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Multiscale evaluation of biochar for the delivery of agronomic and soil health benefits in California

Author

Gelardi, Danielle Leigh

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Multiscale evaluation of biochar for the delivery of agronomic and soil health benefits in California

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DANIELLE LEIGH GELARDI
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Approved:

Dr. Sanjai J. Parikh, Chair

Dr. Daniel J. Geisseler

Dr. Majdi Abou Najm

Committee in Charge

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ABSTRACT

Scientists, policymakers, and growers are increasingly interested in the use of biochar, or pyrolyzed biomass, as an agricultural soil amendment. The number of published biochar studies has increased at a near exponential rate, from one publication per annum in the early 2000s, to over 4,100 in 2020. Policymakers have also taken notice, resulting in biochar included as a leading natural climate solution in the 2018 Intergovernmental Panel on Climate Change (IPCC) Special Report, and in California, the creation of the Biochar Research Advisory Group by the Governor's Office of Planning and Research. As scientific and policy interest in biochar grows, so too does the size of the biochar market. Since 2009, 920 patent applications mentioning biochar have been submitted to the United States Patent and Trademark Office.

While interest in biochar is evident, many questions remain about the efficacy of biochar as a soil amendment. Due to its high surface area, low bulk density, reactive surface functional groups, and recalcitrant carbon, the material is purported to deliver many agronomic and environmental benefits when added to the soil. These benefits include increased water holding capacity, nutrient retention, crop yield, and soil carbon stocks, as well as enhanced microbial activity and the promotion of soil health. Despite the proliferation of biochar studies, research shows inconsistent results on the ability of biochar to deliver these benefits, due to differences in biochar feedstock, production methods, soil properties, climate, and cropping systems. It is especially difficult to interpret results for the fertile agricultural soils of California's Mediterranean climate, as biochar has been shown to have the greatest impact in more acidic, nutrient-limited soils. Furthermore, results from the scientific literature have limited relevance to production agriculture, as biochar studies are dominated by short-term laboratory experiments that are difficult to extrapolate to field-scale. To inform the use and regulation of biochar in California, it is essential that farmers and policymakers have access to reliable, location-based data that evaluates biochar across scales.

This project fills a gap in the literature by providing mechanistic laboratory studies that are linked to pot trials and long-term, field-scale data about the agronomic and soil health potential of biochar as a soil amendment in California. To carry out this work, seven biochars were obtained from commercial companies at multiple production temperatures from various feedstocks. The potential for these biochars to impact the soil physical, chemical, and microbial environment was investigated across scales. In the laboratory, biochars were tested for their ability to physically or chemically retain nitrate and ammonium. Nearly every biochar tested exhibited a strong chemical affinity for ammonium, likely due to the attraction between their negatively charged surfaces and the positively charged ammonium ion. This was evident in that ammonium retention was strongest in biochars with high cation exchange capacity (CEC), oxygen-containing functional groups, and high oxygen to carbon ratios. Biochars exhibited little to no chemical affinity for nitrate, though one biochar reduced nitrate leaching, to a small extent, in soil column studies. This result was linked to the biochar's high surface area and low CEC. The ability of biochar to alter the soil physical environment was most evident in its effect on saturated hydraulic conductivity (K_{sat}). Broadly, biochars increased K_{sat} in a silt loam but had a mixed effect in a sandy loam. An additional small-scale study was carried out in a growth chamber, in which biochar-amended soil was observed to substantially increase the yield of romaine lettuce (*Lactuca sativa*) when compared to the unamended control.

Collectively, the short-term laboratory experiments in this study demonstrated that these biochars could improve ammonium retention, water conductivity, and crop yield when added to the soil. However, in three-year field trials with the same biochars in the same soils, similar benefits were not observed. Seven biochars were amended to soils at two rates, combined with two synthetic nitrogen (N) fertilizer rates, in two California locations. Processing tomatoes (*Solanum lycopersicum*) were grown for three years, and data was collected on the influence of biochar on plant and soil properties. Biochar had minor effects on soil pH, EC, and N content, though the effects varied by biochar, location, and year, and were not substantial enough to impact plant yield or quality parameters. Under no combination of experimental

conditions was biochar observed to increase processing tomato yield, plant nitrogen uptake, or soil moisture. Field trial results are consistent with those from other studies, which indicate biochar may confer limited benefits in soils which do not require conditioning for the successful growth of crops. Furthermore, the discrepancy between results from experiments at different scales demonstrate that short-term laboratory trials are not sufficient to make conclusions about field-scale agriculture.

While biochar did not deliver tangible agricultural benefits in field trials, further investigation was made into its influence on parameters that constitute current notions of soil health. Soils were sampled 2.5 years after amendment with almond shell biochars produced at 500 or 800 °C, or a softwood biochar produced at 500 °C, for a comprehensive soil health assessment. To varying effects, biochars were observed to increase labile carbon, water stable aggregates, pH, and EC in both the silt loam and sandy loam. In the finer textured silt loam, which had higher fertility and organic matter concentration, results were not substantial enough to influence the microbial community. Phospholipid fatty acid (PLFA) analysis from the silt loam revealed that biochar had no effect on community composition or on the PLFA ratios typically interpreted to denote microbial stress. In the coarser, more nutrient-limited sandy loam, however, a canonical correspondence analysis (CCA) revealed microbial communities responded to the increase in water stable aggregates, pH, and potassium conferred by the addition of biochar. This resulted in a distinct community composition, as well as reduced indicators of microbial stress. Results were greatest in plots amended with almond shell biochars, likely due to the high potassium content of almond shell, and to the high pH and ash concentration of these biochars. The soil health assessment indicates that, while biochar may not deliver agronomic improvements in fertile agricultural soils, it may confer other ecological or environmental benefits, or have the potential to deliver agronomic benefits across a longer time horizon.

Importantly, results from multiple scales indicate biochar may be added to agricultural soils with few negative consequences for cropping systems. However, there is a growing body of research which suggests some biochars may contain potentially toxic properties that pose a threat to human health when airborne biochar is inhaled. In order to optimize the ecological benefits of adding biochar to soils, care should be taken to select biochars which conform to quality standards established by the International Biochar Initiative or the European Biochar Certificate. Care should also be taken to amend biochars to soils under conditions which minimize dust emissions, and to equip farmworkers with respirators and appropriate protective attire. As there may be limited financial incentive for California growers to add biochar to their soils, cost-share and incentive programs should be considered. Together, data from this project can assist policymakers and land managers in California in making decisions about amending biochar to working lands. Realistic expectations should be established for the agronomic benefits of adding biochar to California cropping systems. Meanwhile, carbon sequestration or soil health projects may be pursued with minimal consequence, given the safe and appropriate selection of biochars.

