have found that biochars can increase net N immobilization with additions of labile C (Deenik et al., 2010; Rondon et al., 2007; Gundale and DeLuca, 2007), though others have found that this increases microbial activity and mineralization (DeLuca et al., 2015). Biochars may also reduce net mineralization through interactions with organic N substrates, reducing their accessibility to microbes, or by sorbing NH_4^+ and NH_3 on acidic functional groups, removing these products from solution as they are mineralized (Berglund et al., 2004; DeLuca et al., 2015; Asada et al., 2002; Clough and Condron, 2010; Anderson et al., 2014; Taghizadeh-Toosi et al., 2011). Sorption of these substrates may also decrease nitrification rates (Taghizadeh-Toosi et al., 2011), though others have found increased nitrification rates due to stimulation of nitrifying organisms after biochar increases soil pH (DeLuca et al., 2006; Myrold, 2005). A previous mesocosm study, using the same walnut shell (WS) biochar as this current study, found that it doubled net nitrification rates and increased bacterial ammonia oxidizing gene (*amoA*) abundance (Pereira et al., 2015). Although this information is of value, it is important to test these impacts in realistically managed field systems.

Substantial biochar research has been done in highly weathered, lower fertility soils where reduced CEC can limit nutrient retention, soil acidity controls nutrient solubility, and climatic conditions limit accumulation of OM (Quilliam et al., 2012; Lehmann et al., 2011). However, biochar is still widely promoted in temperate agroecosystems as a means of increasing crop yields and C sequestration. It is therefore important to study the long-term impacts of biochar in more productive agricultural soils where CEC, OM, and extreme pH are less limiting and may buffer the effects of biochar.

This study examines the first four years of a continuing, long-term field experiment in a fine-textured, Alfisol soil located in California's agricultural region. We investigated the long-term impacts on soil fertility and crop yields of a high temperature (900 °C) WS biochar applied to an intensively managed soil. Soil nutrient cycling dynamics may differ based on the nutrient management system used; thus we studied biochar's impacts in conjunction with both mineral and organic fertilizers. Our objectives were to determine if WS biochar 1) alters plant-available N pools over the growing season, 2) impacts tomato and corn yields, and 3) has changing impacts as the biochar ages in the soil for several seasons. We hypothesized that 1) soil NH_4^+-N and NO_3^--N concentrations would both increase in plots with WS biochar due to increased mineralization and nitrification, 2) corn and tomato yields would be increased in the first two years of the experiment due to increased N availability, 3) the effects of biochar on plant-available N and yield would decrease over time as the exchange sites on the biochar became saturated and there was less interaction of the biochar with the soil solution.

2. Materials and methods

2.1. Field experimental design

The long-term experimental biochar plots were established in May 2012 at the Russell Ranch Sustainable Agriculture Facility, a division of the Agricultural Sustainability Institute (2016) at the University of California, Davis (http://asi.ucdavis.edu/programs/rr). This facility oversees farming of plots using the same practices and equipment as commercial growers while controlling their management for experimental measurements.

The 2 × 2-factorial treatment design of this experiment compares mineral fertilizer (MF) against composted poultry manure fertilizer (CP) with and without biochar application in an annual crop rotation of processing tomato (*Lycopersicon esculentum* Mill.) and corn (*Zea mays* L.), a common cropping system in California's Central Valley. The plots are arranged in a randomized complete block design with four blocks and one treatment replicate per block, making a total of 16 plots. The soil is mapped as a Rincon silty clay loam (fine, smectitic, thermic Mollic Haploxeralfs). A full analysis of the soil can be found in Supplemental Table S1. During the four seasons reported here, the area received an average of ~282 mm precipitation per water year (Oct. 1-Sept. 30; USGS, 2016) with ~7 mm during the growing season (CIMIS, 2016). All plots were furrow irrigated each season, so it is unlikely that rainfall variation had an effect. The mean air temperature averaged ~21 °C in summers and ~12 °C in winters (CIMIS, 2016).

The WS biochar was applied once in May 2012 (Year 1) at a rate of 10 t ha^{-1} and was incorporated to a depth of 15 cm. Mineral fertilizer and poultry manure compost were applied at appropriate rates prior to each planting of corn or tomato (Table 1). In MF plots, starter fertilizer was applied before planting each season,

Table 1
Summary of important field management and sampling dates.

Year	Crop	Planting date	Harvest date	Cover crop planting date[a]	Soil sampling date(s)
2012 (Year 1)	Tomato	2 May	7 Sept.	14 Nov.	20 April
2013 (Year 2)	Corn	25 March	1 Oct.	16 Nov.	30 July 18 Sept.
2014 (Year 3)	Tomato	27 April	21 Aug.	11 Nov.	20 June 9 July 15 Aug.
2015 (Year 4)	Corn	7 May	25 Sept.	–	27 May 8 July 9 Sept.

[a] Only plots receiving compost (CP) were planted with cover crops.

containing 27.6 kg ha^{-1} N as urea-ammonium-nitrate 32 (UAN-32), 36.2 kg ha^{-1} P as phosphorus pentoxide (P_2O_5), 17.2 kg ha^{-1} K as potassium oxide (K_2O), and 1.7 kg ha^{-1} of zinc chelate. Subsequently, UAN-32 was applied at a rate of 134.5 kg ha^{-1} N three weeks after transplanting in tomato and at a rate of 207.4 kg ha^{-1} N at the four-leaf (V4) growth stage in corn. In all seasons, 8.97 t ha^{-1} of poultry manure compost was added prior to planting, adding on average 225.4 kg ha^{-1} total N, 119.5 kg ha^{-1} total P, and 155.4 kg ha^{-1} total K. A complete annual analysis of the compost can be found in Supplementary Table S2. Beginning in winter prior to the Year 2 growing season, all CP plots also received fertility from a leguminous cover crop mix of woolly pod vetch (*Vicia villosa* ssp. *dasycarpa*) and Austrian winter pea (*Pisum sativum* L. var. *arvense*) with biomass incorporated in early spring.

2.2. Walnut shell biochar source and characteristics

The WS biochar is a locally sourced, commercially available char made by an organic walnut grower and processor in California's Central Valley (Dixon Ridge Farms, 2016www.dixonridgefarms.com). It is a by-product of a gasification system (50 kW Biomax 50, Community Power Corporation, Littleton, CO, USA) running at 900 °C that generates both the char and syngas that powers the farm's storage and drying facilities, reducing electricity use by 526 kWh Mg^{-1} feedstock (Pereira et al., 2016). With nut production and processing well suited to energy and biochar production, widespread adoption of biochar technology has the potential to increase the sustainability and profitability of California's agriculture. Therefore, it is critical to evaluate how amendment of this biochar in particular will impact soils and cropping systems of the Central Valley.

Selected characteristics of this biochar are reported here (Table 2), and a complete characterization and descriptions of the methods used can be found in Mukome et al. (2013). The particle size analysis of the biochar applied (determined by sieving) was 54.4% > 2 mm, 29.4% between 0.25 mm and 2 mm, and 15.3% < 0.25 mm.

2.3. Yield measurements

Crop yield measurements from tomato and corn crops were taken following a combination of hand and machine harvesting. Harvest dates are presented in Table 1. Prior to machine harvest, a 3-m^2 area in tomato and a 1-m^2 area in corn were subsampled by hand from each plot. All aboveground biomass was removed and fruit or cobs were separated from the vegetative biomass, which was then oven-dried at 65 °C. For the corn hand harvest, the cobs were oven-dried before and after shelling to obtain both a cob and hand-harvested grain yield on a dry weight basis. Following hand sampling, each plot was harvested using a commercial-scale combine, and the harvest weight of each plot was measured. Tomato yields are reported in terms of fresh weight of fruit, and corn yields are reported on a dry grain basis in accordance with how yields are reported commercially.

2.4. Soil sampling

Soil samples were collected (0–30 cm) prior to biochar application in Year 1, at mid-season and harvest of the Year 2 corn season, and throughout the Year 3 and 4 growing seasons (explained below) of tomato and corn, respectively (Table 1). For Years 2–4, samples are designated as 1) early season (not present for Year 2), which was just prior to the periods of highest nutrient uptake, during vegetative growth for tomatoes and the five-leaf (V5) stage for corn, 2) mid-season, representing the middle of the period of rapid nutrient uptake, during early fruit set in tomatoes and at tasseling (VT) in corn, and 3) harvest, which was prior to the harvest date of each crop. For all samplings, ten cores were taken from randomized locations within each plot and then consolidated and homogenized. Soils were kept on ice during sampling before being transported back to the lab for analysis. Upon returning to the lab, a representative subsample from each original sample was immediately extracted for NH_4^+-N and NO_3^--N analysis, as described below. The remainder of each soil sample was air-dried.

2.5. Soil nutrient analyses

A comprehensive nutrient analysis was done on the pre-application soil samples from Year 1 and mid-season samples of Years 2–4. Measurements of soil OM, CEC, pH, extractable cations (K^+, Mg^{2+}, Ca^{2+}, Na^+), anions (SO_4-S, PO_4-P), and soil texture were analyzed on air-dried soil samples by A&L Western Laboratories, Inc. (Modesto, CA) following the North American Proficiency Testing (NAPT) program methods outlined in Soil, Plant, and Water Reference Methods for the Western Region (Gavlak et al., 2005). Briefly, soil OM was analyzed by loss on ignition at 360 °C, CEC through the ammonium replacement method, pH by the saturated paste method, exchangeable cations and SO_4-S by 1.0 M ammonium acetate (NH_4OAc) extraction, extractable P using the Olsen sodium bicarbonate ($NaHCO_3$) extraction (Olsen et al., 1954), and soil texture with the hydrometer method.

Exchangeable NH_4^+-N and NO_3^--N were analyzed at each soil sampling time point to evaluate how WS biochar affects available inorganic N pools. From each homogenized field sample, 8.0 g of field-moist soil was extracted with 40 mL of 0.5 M potassium sulfate (K_2SO_4) extraction solution. Samples were shaken at 250 rpm for 1 h and then centrifuged at 7000 rpm for 15 min. The supernatants were pipetted into 2 mL tubes, centrifuged at 10,000 rpm for 2 min, then frozen at −20 °C for subsequent analyses. Subsamples of the field-moist samples were oven-dried for more than 24 h at 105 °C to measure the gravimetric water contents and correct for the moisture. Soil NH_4^+-N and NO_3^--N were analyzed colorimetrically on K_2SO_4 extracts using the salicylate-hypochlorite method (Verdouw et al., 1978) and vanadium (III) chloride reduction method (Doane and Horwath, 2003), respectively. Scaled-down versions of these methods were used in a 96-well microplate (385 μL capacity; Sarstedt, Inc., Newton, NC) with three analytical replicates for each sample. The absorbance values were measured in a Tecan GENios microplate reader at 540 nm (NO_3^--N) and 650 nm (NH_4^+-N).

2.6. Potentially mineralizable N

To look at the effects of biochar on N mineralization, potentially mineralizable nitrogen (PMN) was analyzed through the anaerobic incubation method originally described by Waring and Bremner (1964). These incubations were done using mid-season soil

Table 2
Selected characteristics of the walnut shell biochar used in this study.

Production temp (°C)	pH (1:2 H_2O)	Ash	C	N (% wt)	P	K	Ca	S ($mg\ kg^{-1}$)	CEC ($cmol_c\ kg^{-1}$)	BET surface area ($m^2\ g^{-1}$)
900	9.7	40.4	55.3	0.47	0.64	9.32	5.83	940	33.4	227.1

samples. Two tubes per sample were prepared for extraction at two time points (Day 0 and Day 7). 5.0 g dry weight equivalent of field-moist soil was subsampled (moisture content determined by oven drying at 105 °C) and added to a sterile 50 mL polypropylene tube. It was then covered with 10 mL of deionized water, and nitrogen (N_2) gas was bubbled through the sample for 30 s before the tube was quickly closed to ensure that the sample was anaerobic. One set of samples was extracted immediately (Day 0) while another set was incubated for 7 days (Day 7). For the extraction, 30 mL of 2.67 M potassium chloride (KCl) was added to each sample tube to make a final concentration of 2.0 M KCl. Samples were then handled as in the extraction and NH_4^+-N analysis methods described in the section above. PMN is presented as the difference in NH_4^+-N concentration between Day 7 and Day 0 subsamples for a particular sample.