Chapter 1: Biochar alters hydraulic conductivity and inhibits nutrient leaching in two agricultural soils[*]

Danielle L. Gelardi[1], Irfan Ainuddin[2], Devin A. Rippner[3], Majdi Abou Najm[1], Sanjai J. Parikh[1]
[1]Land, Air and Water Resources, University of California, Davis, 1 Shields Ave, Davis CA 95616, USA
[2]California State University Chico, 400 West First Street, Chico, CA, 95929, USA
[3]United States Department of Agriculture, Horticulture Crops Research Unit, Davis, Prosser, WA

ABSTRACT

Biochar is purported to provide agricultural benefits when added to the soil, through changes in soil water hydraulic conductivity (K_{sat}), and increased nutrient retention through chemical or physical means. Despite increased interest and investigation, there remains uncertainty regarding the ability of biochar to deliver these agronomic benefits due to differences in biochar feedstock, production method, production temperature and soil texture. In this project, a suite of experiments was carried out using biochars of diverse feedstocks and production temperatures, in order to determine the biochar parameters which may optimize agricultural benefits. Sorption experiments were performed with seven distinct biochars to determine sorption efficiencies for ammonium and nitrate. Only one biochar effectively retained nitrate, while all biochars bound ammonium. The three biochars with the highest binding capacities (produced from almond shell at 500 and 800 °C (AS500 and AS800) and softwood at 500 °C (SW500)) were chosen for column experiments. Biochars were amended to a sandy loam and a silt loam at 0 and 2% (w/w) and saturated hydraulic conductivity (K_{sat}) was measured. Biochars reduced K_{sat} in both soils by 64-80%, with the exception of AS800, which increased K_{sat} by 98% in the silt loam. Breakthrough curves for nitrate and ammonium, as well as leachate nutrient concentration, were also measured in the sandy loam columns. All biochars significantly decreased the quantity of ammonium in the leachate, by 22 to 78%, and slowed its movement through the soil profile. Ammonium retention was linked to high cation exchange capacity and a high oxygen to carbon ratio, indicating that the primary control of ammonium retention in biochar-

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amended soils is the chemical affinity between biochar surfaces and ammonium. Biochars had little to no effect on the timing of nitrate release, and only SW500 decreased total quantity, by 27 to 36%. The ability of biochar to retain nitrate may be linked to high surface area, suggesting a physical entrapment rather than a chemical binding. Together, this work sheds new light on the combined chemical and physical means by which biochar may alter soils to impact nutrient leaching and hydraulic conductivity for agricultural production.

1.1 INTRODUCTION

The ability of biochar to chemically and physically alter soil environments for specific agronomic benefits is the subject of increased investigation, as evidenced by the recent rise in published biochar studies[1] and United States trademark and patent applications listing the word “biochar.”[2] Biochar, or the carbonaceous material created from the thermochemical conversion of biomass in an oxygen-limited environment,[3] possesses unique chemical and physical properties, determined by variables such as its feedstock, production method, and production temperature. Biochar properties typically include a low bulk density, high porosity, high surface area, reactive surface functional groups, and recalcitrant carbon.[4] These attributes make it a promising material for amendment to agricultural soils, as biochar may help improve soil water holding capacity, hydraulic conductivity, and nutrient retention. Despite increased interest and investigation, there remains uncertainty regarding the ability of biochar to deliver these agronomic benefits. While many studies show promising results where nutrient retention and soil water dynamics are concerned,[5–10] others have demonstrated no or only minor effects.[11–13] Several authors have concluded that, due to differences in biochar production parameters and those of the soil environment, material and site-specific investigation is required before conclusions can be drawn about the potential of biochar to provide agricultural benefits.[14–16]

The ability of biochar to remove nitrate and ammonium from aqueous environments has been widely investigated, as it may indicate whether biochar can improve crop nutrient use efficiency and supress fertilizer pollution through leaching and volatilization. To this effect, batch sorption experiments are commonly carried out to determine the electrostatic affinity between biochars and nitrate and ammonium. Due to the deprotonation of surface functional groups at agronomic soil pHs, biochar is typically negatively charged. It is expected, then, that it would not bind to nitrate, which exists in the anionic form in aqueous environments. Electrostatic repulsion between nitrate and biochar has indeed been regularly cited as the reason behind little to no nitrate removal in batch sorption experiments. Zhou et al. (2019) tested biochars from four feedstocks, each produced at three temperatures, to find minimal nitrate sorption or even nitrate release. Similarly, Sanford et al. (2019) found that five biochars from diverse feedstocks and production temperatures had zero nitrate binding capacity. Little to no nitrate sorption capacity has been commonly observed for biochars produced from a broad range of feedstocks, productions methods, and temperatures.[19–24] Though exceptions have been observed in which biochars exhibited high nitrate binding capacities,[25,26] a recent study determined the average published maximum adsorption capacity (Q_{max}) of unmodified biochar for NO_3-N to be as low as 1.95 mg g^{-1}.[27]

This same study determined the average published Q_{max} of unmodified biochar for NH_4^+-N to be 11.19 mg g^{-1}.[27] Higher Q_{max} values for biochar and ammonium are to be expected, as ammonium exists in the cationic form in aqueous environments and would more readily adsorb to negatively charged biochar surfaces. While this theoretical electrostatic affinity is supported by higher Q_{max} values throughout published sorption experiments, inconsistencies can still be found. Q_{max} values lower than 2 mg NH_4^+ g^{-1} are commonly observed, for biochars produced from a broad range of temperatures and feedstocks.[28–35]. While most reported Q_{max} values are less than 20 mg NH_4^+-N g^{-1},[27] values as high as 93.6 mg NH_4^+ g^{-1} [36] and 243.3 mg NH_4^+ g^{-1} have been observed.[37] Biochars exhibit a broad range of ammonium sorption capacities and conflicting trends have emerged. Multiple authors have observed that sorption capacity decreases with increasing production temperature.[36–38] Lower temperatures have been correlated with higher cation exchange capacity (CEC),[38] and higher O/C ratios.[39] These properties may contribute to biochars with the ability to remove ammonium from solution, as they provide a greater number of exchange sites and oxygen-containing functional groups which can react with ammonium.[39] The reverse trend has also been observed, however, with authors noting that an increase in production temperature resulted in higher ammonium Q_{max} values.[19,25,40] These authors point towards the higher specific surface area (SA) of biochar at higher production temperatures as a critical parameter to predicting ammonium adsorption.

Chemical bonding and electrostatic interactions may not be the only mechanism by which biochar retains nitrate and ammonium in soils. Despite the lack of chemical affinity between nitrate and biochar, studies frequently demonstrate the ability of biochar to reduce nitrate leaching in soil column studies and pot trials.[41–44] While some authors hypothesize the mechanism to be microbial immobilization,[45] others have found the addition of biochar to stimulate N mineralization.[46] In addition to chemical and microbial mechanisms, biochar may retain N through physical means.[47] One study determined that biochar decreased soil bulk density by 3 to 31%, and increased porosity by 14 to 64%.[10] Biochar can also alter mean pore size and pore architecture, thereby influencing tortuosity and the residence time of water and nutrients within the soil profile.[48,49] The impact of biochar on hydraulic conductivity largely appears dependent on soil texture, which highly influences pore structure. While exceptions have been observed, biochar has largely been shown to decrease the ability of a saturated soil to transmit water (saturated hydraulic conductivity (K_{sat})) in coarse textured soils and increase K_{sat} in finer soils.[10] The impact of biochar on these soil physical properties may influence nitrate retention through a mechanism known as "nitrate capture," in which nitrate molecules become physically entrapped within biochar pores,[42] potentially leading to increased residence time in crop rooting zones and a greater opportunity for plant uptake.[8,41,50]

In this project, a suite of experiments was carried out using biochars of diverse feedstocks and production temperatures, in order to determine to what degree these biochars: 1) chemically bind nitrate and ammonium; 2) physically alter the soil to influence saturated hydraulic conductivity; or 3) influence nutrient leaching, through either chemical or physical means. This information was used to determine the soil and biochar parameters which may optimize hydrologic and nutrient retention benefits in two agricultural soils, and to investigate the combination of chemical and physical mechanisms by which these benefits are delivered. Sorption experiments were performed with seven distinct, commercially available biochars to determine nutrient removal efficiencies for ammonium and nitrate. Due to their high sorption capacities, almond shell biochars produced at 500 and 800 °C (AS500 and AS800) and softwood at 500 °C (SW500) were selected for a series of soil column experiments. These biochars were amended to a sandy loam and a silt loam at 0 and 2% (w/w) and K_{sat} was measured. Breakthrough curves for nitrate and ammonium, as well as leachate nutrient concentrations, were also determined in the sandy loam columns. Together, these data elucidate the combination of chemical and physical means by which biochar impacts nutrient leaching and hydraulic conductivity. Data can be used to inform the production or modification of biochars for these specific purposes, as well as for predicting how biochars may behave in specific agricultural conditions.