2.7. Statistical analyses

All data were analyzed with mixed models using the *lmer()* function and one-way analysis of variance (ANOVA) in the *lme4* package in R (R-3.2.2, R Core Team, 2015; Bates et al., 2015). The two treatment factors, fertilizer type and biochar application, were fixed effects while block was a random effect. The mixed models tested the treatment factors individually and the interactions between them. To observe the changing effects of biochar over time, all data were first analyzed using a repeated measures model with year (for yield and soil quality measurements) or sampling date (for inorganic N data) as a fixed effect interacting with the treatment factors and plot as a random effect to designate that repeated measurements were made on the same plot. When repeated measures analysis showed a significant interaction between a treatment factor and year, indicating that the treatment had different effects in different years, each year was then analyzed separately for that parameter. Inorganic N data were analyzed only as a repeated-measures model within each season and not between years as different crops were being grown. Before analysis, each model and response variable was tested for assumptions of normality and homogeneity of variances. If the data set did not meet these assumptions, it was transformed in order to best meet the assumptions. Plots were generated using the *ggplot2* package in R (Wickham, 2009). Box plots show medians with the middle horizontal line and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of the "whiskers" on the boxes represent the highest and lowest values within 1.5 times the inter-quartile range. Outliers beyond this range are represented as points. For analysis of the results, all effects with p-values < 0.05 were considered significant.

3. Results

3.1. Crop yields

Walnut shell biochar had an effect on crop yields only in Year 2, after it had aged in the field for one year (Fig. 1a and b). In this year,

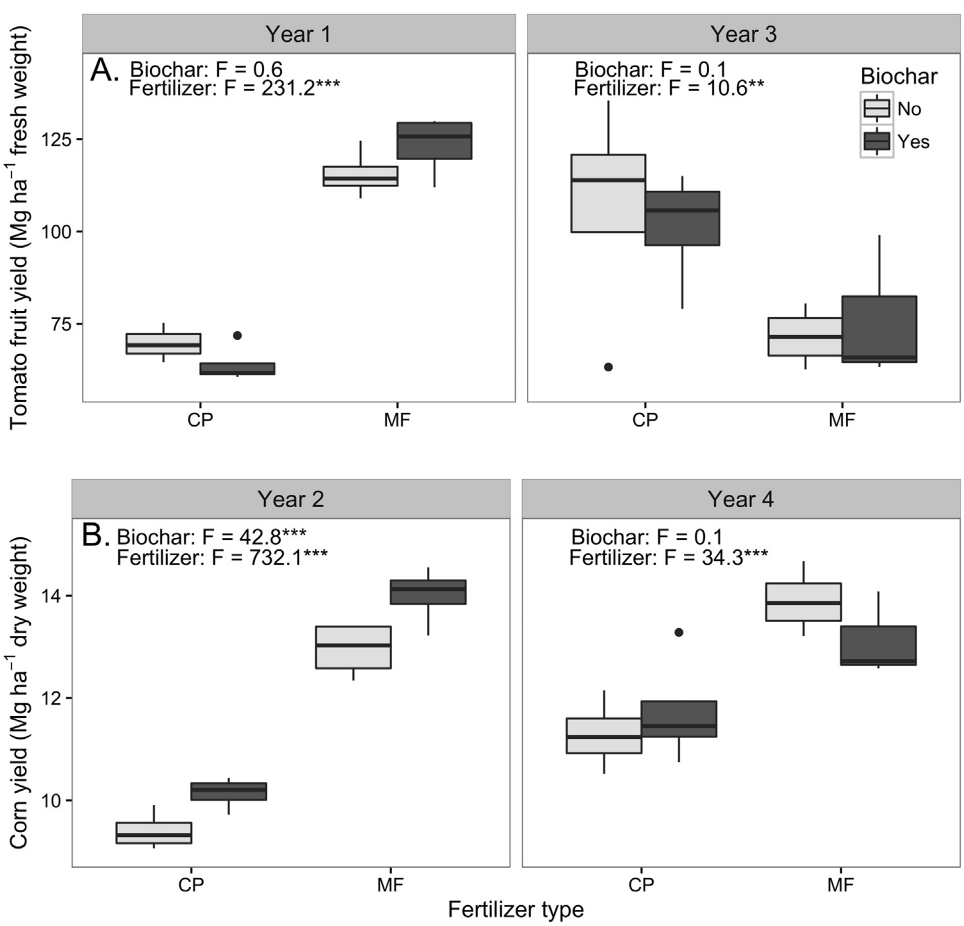

Fig. 1. Crop yields each year for (A.) tomato fruit yields (fresh fruit weight) and (B.) corn grain yield (dry grain weight) with 0 and 10 t ha^{-1} biochar applications and compost (CP) and mineral fertilizer (MF) treatments. F-statistics are shown for each treatment factor from mixed-model ANOVAs for each year, and asterisks indicate significance level ($^{*}p < 0.05$, $^{**}p < 0.01$, $^{***}p < 0.001$). There were no significant interactions between treatment factors. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of the "whiskers" represent the highest and lowest values within 1.5 times the inter-quartile range. Outliers beyond this range are represented as points.

biochar increased corn yields by 8.1% and 7.8% in mineral fertilizer and compost-fertilized plots, respectively ($p = 0.0001$). This positive effect was not seen in Year 1, the year of biochar application, and it faded in subsequent years as the biochar aged in the field. In contrast, the type of fertilizer used had a significant effect in each season. In three out of four years, plots fertilized with mineral fertilizer had higher yields than those fertilized with compost and cover crops. However, in Year 3 the opposite was true, a trend that was consistent with other experimental plots at the Russell Ranch research station (data not shown).

3.2. Soil nutrient availability

Contrary to our hypothesis, the WS biochar did not change plant-available inorganic N pools during the growing season for each year (Table 3; Fig. S1). In all years, soil NH_4^+-N concentrations were affected by the fertilizer type applied, but not by the presence of biochar. Soil NO_3^--N concentrations were similarly affected by fertilizer type in Year 3, though not in Years 2 or 4 when the corn crops were grown. In all seasons, the effect of sampling date was significant in the repeated measures statistical analyses, confirming that nitrate and ammonium concentrations are changing throughout the growing season. As with yield, these inorganic N concentrations are more impacted by fertilizer management than biochar addition.

The WS biochar application did, however, increase exchangeable K^+, Ca^{2+}, and PO_4-P in the soil (Fig. 2; Table 4). These effects on nutrient availability were seen only in Year 2, one year after biochar application, corresponding to the increased corn yields seen in the plots with biochar in that year. Soil nutrient concentrations were not different among the plots before biochar was applied in Year 1,

Table 3
F-statistics of treatment factors (biochar and fertilizer type) on extractable soil NH_4^+-N and NO_3^--N from repeated measures statistical analysis for each year.

	NH_4^+-N		NO_3^--N	
	Biochar	Fertilizer	Biochar	Fertilizer
Year 2	0.17	21.80***	0.17	0.22
Year 3	0.26	6.52*	<0.01	28.52***
Year 4	0.30	7.02*	<0.01	1.39

*$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

and there were no significant effects in Years 3 and 4 ($p < 0.05$). However, in Year 3, exchangeable K^+ was slightly higher in plots with biochar, indicating that the influence of biochar is fading gradually in the years after application. Biochar application also increased soil pH in Years 2 and 3, though to a lesser extent in the latter (Table 4). These trends with WS biochar were true regardless of whether mineral fertilizer or compost was applied as the ANOVAs showed no significant interactions between biochar application and fertilizer type. Biochar application did not alter exchangeable SO_4-S, Na^+, Mg^{2+} concentrations, soil OM content or CEC (data not shown).

3.3. Potentially mineralizable N

Assays performed in the mid-season of Year 3, when tomatoes were planted, showed that biochar had a negative effect on PMN ($p = 0.0407$; Fig. 3). Fertilizer type also had a significant effect ($p = 0.01474$), with lower PMN in MF treatments. In mid-season Year 4, however, there were no differences between treatments. In both years, PMN values for all treatments were very low. Negative PMN values may be the result of variability between subsamples as

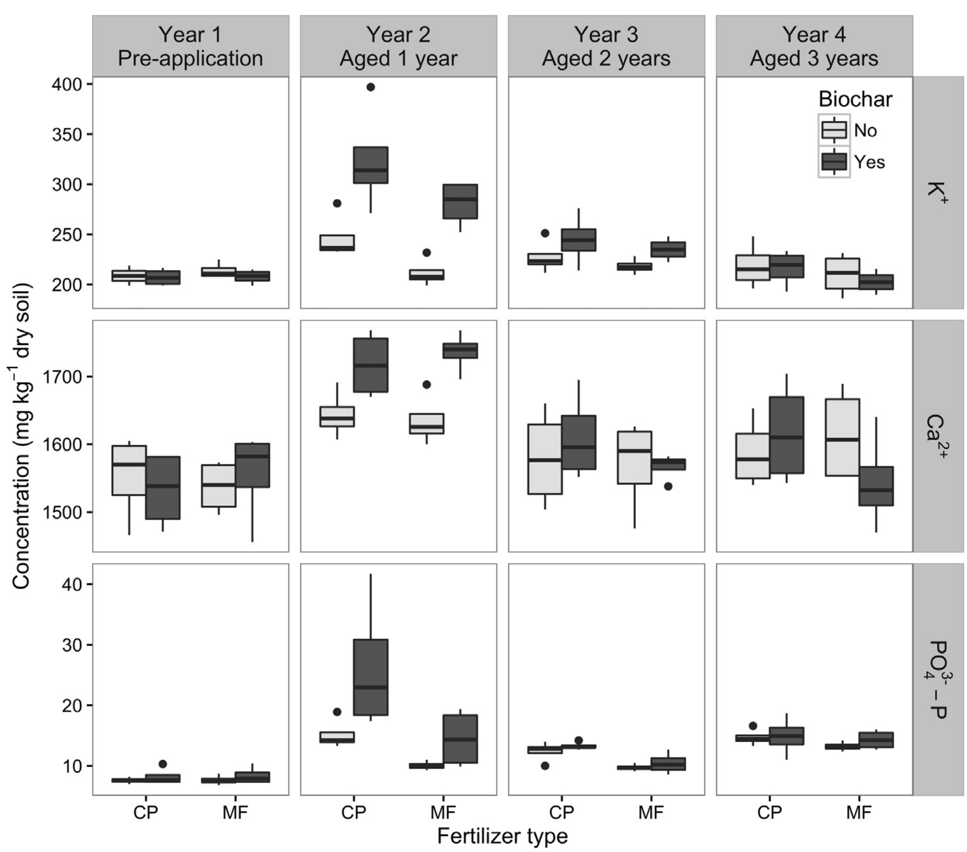

Fig. 2. Concentrations of extractable K^+, Ca^{2+}, PO_4-P with 0 and 10 t ha^{-1} biochar applications and compost (CP) and mineral fertilizer (MF) treatments. The samples analyzed are from prior to biochar application in Year 1 (2012) and from mid-season (July) of subsequent years.

Table 4
F-statistics for biochar and fertilizer type treatment factors from ANOVAs.

	K^+		Ca^{2+}		PO_4-P		pH	
	Biochar	Fertilizer	Biochar	Fertilizer	Biochar	Fertilizer	Biochar	Fertilizer
Year 1	NS	NS	NS	NS	NS	NS	NS	NS
Year 2	21.15***	6.11*	30.30***	NS	7.55*	8.92*	6.75*	NS
Year 3	NS	NS	NS	NS	NS	24.27***	5.65*	5.65*
Year 4	NS	NS	NS	NS	NS	NS	NS	NS

NS: Non-significant; *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$.

these incubations were done with destructive sampling for each time point.

4. Discussion

This long-term field study offers a realistic view of WS biochar's integration into farming systems and allows extrapolation across years to determine whether biochar application, an irreversible practice, will have lasting effects. As is the case in all field settings, annual crop productivity is subject to variable factors, such as the timing of water and nutrient availability with demand. Our experiment allowed us to see how the WS biochar's effects may be changing not only with climatic variations, but also with aging of the biochar itself.

Although crop yields vary over the observed seasons due to climatic differences or nutrient management strategies, WS biochar does not have a significant long-term effect on yield. Across all years, the type of fertilizer used had a greater effect on crop yields and inorganic N pools than did the application of biochar, a result that agrees with Biederman and Harpole's meta-analysis (2013), which stated that fertilizer management had a larger mean effect size for yield than did biochar addition. In our study, mineral fertilizer produced higher yields than compost fertilizer in three out of four seasons, likely due to greater synergism between the timing of nutrient demand and availability. However, yields improved in compost-fertilized plots over time, most likely due to the accumulation of nutrients from continual annual compost and cover crop additions. Importantly, though the effects of the fertilizer systems varied, WS biochar had a similar impact in each. We found that WS biochar had an effect on crop yields only in Year 2, one year after biochar application, when corn yields increased by approximately 8% in both mineral fertilizer and compost fertilized plots. This increase in Year 2 yields corresponds to higher soil extractable K^+, Ca^{2+}, and PO_4-P (Fig. 2) and soil pH (Table S3) in plots containing biochar, an effect that diminishes in subsequent years. There was, however, no effect of biochar on inorganic N pools. Therefore, increased corn yields in Year 2 were likely caused by higher bioavailable concentrations of these other essential plant nutrients.