1.2 MATERIALS AND METHODS

1.2.1 Biochar characterization

Seven biochars from four commercial companies were obtained from the following feedstocks and produced at the following temperatures: almond shell at 500 and 800 °C (AS500, AS800), coconut shell at 650 °C (CS650), softwood at 500, 650, and 800 °C (SW500, SW650, SW800), and an additional softwood biochar produced at 500 °C and inoculated with a microbial formula (SW500-I). Unless otherwise stated, biochars were sieved to 2 mm and characterized using procedures recommended by the International Biochar Initiative (IBI, 2015): pH and electrical conductivity (EC) were measured at a 1:20 biochar to 18.2 MΩ-cm water (Barnstead nanopore, Thermo Fisher) dilution (w:v) after solutions were shaken for 90 minutes; total carbon, nitrogen, hydrogen, and oxygen were measured using a dry combustion-elemental analyzer (Costech ECS4010); and moisture, volatile, and ash content were measured as a percent of total dry weight through sequential increases in furnace temperature (105, 750, and 950 °C, respectively). Particle size distribution was measured by laser diffraction (Coulter LS230). CEC was measured using a combination of the modified ammonium acetate compulsory displacement method[51] and the rapid saturation method:[52,53] 0.25g of biochar was leached with 18.2 MΩ-cm water (w:v) under vacuum (-20 to -40 kPa). Leachate was stored and analyzed for dissolved organic carbon

(DOC) through combustion (Shimadzu TOC-V). Biochar samples were then washed with 1 M sodium acetate (pH 8.2) until the EC of the elute was the same as the eluant. Samples were rinsed three times with 10 ml of 2-proponal, then dried under vacuum for 10 minutes. To displace sodium ions, biochars were washed with 1 M ammonium acetate in same volume as was required sodium acetate. Leachate was collected and analyzed for sodium concentration through atomic absorption spectroscopy (Perkin Elmer AAnalyst 800).

Specific surface area was determined by Micromeritics' Particle Testing Authority (https://www.particletesting.com/) from CO_2 adsorption isotherms according to the Brunauer, Emmet, Teller (BET) method.[54] Fourier transform infrared (FTIR) spectra of AS500, AS800, and SW500 biochars were collected using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT; PIKE Technologies EasiDiff) with air dried samples diluted to 3% with potassium bromide. All FTIR spectra were collected using a Thermo Nicolet 6700 FTIR spectrometer (Thermo Scientific) using 256 scans, 4 cm^{-1} resolution, and a DTGS detector. FTIR bands were assigned as in Parikh et al. (2014). Gross morphological differences among AS500, AS800, and SW500 were visualized by X-ray micro-computed tomography (X-ray microCT) at the Lawrence Berkeley National Laboratory Advance Light Source on beamline 8.3.2, using a beam energy of 21 KeV. Biochars were sieved to 2mm and mounted in syringes of 8.3mm diameter for imaging. A total of 1025 projections were acquired using continuous tomography mode with a 4x objective, for a final pixel size of 1.7 µm. Images were reconstructed using Gridrec methods via TomoPy and Xi-CAM.[56,57] Image analysis was completed in Dragonfly, a 3D image analysis software free for non-commercial use (Object Research Systems, Canada).

1.2.2 Soil characterization

Hanford sandy loam (HSL) and Yolo silt loam (YSiL) soils were chosen for continuity between laboratory experiments and ongoing field trials. Collectively, these soils represent over 260,000 hectares of arable land in California and offer textural distinctions within a range of soils commonly farmed in the Central Valley of California.[58] Soils were located via Web Soil Survey (http://websoilsurvey.sc.egov.usda.gov/) and collected from the top 30 cm in fallowed agricultural fields in Parlier, California (HSL) and Davis, California (YSiL). Soils were homogenized and sieved to 2 mm for characterization and column experiments. Colorimetric NO_3^- and NH_4^+ measurements were made according to Doane and Horwath (2003) and Verdouw et al. (1978) (Shimadzu UV-1280). Extractable P was measured using the Olsen sodium bicarbonate extraction.[61] Concentrations of potassium, calcium, magnesium, and sodium were measured by extracting 4 g of soil with 40 ml of 1 M ammonium acetate on a shaker for 30 minutes. Nutrient concentrations of filtered extracts were determined through atomic absorption spectroscopy (Perkin Elmer AAnalyst 800). Total porosity was calculated as the pore volume divided by the total soil volume in representative cores. Pore volume was determined as the difference in weight between saturated and oven-dried (105 °C for 24 h) cores. The pH and EC of soils with and without biochar were measured via 1:2 soil to 18.2 MΩ-cm water (w:v) dilution, after 15 minutes on the shaker and 60 minutes at rest.[62] Soil texture analysis was performed by the Analytical Lab at the University of California, Davis (Davis, CA, USA) using the hydrometer method.[63]

1.2.3 Sorption experiments

To investigate the ability of biochar to adsorb ammonium and nitrate, 0.1 g of biochar was added to 40 ml of solution containing either 0, 50, 100, 200, 400, or 600 mg L^{-1} of NO_3^- (as KNO_3) or NH_4^+ (as NH_4Cl), along with method blanks. All solutions were prepared in 5.84 mg L^{-1} NaCl and, as in Hale et al. (2013a), spiked at 1% volume with a stock solution of 20 g L^{-1} of the bactericide sodium azide. All sorption experiments were performed in triplicate at 22 ± 1 °C. Tubes were placed on an end-over shaker at 8 rpm for 24 h. Supernatants were passed through a 0.45 µm filter and analysed for colorimetric NO_3^- and NH_4^+ (Shimadzu UV-1280).[59,60] Single point sorbed ion concentration was determined at initial concentrations of 100 mg NO_3^- or NH_4^+ g^{-1} biochar using Eq. (1).

$$q = \frac{C_0V_0 - C_fV_f}{m} \tag{1}$$

Here, q is the sorbed ion concentration (mg g^{-1}), C_0 and C_f are the initial and final sorbate concentrations, respectively (mg L^{-1}), V_0 and V_f are the initial and final solution volumes, respectively

(L), and m is the mass of biochar (g). Multiple equations were tested to model the adsorption isotherms, with the Freundlich equation (Eq. (2)) demonstrating the best fit based on r^2 values.

$$q = K_f C_f^{\frac{1}{n}} \qquad (2)$$

Here, q and C_f are the same as in equation 1, K_f is the Freundlich constant (mg g^{-1}), and $1/n$ is the degree of nonlinearity of the isotherm. Excel was used to determine the parameters for the equations. Using batch sorption results, AS500, AS800, and SW500 were selected for further experimentation.

1.2.4 Column experiments

To investigate the influence of biochar on saturated hydraulic conductivity (K_{sat}), constant head column experiments were performed in five replicates using the 5 station Chameleon Kit (Soilmoisture Equipment Corporation (SEC) 2816GX). SEC tempe cells were packed with soils amended with 0 and 2% (w/w) AS500, AS800, or SW500 biochars, to a bulk density of 1.34 ± 0.02 g cm^{-3}. An application rate of 2% was chosen as the midrange of those represented in similar experiments.[10] Columns were saturated for 24 h before the start of each experiment. Each column was gravity-fed a solution of 11.1 mg L^{-1} $CaCl_2$ at a pressure head of 34 cm for 10 pore volumes. K_{sat} was calculated using data produced by SEC pressure transducers and PressureLogger software, which monitored head and flow over time. Columns were also used to investigate the nutrient retention and leaching in HSL amended with 0 and 2% biochar. Native soil nitrogen was flushed for 10 pore volumes with 11.1 mg L^{-1} $CaCl_2$, after which 50 mg L^{-1} of both NO_3^- and NH_4^+ (as NH_4Cl and KNO_3) was gravity-fed through columns for 15 pore volumes. Leachate was collected every 0.5 pore volumes and analysed for colorimetric NO_3^- and NH_4^+ as in sorption experiments.[59,60]

1.2.5 Statistical analysis

All data were analyzed with mixed models and two-way analysis of variance (ANOVA) in the stats and Tidyverse packages in R.[64,65] If a significant interaction between the fixed effects (biochar and soil type) was found, the effect of biochar within each soil type was analysed separately. For analysis of results, all effects with p-values < 0.05 were considered significant. P-values were generated using the emmeans package in R[66] and corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method. Plots were generated in R using the ggplot2 package[67] and visualized as the mean plus or minus the standard error of the means.

1.3 RESULTS

1.3.1 Biochar characterization

Biochars exhibited a broad range of chemical and physical properties depending on their production temperature and feedstock (Tables 1.1 and 1.2). Generally, increased production temperature was associated with higher ash content, pH, EC, and surface area, as well as decreased carbon, hydrogen, and DOC. These trends are consistent with those of a recent meta-analysis on temperature and biochar properties [16]. Softwood biochars produced at 500 and 800 °C had substantially higher surface areas than almond shell biochars produced at the same temperatures. All biochars contained less than 1% nitrogen, spanning from SW800 at 0.13% to CS650 at 0.79%. Almond shell biochars contained 4-6x more nitrogen than softwood biochars produced at the same temperature. Overall, AS800 possessed the most unique properties, with the lowest carbon content at 35.3%, the highest ash content at 55.4%, the highest EC at 27.2 mS cm^{-1}, and a basic pH of 10.13. Contrary to trends observed in the literature regarding high temperature biochars, AS800 had the highest O/C ratio at 0.56, and the second highest CEC at 53.77 cmolc kg^{-1}.[16] The unusual O content of AS800 suggests it may have been oxidized through exposure to air immediately after pyrolysis while still hot.

Table 1.1 Select chemical and physical biochar properties (n=3) ± standard error of the means

	AS500	AS800	CS650	SW500	SW500-I	SW650	SW800
Carbon (%)	65.8 ± 0.45	35.33 ± 0.25	71.23 ± 0.73	70.89 ± 0.25	63.49 ± 0.33	78.32 ± 0.41	41.76 ± 0.47
Nitrogen (%)	0.76 ± 0.01	0.55 ± 0.02	0.79 ± 0.04	0.13 ± 0.03	0.69 ± 0.01	0.29 ± 0.01	0.13 ± 0.03
Oxygen (%)	17.11 ± 0.75	26.44 ± 0.75	13.66 ± 0.64	17.07 ± 0.58	20.11 ± 0.23	10.18 ± 0.16	15.3 ± 0.88
Hydrogen (%)	3.05 ± 0.04	1.83 ± 0.02	3.23 ± 0.06	3.76 ± 0.01	3.79 ± 0.03	2.92 ± 0.07	1.48 ± 0.05
Molar O/C ratio	0.19 ± 0.01	0.56 ± 0.01	0.15 ± 0.01	0.18 ± 0.01	0.24 ± 0	0.1 ± 0	0.27 ± 0.01
Molar H/C ratio	0.55 ± 0.01	0.62 ± 0.01	0.54 ± 0.01	0.63 ± 0	0.71 ± 0.01	0.44 ± 0.01	0.42 ± 0.02
Volatile (%)	30.74 ± 2.67	28.17 ± 0.5	32.14 ± 0.36	37.99 ± 0.86	38.83 ± 1.21	26.87 ± 0.29	21.67 ± 0.17
Ash (%)	19.01 ± 0.99	55.35 ± 0.78	5.28 ± 0.15	4.48 ± 0.06	9.21 ± 0.53	4.45 ± 0.29	31.45 ± 1.21
pH	9.34 ± 0.02	10.13 ± 0.01	7.77 ± 0.02	7.85 ± 0.02	10.43 ± 0.01	8.03 ± 0.03	10.29 ± 0.01
EC (mS cm^{-1})	3.17 ± 0.01	27.2 ± 0.12	0.28 ± 0	2.54 ± 0.02	2.05 ± 0.02	0.12 ± 0	2.71 ± 0.01
DOC (mg kg^{-1})	38322.1 ± 1776.6	1055.9 ± 52.9	644.5 ± 77.1	43776.2 ± 1103.8	32171.2 ± 934.8	423.4 ± 50.6	475.2 ± 66.9
CEC (cmolc kg^{-1})	24.02 ± 0.57	52.74 ± 0.81	26.82 ± 1.06	16.46 ± 0.39	34.13 ± 0.18	21.65 ± 0.43	60.83 ± 0.75
Mean particle size (µm)	464	269.8	609.1	493.6	241.1	212.3	139.4
Median particle size (µm)	590.6	334.8	931.2	763.5	312.8	446.3	171.2
Surface Area (m^2 g^{-1})	54.7	188.2	233.6	93.5	152.6	305.6	363.6

EC = electrical conductivity; DOC = dissolved organic carbon; CEC = cation exchange capacity

The IR spectra of AS500 and SW500 were notably similar, with carboxyl and aromatic functional groups present at 1697 and 1703 cm^{-1} (C=O) and 1410 and 1418 (COO^-); aromatic bands around 1580 cm^{-1}; C=C skeletal vibrations; out of plane C-H bending vibrations (700 to 900 cm^{-1}) associated with adjacent aromatic hydrogen bonds; and aromatic C=C and C=O stretching vibrations (1581 and 1589 cm^{-1}) (Figure 1.1a, Table 1.2). The similarity between these biochars was expected, as each was produced at the same temperature by the same company via fractional hydropyrolysis. Additionally, the AS500 biochar included 25% softwood chips to aid the pyrolysis process. By contrast, AS800 was produced via gasification. AS800 spectra contained a strong band at 1405 cm^{-1} representing substantial contributions of COO^-, and multiple sharp IR peaks from ~1000 to 700 cm^{-1} arising from metal oxide vibrations (Figure 1.1a, Table 1.2). The high contribution of O-rich functional groups and metal oxide vibrations is consistent with the elemental analysis of AS800, which showed high oxygen and ash content (Table 1.1). Each biochar was visually distinct at the macroscale (Figure 1.1b). Animated reconstructions of biochar particles have been uploaded to a data repository and can be located as follows: AS500 (Figure 1.S1a): https://doi.org/10.5446/53407; AS800 (Figure 1.S1b): https://doi.org/10.5446/53406 ; and SW500 (Figure 1.S1c): https://doi.org/10.5446/53408. The macro-pores (>50 µm) of SW500 were more uniform in size compared to those of AS500 and AS800 (Figure 1.1b, 1.S1a, 1.S1b, and 1.S1c). The softwood chips added to the AS500 feedstock matrix are visible in the background, and contrast sharply with the almond shells (Figure 1.1b and 1.S1a). The macro-pores of AS800 appeared to increase in size (most visible in the bottom right of AS800 Figure 1.1a, and in the animated reconstruction in figure 1.S1b), due to the collapse of the lacy carbon pores that were visible in AS500 (Figure 1.1b and 1.S1a). The increase in production temperature resulted in more binomial pore size distribution in AS800, with larger macropores as well as increased quantity of micro-pores, leading to an overall increase in surface area as confirmed by BET (Table 1.1, Figure 1.1b, Figure 1.S1b)