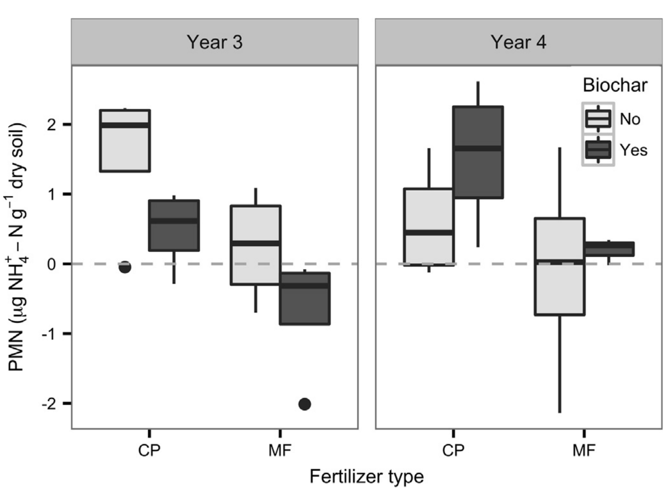

Fig. 3. NH_4^+-N produced in a 7-day anaerobic PMN incubation of mid-season soils from each treatment (CP: compost; MF: mineral fertilizer). The horizontal dashed line represents a difference of 0 μg g^{-1}, where no net NH_4^+-N is produced.

4.1. Increased nutrient concentrations through direct addition

Though WS biochar did cause a slight, though significant, increase in soil pH, higher concentrations of exchangeable K, Ca, and PO_4-P are most likely due to direct addition rather than to indirect mechanisms, such as enhanced nutrient solubility. In their meta-analysis, Biederman and Harpole (2013) also found that, across various biochar and soil types, biochars increased soil K ($n = 31$) and P ($n = 53$) concentrations and noted direct addition as a main mechanism for these increases in neutral pH soils. The soil at this site began with an average pH of 6.74 ± 0.03 before biochar application, and in Year 2 increased to 7.30 with biochar addition in both mineral fertilizer (± 0.06) and compost plots (± 0.04; Table S3). These soil pH values, both with and without biochar, are within an ideal range for nutrient solubility (Brady and Weil, 2008). Therefore, pH-induced changes to nutrient availability, which are often seen when biochar is added to acidic soils (*e.g.* Rondon et al., 2007; Major et al., 2010; Steiner et al., 2007), are likely not a factor here. Additionally, there was no effect of biochar addition on CEC, so WS biochar is likely not altering the nutrient retention capacity of the soil. Instead, this biochar is directly adding high levels of K, Ca, and P to the soil. Even in this high fertility system where K and P (and Ca in the case of compost) are being added at recommended levels, biochar is contributing an additional supply of these nutrients at a significant level. "Luxury consumption" of K^+ by plants is known to occur when concentrations are plentiful (Marschner, 1995), which may explain the substantial drop in available K^+ in seasons following Year 2.

The high production temperature (900 °C) of the WS biochar results in a relatively greater ash content compared to many biochars produced at lower temperatures (<700 °C; Ippolito et al., 2015). The WS biochar is 9.32% K by weight (Mukome et al., 2013) and is therefore adding 932 kg ha^{-1} K with an application rate of 10 t ha^{-1}. Though it is unlikely that all of this K is plant-available, it is a substantially greater concentration than the 17.2 kg ha^{-1} K added as K_2O to the MF plots each season. Similarly, 64 kg ha^{-1} PO_4-P is being added in a 10 t ha^{-1} application of biochar (Mukome et al., 2013), supplementing the 36.2 kg ha^{-1} P_2O_5-P applied to the MF plots. Biochar application brought 583 kg ha^{-1} Ca to MF plots that otherwise did not receive Ca inputs. Even in CP plots, where the compost is contributing approximately 155.4 kg ha^{-1} K, 119.5 kg ha^{-1} P, and 307 kg ha^{-1} Ca each year (Table S2), the WS biochar application significantly increased concentrations of these nutrients in Year 2. Further analyses should be done exploring the relative availability of these nutrients in WS biochar and compost.

4.2. Delayed but short-lived effects

The effects of WS biochar on nutrient concentrations and soil pH diminished after the second season, one year after application, and impacted yields only in that season. This suggests that the additional nutrients added by the biochar were removed through uptake by the corn crop in Year 2, leaching from the soil, or sorption to minerals and OM, and thus had no effect in the following years. However, the fact that effects of biochar did not appear until one year after application calls into question the immediate bioavailability of these nutrients from the biochar. Soil data from Year 1 post-application is not available, but no effects on yield were found in the tomato season that year. Several other studies have found a similar delayed and short-lived effect of biochar on yields and soil fertility (Jones et al., 2012; Major et al., 2010; Steiner et al., 2007). Jones et al. (2012) found no effect of biochar on maize production or nutrient content in the first season after application, but did find increased orchard grass biomass and quality with biochar in years 2 and 3. While this result may be attributed to differences in crop physiology, Jones et al. (2012) also found increased pH and microbial activity starting in year 2 and higher soil exchangeable K^+ in year 3. These results indicate that some biochars may require several months to a year before they interact with and influence the surrounding soil chemical and microbial environment. Biochar hydrophobicity and density may be some factors that determine the rate at which a char's effects will be seen at the field scale. Many biochars, particularly those with high ash content and including the WS char used in this experiment, are very hydrophobic when fresh, a quality that may prevent interactions of the fresh biochar and the soil solution soon after application (Joseph et al., 2010; Basso et al., 2013). Biochars become more hydrophilic over time as surface oxidation occurs, creating more polar, ionizable functional groups such as carboxylic acids that facilitate interactions with the surrounding soil environment (Joseph et al., 2010). Meanwhile, a biochar's density and porosity will determine the degree to which the char's surfaces are accessible to the soil solution. Additionally, microbial activity that is responsible for much of the oxidation of biochar structures has been found to be inhibited by compounds released from some fresh biochars (Lehmann et al., 2011). For example, biochars can contain and retain polyaromatic hydrocarbons (PAHs) that may be toxic to microorganisms, reducing microbial activity and slowing degradation of the biochar (Quilliam et al., 2013).