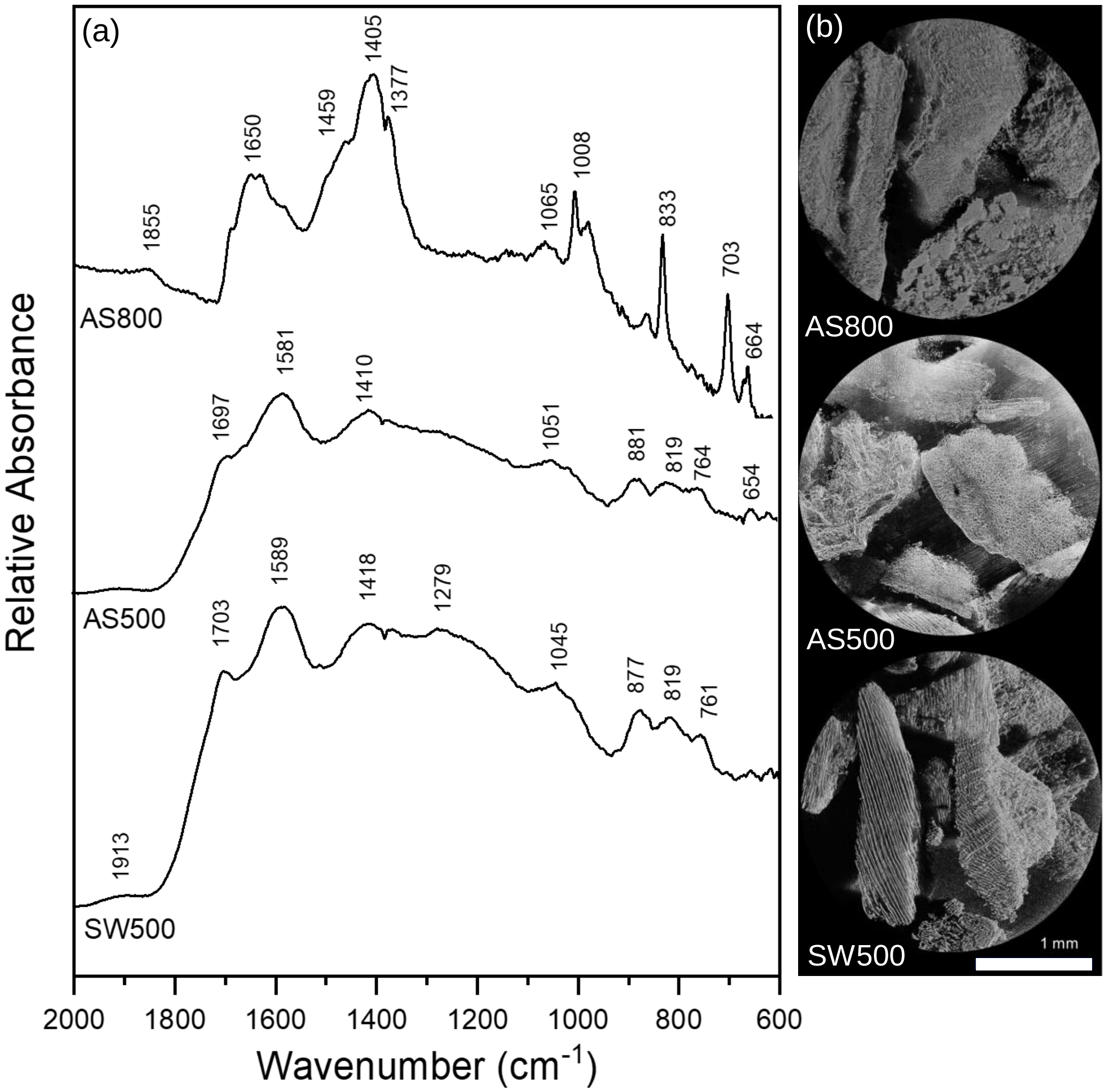

Figure 1.1 a) DRIFT spectra of AS800, AS500, and SW500 biochars. Samples diluted with potassium bromide to 3% sample, and collected with 256 cm^{-1} scans with a 4 cm^{-1} resolution; b) X-ray microCT images of AS800, AS500, and SW500 biochars.

Table 1.2 Functional group assignments corresponding to organic biomass

Wavenumber (cm^{-1})	Assignment*
1695-1720	ν(C=O) vibration aromatic carbonyl/ carboxyl C=O stretching
1640-1660	ν(C=C) vibration, C=C aromatic ring
1540-1650	ν_{as}(COO)
1580-1590	Skeletal C=C vibration
1459	δ(C-H) vibrations in CH_3 and CH_2
1400-1380	ν_s(COO)
1377	ν(C-O) vibration aromatic and δ(C-H) vibrations in CH_3 and CH_2
1154	Aromatic C-O stretching
1080-1040	ν(C-O) stretch of polysaccharides
1000-1010	ν(Si-O)
870-881	1 adjacent H deformation
833	ν(metal-O)
819	2 adjacent H deformation
703	ν(metal-O)
760-765	4 adjacent H deformation
654-664	γ(OH) bend

*** FTIR band assignments from Parikh et al. (2014)**

1.3.2 Soil characterization

Table 1.3 contains select chemical and physical properties of soils used in this study. The finer textured YSiL had a porosity of 42.5%, a sand concentration of 24%, and a clay concentration of 32.7%, compared to the coarser HSL with a porosity of 29.9%, and sand and clay concentrations of 58.7%, and 12%, respectively. Both HSL and YSiL contained substantial levels of nitrate, calcium, magnesium, and potassium, and were slightly above neutral at a pH of 7.30 and 7.31, respectively.

Table 1.3 Select physical and chemical properties of Hanford Sandy Loam (HSL) and Yolo Silt Loam (YSiL) (n=3) ± standard error of the means

	HSL	YSiL
NH_4^+ (mg kg^{-1})	0.74 ± 0.05	1.02 ± 0.14
NO_3^- (mg kg^{-1})	34.49 ± 0.50	40.40 ± 1.05
Ca (mg kg^{-1})	943.41 ± 11.56	2191.26 ± 7.19
Mg (mg kg^{-1})	58.05 ± 1.62	508.50 ± 11.60
K (mg kg^{-1})	55.91 ± 0.99	360.05 ± 0.70
Na (mg kg^{-1})	118.09 ± 2.27	146.56 ± 0.73
Olsen P (mg kg^{-1})	9.19 ± 0.12	9.83 ± 0.15
pH	7.30 ± 0.09	7.31 ± 0.05
EC (μs cm^{-1})	427.33 ± 2.84	269.25 ± 1.92
Porosity (%)	29.9 ± 0.35	42.5 ± 0.42
Sand (%)	58.7 ± 1.4	24.0 ± 0.9
Clay (%)	12.0 ± 0.9	32.7 ± 0.5

EC = electrical conductivity

1.3.3 Sorption

All biochars exhibited the capacity to remove ammonium from solution (Figure 1.2), though K_f values were low (Table 1.4). Single point concentration tests at a C_0 of 100 mg L^{-1} revealed the following hierarchy of sorption capacities, in order of lowest to highest: SW650 < SW500 < CS650 < SW500-I < AS500 < SW800 < AS800 (Table 1.4). These q values spanned 0.70 (SW650) to 7.15 (AS800) mg g^{-1}, or removal efficiencies of 0.70 and 7.15%. AS800 exhibited the greatest K_f value at 0.16 mg NH_4^+ g^{-1}. Isotherms for nitrate and biochar are not provided, as only AS500 exhibited the capacity to remove nitrate from solution. The other six biochars released, rather than removed, nitrate. For AS500, the single point concentration test at a C_0 of 100 mg L^{-1} revealed a removal efficiency of 1.74%, or a q of 1.74 mg g^{-1} (Table 1.4). All tested models were poor fits for the AS500 and nitrate isotherm, including the Freundlich equation with an r^2 of 0.57. As such, K_f and 1/n values provided in Table 1.4 should be regarded with caution.

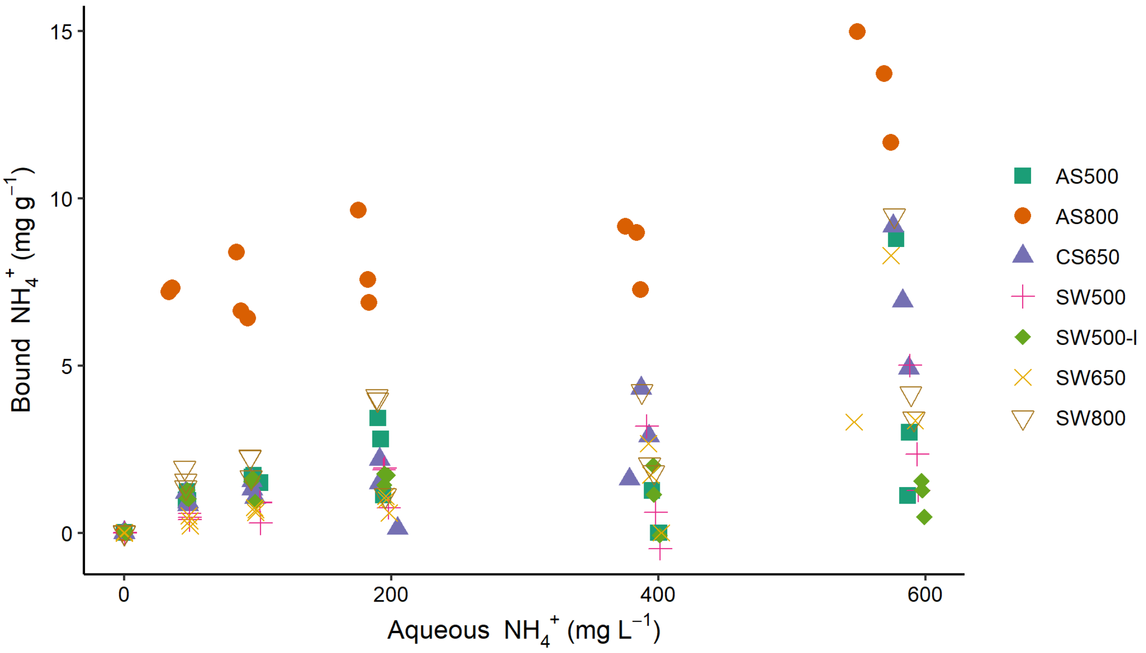

Figure 1.2 Sorption isotherms for ammonium and biochars, performed in at 22 ± 1 °C. All solutions were prepared in 5.84 mg L^{-1} NaCl and spiked at 1% volume with a stock solution of 20 g L^{-1} of the bactericide sodium azide.

Table 1.4 Concentration of ions bound to biochars (mg NH_4^+ or NO_3^- g^{-1}) at single point concentration of 100 mg L^{-1}, and Freundlich model parameters (n=3). Nitrate parameters reported for only one biochar (AS500), as all other biochars released rather than removed nitrate.

	Single point concentration		Freundlich parameters		
Biochar	q (mg NH_4^+ g^{-1})	standard error	1/n	K_f (mg NH_4^+ g^{-1})	r^2
AS500	1.63	0.05	0.71	0.05	0.90
AS800	7.15	0.51	0.77	0.16	0.84
CS650	1.30	0.12	0.65	0.06	0.75
SW500	0.70	0.17	0.83	0.01	0.91
SW500-I	1.37	0.18	0.52	0.08	0.73
SW650	0.69	0.03	0.68	0.03	0.89
SW800	2.06	0.17	0.77	0.04	0.90
Biochar	q (mg NO_3^- g^{-1})	standard error	1/n	K_f (mg NO_3^- g^{-1})	r^2
AS500	1.74	0.47	0.49	0.22	0.57

1.3.4 Soil columns- hydraulic conductivity and breakthrough curves

There was a main effect of biochar and soil texture, as well as a significant interaction between biochar and soil texture, on saturated hydraulic conductivity ($p = 0.001$, < 0.001, and 0.006, respectively). In HSL soil, AS500 and SW500 each decreased K_{sat} by 75%, from the control at 1.2 cm s^{-1} to 0.3 cm s^{-1} ($p = 0.023$) (Figure 1.3). AS800 caused a 12.5% decrease in K_{sat} to 1.05 cm s^{-1}, though the effect was not significant ($p = 0.939$). In YSiL soil, AS500 decreased K_{sat} by 63.6%, from the control at 0.044 cm s^{-1} to 0.016 ($p < 0.001$). SW500 caused a decrease of 79.5%, to 0.009 cm s^{-1} ($p < 0.001$). In contrast to its effect on HSL, AS800 increased K_{sat} in YSiL by 97.7%, to 0.087 cm s^{-1} ($p < 0.001$).