Among the few multi-season field experiments looking at biochar, both Major et al. (2010) and Steiner et al. (2007) studied the effects of biochars in lower fertility Oxisols and found that their biochars took approximately a year to show their fullest impacts. Major et al. (2010) reported no yield effects in the first season but increased maize yields in all subsequent years, up to three years after application. Similarly, Steiner et al. (2007) found that the charcoal had its greatest effect on plant productivity after the first season, in this case peaking in season 2. Both studies attributed the delayed effects to the recalcitrant nature of biochars, causing a slow breakdown and release of nutrients and concluded that higher productivity with biochar was primarily due to greater Ca^{2+} and Mg^{2+} retention on biochar surfaces, lower Al^{3+} toxicity from increased pH, and higher K^+ availability from direct addition. For Major et al. (2010), K^+ availability in biochar treatments was highest in the year following application, as was the case in our study, but concentrations decreased again as this ion was leached or taken up. The biochar's effects on Ca and Mg stocks and yield were longer-lived, with the greatest effect occurring 3 years after application.

In each of these experiments on Oxisol soils, the biochars still showed some significant benefits in the fourth season after application; their systems have not yet reached a steady state where biochar's influences have diminished completely (Major et al., 2010; Steiner et al., 2007). Effects from increased soil pH, reduced exchangeable Al^{3+}, and greater retention of base cations are still exhibited several seasons after application. Alternatively, in our temperate system on an Alfisol soil, where soil pH is near neutral, base cations dominate the exchange complex, and nutrient retention and availability are high, WS biochar's effects have completely faded by the fourth season after application in both MF and CP plots. Quilliam et al. (2012), also working in a temperate system on a non-acid soil, found similar results with short-lived increases in available PO_4-P, K^+, and Ca^{2+} immediately after biochar application but with no lasting effects 3 years after application. Jones et al. (2012), working in the same experiment as Quilliam et al. (2012), found that the 3-year field-aged biochar had 90% lower exchangeable K, 30% lower exchangeable Ca, and a pH over 2 units lower than the fresh biochar used. It is likely that a similar mechanism is occurring in our system, and given the intrinsic fertility of the system, the short-term flux of increased nutrients does not have long-term benefits.

4.3. Effects on inorganic N pools and potentially mineralizable N

Biochar effects on the N cycle have been proposed as one of the main mechanisms through which biochars improve soil fertility. As a result, there have been numerous studies investigating the interactions of biochars with the N cycle, particularly concerning nitrification and reduction of N losses. In our study, the WS biochar application had no effect on extractable NH_4^+-N and NO_3^--N concentrations in soil samples collected during the growing seasons of Years 2, 3, and 4 (Fig. S1). Concentrations of these ions were more influenced by the fertilizer type used. Additionally, there were no significant interactions between biochar application and fertilizer type, indicating that biochar did not affect the N cycle differently depending on whether a mineral or organic source of N was applied.

Many of the studies that have identified complex interactions of biochar with N cycling, both in fertile and non-fertile soils, have been incubation experiments where conditions are more controlled than in the field (*e.g.* Nelissen et al., 2015; DeLuca et al., 2006; Taghizadeh-Toosi et al., 2012). For example, Nelissen et al. (2015), working in a sandy loam with pH of ~6.4, found that biochar increased N mineralization and nitrification rates as well as N immobilization immediately after application, but that one year after application, biochar had no effect on N cycling. The authors attribute these results to more labile C and a pH increase from fresh biochar that stimulate microbial activity in the first year but that fade in the following year. We did not collect soil samples during the first year of this study, so it may be that biochar-induced changes to N transformations occurred during this time. However, we saw no differences in yield with biochar during the first year (Fig. 1a), indicating that any changes to N cycling did not result in N being significantly more or less limiting to the tomato plants that season.

Other experiments showing the interactions of biochar and N have focused on lower fertility agricultural or forest systems (*e.g.* DeLuca et al., 2015; MacKenzie and DeLuca, 2006; Berglund et al., 2004). Increases in nitrification rates have been observed in forest systems where nitrifying organism abundance is naturally low and phenolic compounds from plant litter can inhibit nitrification rates (DeLuca et al., 2006; Mackenzie and DeLuca, 2006). Additionally, biochar has increased nitrification rates in acidic soils by raising soil pH to a level more suitable for most nitrifying organisms (DeLuca et al., 2006; Myrold 2005). However, DeLuca et al. (2006) found that char had no effect on nitrification in grasslands where nitrifiers are naturally in higher numbers. Similarly, Anderson et al. (2014) found biochar addition to a pastured silt loam soil did not affect NH_4^+-N or NO_3^--N pool sizes. In agricultural soils of the California, nitrifier populations are already abundant due to high fertilizer inputs and a suitable pH. Therefore, biochar is not expected to increase nitrification when amended to these soils. Biederman and Harpole (2013) found in their meta-analysis that on average, across both temperate and tropical systems, there were no significant effects of biochar on inorganic N pools ($n = 33$), challenging the theory that biochar increases soil fertility by altering N dynamics in a variety of systems. Major et al. (2010) and Steiner et al. (2007) did not find any effects of biochar on inorganic N pools in an acidic tropical Oxisol, nor did Quilliam et al. (2012) and Jones et al. (2012), studying impacts in a temperate, more neutral pH soil.

The only evidence in this experiment that WS biochar may affect N cycling was the reduction of PMN in soils with biochar in mid-season of Year 3. These reductions were small, dropping from an average of 1.53 to 0.48 μg NH_4^+-N g^{-1} soil with CP and 0.24 to -0.68 μg NH_4^+-N g^{-1} with MF, but were statistically significant ($p = 0.0407$). This indicates that biochar may reduce mineralization of microbial biomass or availability of the resulting NH_4^+. Several studies have indeed found that many biochars sorb NH_4^+ through cation exchange sites, a mechanism that is favorable in terms of nutrient retention, and have also shown binding of NH_3 through acidic functional groups, such as carboxyl groups (Asada et al., 2002; Clough and Condron, 2010; Anderson et al., 2014; Taghizadeh-Toosi et al., 2011; DeLuca et al., 2015). Biochar aging may increase these phenomena as competing K^+ ions are removed from fresh char and surfaces are oxidized. There are still knowledge gaps concerning the bioavailability of these sorbed compounds, but it is possible that some NH_4^+ and NH_3 bind strongly to the WS biochar, preventing their extraction. Taghizadeh-Toosi et al. (2011) found that $^{15}NH_3$ pre-sorbed to four pine biochars, all with lower surface area and CEC than the WS biochar, was subsequently taken up by plants. However, the authors also saw a positive correlation between biochar acidity and the degree of NH_3 sorption. With a pH of 9.7, no measurable acidity, and a higher basicity than many other biochars (11.7 meq g^{-1}; Mukome et al., 2013), the WS biochar may be unlikely to sorb significant NH_3. Batch sorption experiments with the WS biochar showed that it has a strong capacity to sorb organic N compounds, which could indeed prevent mineralization (Parikh and Ghazal, unpublished data). However, we did not see any indication of reduced NH_4^+ in the *in situ* inorganic N data, and with such low PMN values in all treatments at mid-season, it is unlikely that WS biochar negatively affected availability of N to plants.