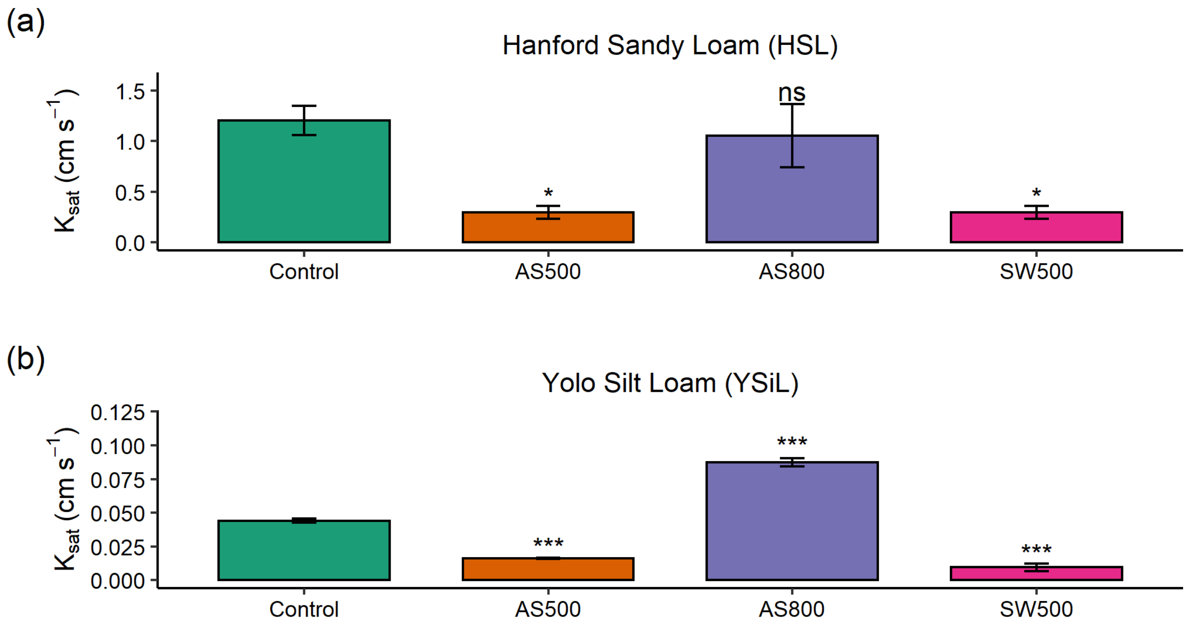

Figure 1.3 Impact of 0 and 2% addition of AS500, AS800, and SW500 biochars on saturated hydraulic conductivity (K_{sat}) in a) a Hanford Sandy Loam (HSL) soil and b) a Yolo Silt Loam (YSiL) soil (n=5). Symbols denote significance levels as follows: ns = not significant, *p<0.05, **p<0.01, ***p<0.001. P-values refer to comparisons between treatments and the control within each pore volume, and were corrected for multiple comparisons using Tukey's honestly significant difference method.

Figure 1.4 illustrates the ammonium and nitrate breakthrough curves for HSL amended with 0 and 2% AS500, AS800, and SW500. Biochar affected the timing and quantity of ammonium (introduced in pore volumes 11-25 at 50 mg L^{-1}) leached from the soil column (Figure 1.4a). The estimated breakthrough point, or the pore volume at which the concentration of the leachate equals 0.5x the concentration of the incoming solution ($C/C_0 = 0.5$), was reached as follows, in order of fastest to slowest for ammonium: HSL at pore volume 14.3, SW500 at 15.5, AS500 at 16.2, and AS800 at 18.1. Biochar also significantly decreased the total amount of ammonium in the leachate at all pore volumes, as follows, in order of least to most retention: HSL < SW500 < AS500 < AS800 (Figure 1.5a). At pore volume 15, AS500 decreased the ammonium concentration of the leachate compared to the control (HSL = 37.33 mg L^{-1}) by 30.5% ($p < 0.001$), AS800 by 78.1% ($p < 0.001$), and SW500 by 24.4% ($p = 0.002$). This effect was diminished by pore volume 25, where differences from the control (HSL= 41.69 mg L^{-1}) were decreased to 21.8% by AS500 ($p < 0.001$), 28.9% by AS800 ($p < 0.001$), and 8.5% by SW500 (not statistically significant at $p = 0.463$).

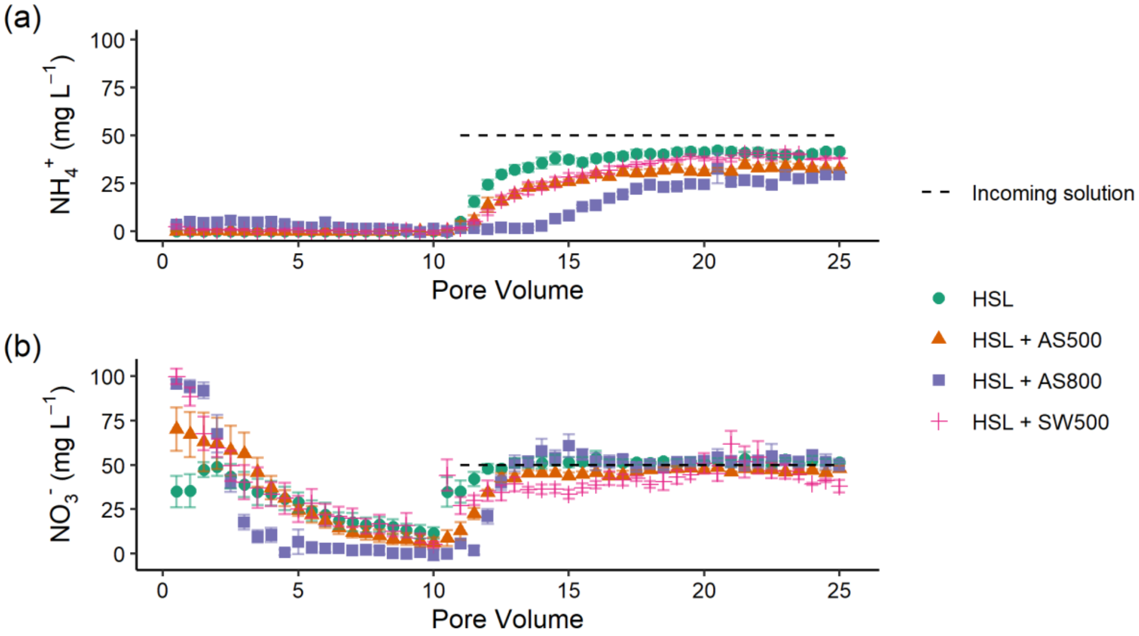

Figure 1.4 Breakthrough curves for a) ammonium and b) nitrate in a Handford Sandy Loam (HSL) soil with 0 and 2% additions of AS500, AS800, and SW500 biochars. Native soil nitrogen was flushed in pore volumes 0-10 with a 11.1 mg L^{-1} $CaCl_2$ solution, after which 50 mg L^{-1} solutions of NH_4^+ and NO_3^- were gravity-fed through soil columns (n=5). Error bars represent standard error of the means.

Estimated nitrate breakthrough points for biochar amended soils were each within 0.5 pore volumes of the control (pore volume 11.4), indicating that biochar had little to no effect on the timing of nitrate release from HSL. The effect of biochar on the total quantity of nitrate released was also less substantial than for ammonium (Figure 1.4b). Only SW500 significantly decreased the concentration of nitrate in the leachate compared to the control. At pore volume 15, SW500 inhibited nitrate transport by 35.01% (p = 0.002) (Figure 1.5b). This effect was not present at pore volume 20, and was slightly lessened to 26.5% by pore volume 25 (marginally significant at p = 0.098).