5. Conclusions

Our study explored the long-term effects of WS biochar on crop productivity and soil nutrient availability in conjunction with both organic and mineral fertilizers. The one-time addition of biochar to a high fertility, fine-textured, agricultural soil increased yield only in the second of four seasons. This delayed and short-lived effect can be attributed to significant increases in exchangeable K^+, Ca^{2+}, and PO_4-P one year after biochar application that did not persist in following years. Based on the elemental composition of the biochar itself and characteristics of the soil (*e.g.* neutral pH), greater concentrations of these nutrients are most likely due to direct additions from this high ash biochar rather than from indirect mechanisms, such as increased nutrient retention or solubility of non-biochar sourced ions. Going forward, it will be important to study this mechanism and the rate at which ions are released from the biochar. The fertilizer type used did not alter the biochar's effects for any of the parameters measured, though the mineral vs. compost fertilizer treatments had their own effects independent from the biochar factor. Additionally, biochar application did not change inorganic N pools, suggesting that this biochar will not substantially alter N cycling and availability to plants.

The WS biochar's effects faded after the second season as the excess nutrients were likely removed by crop uptake, leaching, and sorption to minerals and OM. Therefore, we conclude that a one-time application of this and other high ash biochars has short-term nutrient benefits but neither positive nor negative long-term impacts on soil fertility and crop productivity, despite the persistence of biochar particles in the soil. However, it will be important to continue this evaluation beyond four seasons as the biochar continues to age.

Acknowledgements

We are grateful to Jessica Schweiger, Dr. Daniel Bair, Tom Hollemans, and Andrew Margenot for their work in setting up and sampling the experimental plots in 2012, Charlotte Oriol and Phirun Khim for field and lab assistance, Israel Herrera, Luis Loza, and the staff at the Russell Ranch Sustainable Agriculture Facility for their management of the plots, and Russ Lester at Dixon Ridge Farms for donation the walnut shell biochar. This publication was made possible by the United States Department of Agriculture (USDA),National Institute of Food and Agriculture (NIFA) through Hatch Formula Funding CA 2122-H and multistate regional project W-2082. Additionally, this research was supported by funds from the College of Agricultural and Environmental Sciences Dean's Office and the Agricultural Sustainability Institute at UC Davis. D. Griffin was supported by a Henry A. Jastro Graduate Research Award, a Beatrice Oberly and S. Atwood McKeehan Fellowship, and a National Science Foundation (NSF) Graduate Research Fellowship (NSF DGE-1148897). Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the NIEHS, NIH, NIFA, USDA, or NSF.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.agee.2016.11.002.

References

Agricultural Sustainability Institute, 2016. Russell Ranch Sustainable Agriculture Facility. The Regents of the University of California, Davis campus http://asi.ucdavis.edu/programs/rr (Accessed 27 July 2016).

Anderson, C.R., Hamonts, K., Clough, T.J., Condron, L.M., 2014. Biochar does not affect soil N-transformations or microbial community structure under ruminant urine patches but does alter relative proportions of nitrogen cycling bacteria. Agric. Ecosyst. Environ. 191, 63–72.

Asada, T., Ishihara, S., Yamane, T., Toba, A., Yamada, A., Oikawa, K., 2002. Science of bamboo charcoal: study on carbonizing temperature of bamboo charcoal and removal capability of harmful gases. J. Heal. Sci. 48, 473–479.

Basso, A.S., Miguez, F.E., Laird, D. a., Horton, R., Westgate, M., 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. GCB Bioenergy 5, 132–143.

Bates, D., Maechler, M., Bolker, B., Walker, S., 2015. Fitting linear mixed-effects models using lme4. J. Stat. Softw. 67, 1–48.

Berglund, L.M., Deluca, T.H., Zackrisson, O., 2004. Activated carbon amendments to soil alters nitrification rates in Scots pine forests. Soil Biol. Biochem. 36, 2067–2073.

Biederman, L.A., Harpole, W.S., 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. GCB Bioenergy 5, 202–214.

Brady, N.C., Weil, R.R., 2008. The Nature and Properties of Soils, 14th ed. Pearson, New Jersey.

CIMIS, 2016. California Irrigation Management Information System. Internet Resource. http://www.cimis.water.ca.gov/WSNReportCriteria.aspx (Accessed 31 October 2016).

Clough, T.J., Condron, L.M., 2010. Biochar and the nitrogen cycle: introduction. J. Environ. Qual. 39, 1218.

DeLuca, T.H., MacKenzie, M.D., Gundale, M.J., Holben, W.E., 2006. Wildfire-produced charcoal directly influences nitrogen cycling in ponderosa pine forests. Soil Sci. Soc. Am. J. 70, 448–453.

DeLuca, T.H., MacKenzie, M.D., Gundale, M.J., 2015. Biochar effects on soil nutrient transformations, In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. second ed. Earthscan, London, pp. 421–445.
Deenik, J.L., McClellan, T., Uehara, G., Antal Jr, M.J., Campbell, S., 2010. Charcoal volatile matter content influences plant growth and soil nitrogen transformations. Soil Sci. Soc. Am. J. 74, 1259–1270.
Dixon Ridge Farms, 2016. http://www.dixonridgefarms.com (Accessed 27 July 2016).
Doane, T.A., Horwath, W.R., 2003. Spectrophotometric determination of nitrate with a single reagent. Anal. Lett. 36, 2713–2722.
Gavlak, R., Horneck, D., Miller, R.O., Soil, plant, and water reference methods for the western region, third ed., *Western Region Extension Publication* **no. 125**, 2005.
Gul, S., Whalen, J.K., Thomas, B.W., Sachdeva, V., Deng, H., 2015. Physico-chemical properties and microbial responses in biochar-amended soils: mechanisms and future directions. Agric. Ecosyst. Environ. 206, 46–59.
Gundale, M.J., DeLuca, T.H., 2007. Charcoal effects on soil solution chemistry and growth of *Koeleria macrantha* in the ponderosa pine/Douglas-fir ecosystem. Biol. Fertil. Soils 43, 303–311.
Huang, M., Yang, L., Qin, H., Jiang, L., Zou, Y., 2013. Quantifying the effect of biochar amendment on soil quality and crop productivity in Chinese rice paddies. Field Crop. Res. 154, 172–177.
Ippolito, J.A., Spokas, K.A., Novak, J.M., Lentz, R.D., Cantrell, K.B., 2015. Biochar elemental composition and factors influencing nutrient retention, In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. second ed. Earthscan, London, pp. 139–163.
Jeffery, S., Verheijen, F.G.A., van der Velde, M., Bastos, A.C., 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. Agric. Ecosyst. Environ. 144, 175–187.
Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H., Murphy, D.V., 2012. Biochar-mediated changes in soil quality and plant growth in a three year field trial. Soil Biol. Biochem. 45, 113–124.
Joseph, S.D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C.H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J., Foidl, N., Smernik, R.J., Amonette, J.E., 2010. An investigation into the reactions of biochar in soil. Aust. J. Soil Res. 48, 501–515.
Lehmann, J., Rillig, M.C., Thies, J.E., Masiello, C.A., Hockaday, W.C., Crowley, D., 2011. Biochar effects on soil biota – a review. Soil Biol. Biochem. 43, 1812–1836.
Lehmann, J., Abiven, S., Kleber, M., Pan, G., Singh, B.P., Sohi, S.P., Zimmerman, A.R., 2015. Persistence of biochar in soil, In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. second ed. Earthscan, London, pp. 235–282.
Lone, A.H., Najar, G.R., Ganie, M.A., Sofi, J.A., Ali, T., 2015. Biochar for sustainable soil health: A review of prospects. Pedosphere Int. J. 25, 639–653.
MacKenzie, M.D., DeLuca, T.H., 2006. Charcoal and shrubs modify soil processes in ponderosa pine forests of western Montana. Plant Soil 287, 257–266.
Major, J., Rondon, M.A., Molina, D., Riha, S.J., Lehmann, J., 2010. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. Plant Soil 333, 117–128.
Marschner, H., 1995. Functions of mineral nutrients: macronutrients, In: Marschner, H. (Ed.), Mineral Nutrition of Higher Plants. second ed. Academic Press, London, pp. 229–312.
Mukome, F.N.D., Zhang, X., Silva, L.C.R., Six, J., Parikh, S.J., 2013. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. J. Agric. Food Chem. 61, 2196–2204.
Myrold, D.D., 2005. Transformations of nitrogen. In: Sylvia, D.M., Fuhrmann, J.J., Hartel, P.G., Zuberer, D.A. (Eds.), Principles and Applications of Soil Microbiology. Pearson, New Jersey, pp. 333–372.
Nelissen, V., Rütting, T., Huygens, D., Ruysschaert, G., Boeckx, P., 2015. Temporal evolution of biochar's impact on soil nitrogen processes – a ^{15}N tracing study. GCB Bioenergy 7, 635–645.
Olsen, S.R., Cole, C.V., Watanabe, T.S., Dean, L.A., 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circular **939**. US Government Printing Office, Washington DC, pp. 1–19.
Pereira, E.I.P., Suddick, E.C., Mansour, I., Mukome, F.N.D., Parikh, S.J., Scow, K.M., Six, J., 2015. Biochar alters nitrogen transformations but has minimal effects on nitrous oxide emissions in an organically managed lettuce mesocosm. Biol. Fertil. Soils 51, 571–582.
Pereira, E.I.P., Suddick, E.C., Six, J., 2016. Carbon abatement and emissions associated with the gasification of walnut shells for bioenergy and biochar production. PLoS One 11, 1–15.
Pignatello, J.J., Uchimiya, M., Abiven, S., Schmidt, M.W.I., 2015. Evolution of biochar properties in soil, In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. second ed. Earthscan, London, pp. 195–233.
Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H., Jones, D.L., 2012. Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time since application and reapplication rate. Agric. Ecosyst. Environ. 158, 192–199.
Quilliam, R.S., Rangecroft, S., Emmett, B.A., DeLuca, T.H., Jones, D.L., 2013. Is biochar a source or sink for polycyclic aromatic hydrocarbon (PAH) compounds in agricultural soils? GCB Bioenergy 5, 96–103.
R Core Team, 2015. R: A Language and Environment for Statistical Computing, 3.2.2 ed. The R Foundation for Statistical Computing, Vienna, Austria.
Rondon, M.A., Lehmann, J., Ramírez, J., Hurtado, M., 2007. Biological nitrogen fixation by common beans (*Phaseolus vulgaris* L.) increases with bio-char additions. Biol. Fertil. Soils 43, 699–708.
Spokas, K.A., Cantrell, K.B., Novak, J.M., Archer, D.W., Ippolito, J.A., Collins, H.P., Boateng, A.A., Lima, I.M., Lamb, M.C., McAloon, A.J., Lentz, R.D., Nichols, K.A., 2012. Biochar: a synthesis of its agronomic impact beyond carbon sequestration. J. Environ. Qual. 41, 973–989.
Steiner, C., Teixeira, W.G., Lehmann, J., Nehls, T., de Macêdo, J.L.V., Blum, W.E.H., Zech, W., 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. Plant Soil 291, 275–290.
Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condron, L.M., 2011. A wood based low-temperature biochar captures NH_3-N generated from ruminant urine-N, retaining its bioavailability. Plant Soil 353, 73–84.
Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R., Condron, L.M., 2012. Biochar adsorbed ammonia is bioavailable. Plant Soil 350, 57–69.
USGS, 2016. Explanations for the National Water Conditions. United States Geologic Survey http://water.usgs.gov/nwc/explain_data.html (Accessed 31 October 2016).
Verdouw, H., Van Echteld, C.J.A., Dekkers, E.M.J., 1978. Ammonia determination based on indophenol formation with sodium salicylate. Water Res. 12, 399–402.
Verheijen, F., Jeffery, S., Bastos, A.C., van der Velde, M., Diafas, I., 2010. Biochar Application to Soils: a Critical Scientific Review of Effects on Soil Properties, Processes, and Functions. Office for the Official Publication of the European Communities, Luxembourg.
Waring, S.A., Bremner, J.M., 1964. Ammonium production in soil under waterlogged conditions as an index of nitrogen availability. Nature 201, 951–952.
Wickham, H., 2009. ggplot2: Elegant Graphics for Data analysis. Springer-Verlag, New York.
Wiedner, K., Glaser, B., 2015. Traditional use of biochar, In: Lehmann, J., Joseph, S. (Eds.), Biochar for Environmental Management. second ed. Earthscan, London, pp. 15–37.