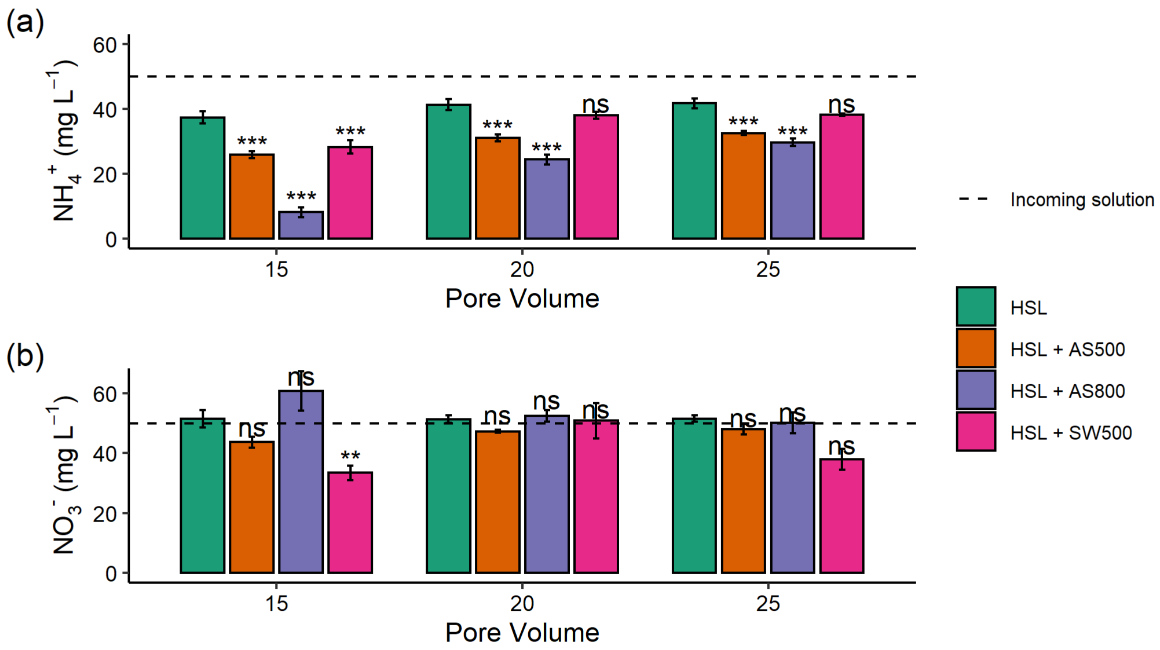

Figure 1.5 Quantity of a) ammonium and b) nitrate in Hanford Sandy Loam (HSL) soil columns with 0 and 2% additions of AS500, AS800, and SW500 biochars in pore volumes 15, 20, and 25 (n=5). Error bars represent standard error of the means. Symbols denote significance levels as follows: ns = not significant, *p<0.05, **p<0.01, ***p<0.001. P-values refer to comparisons between treatments and the control within each pore volume, and were corrected for multiple comparisons using Tukey's honestly significant difference method.

1.4 DISCUSSION

1.4.1 Sorption and biochar properties

The ability of all seven biochars to retain ammonium, and within the demonstrated ranges, is consistent with other published studies.[27] AS800 exhibited substantially higher ammonium binding capacity than the other biochars tested. While it is typical for biochars produced at high temperatures to have low O/C ratios and low CEC,[16] AS800 had the largest O/C ratio at 0.56 (presumably due to post-pyrolysis oxidation), and the second highest CEC at 52.75 cmolc kg^{-1}. These properties, as well as the IR band at 1405 cm^{-1}, likely explain the high ammonium retention, as they indicate increased exchange sites and oxygen-containing functional groups which can react with ammonium. The relationship between these biochar properties and ammonium binding capacity was also demonstrated with SW800, which had the highest CEC at 60.83 cmolc kg^{-1}, the second highest O/C ratio at 0.27, and the second highest ammonium binding capacity. These observations are consistent with those of other studies.[38,39] No clear trends between surface area and ammonium retention emerged in this study.

That six of the seven biochars did not retain nitrate, and in most cases released nitrate, is consistent with other published studies.[27] Though data are inconclusive and show no clear trends to explain the chemical affinity between AS500 and nitrate, it is possible that the relatively high ash content and low CEC enabled anionic binding, as positively charged ions from biochar ash could bind to nitrate without being repelled by surface cation exchange sites. While AS800 and SW800 had higher ash contents, they also had substantially larger CECs. Electrostatic repulsion, then, may have prevented binding between the positively charged metals in the ash and the aqueous nitrate.

1.4.2 Column experiment- nutrient retention

As in the sorption trials, AS800 retained the greatest quantity of ammonium in the column studies, followed by AS500 and SW500. This suggests that the chemical affinity between biochar and ammonium is the controlling factor on the flow of ammonium through biochar-amended soils. By contrast, the flow of nitrate appears to be dictated, though minor in effect, by physical means. Unlike in sorption trials, AS500 did not retain significant quantities of nitrate. This suggests a weak chemical affinity between AS500 and nitrate, in which nitrate is readily desorbed from AS500. SW500, however, significantly inhibited the flow of nitrate, despite not exhibiting chemical affinity in sorption trials. This suggests the physical retention mechanism known as nitrate capture, which is believed to be facilitated by increased surface area and porosity.[8,41,42,50] Indeed, SW500 had a substantially larger surface area than AS500 (93.5 compared to 54.7 m^2 g^{-1}). AS800, however, had an even greater surface area at 188.2 m^2 g^{-1}, but exhibited no capacity to retain nitrate. This may have been due to the formation of larger macropores in AS800 (Figure 1.1b), which allowed water to move through the biochar more quickly and limited the flow of nitrate into micropores where it could be retained. The strong ammonium binding capacity and high CEC of AS800 suggests a strongly negatively charged surface. Electrostatic repulsion between AS800 and nitrate, therefore, may have prevented nitrate capture. Together with sorption results, these breakthrough curves add to a growing body of literature which suggests that biochar may have a strong role in decreasing ammonium mobility in soils, but is unlikely to do so for nitrate without chemical or physical modification.[27]

1.4.3 Column experiment- saturated hydraulic conductivity

AS500 and SW500 significantly decreased K_{sat} by 75% in HSL. AS800 also decreased K_{sat} in HSL, though to a lesser extent and without statistical significance. This effect is in agreement with the literature, which consistently demonstrates decreased K_{sat} in coarse textured soils after biochar amendment, and is hypothesized to be the result of increased surface area, microporosity, and tortuosity, which can slow the movement of water through soils.[10] By contrast, biochar typically increases K_{sat} in fine textured soils due to decreased bulk density and an increase in total porosity and mean pore size.[10] This is in agreement with the 98% increase in K_{sat} in YSiL after amendment with AS800, but contrasts with the 64 and 80% reduction after the addition of AS500 and SW500, respectively. AS500 and SW500 had substantially larger particle sizes and smaller surface areas than AS800. Though pore size was not quantitatively measured in this study, it is possible that the pores of AS500 and SW500 were small enough to decrease mean pore size in the coarse soil as in Devereux et al. (2013) but were not large or numerous enough to increase K_{sat} in a fine soil. By contrast, the collapse of the lacy carbon pores in the AS500 compared to AS800 lead to the formation of both additional small pores with greater surface area (confirmed by BET), and larger macro-pores (as visualized by X-ray microCT) in AS800. This may indicate an ability for AS800 to increase overall porosity, mean pore size, and pore connectivity in YSiL, as seen in other studies.[49] Broadly, the ability of each biochar to substantially influence the movement of water through each soil underscores its effect on the physical composition of soils. This fact contributes to the hypothesis that nitrate capture may have occurred in the case of SW500.

1.5 CONCLUSION

This project contributes to the literature by investigating the combination of chemical and physical mechanisms through which biochar influences nutrient retention and hydraulic conductivity. Biochar was demonstrated to control the flow of ammonium primarily through chemical affinity. Ammonium retention was linked to biochar properties such as high CEC, high O/C ratios, and the presence of oxygen-containing surface functional groups. Nitrate transport was shown to be controlled, though slightly, through physical means. This effect could perhaps be optimized by producing biochars, like SW500, which minimize CEC but maximize surface area, to encourage the physical entrapment of nitrate. Biochar also had a large effect on saturated hydraulic conductivity, though this effect was not consistent across biochars and soils. Broadly, the results of this study suggest that biochar may increase the residence time of water in sandy soils and increase drainage in fine textured soils, though soil- and biochar- specific investigation is required.

This study demonstrates that biochar can provide a suite of agronomic benefits, from nutrient retention to improvements in soil-water dynamics for crop production. This may be particularly relevant for flooded agricultural systems such as rice, where ammonium is the primary source of N and water retention is a key parameter for success. Additional research and quantitative analysis at the micron and sub-micron scale is required to assess the influence of biochar on soil porosity and pore architecture. Field-scale investigation using these soils and biochars is also ongoing, in order to link the impact of biochar on hydraulic conductivity and nutrient leaching to its influence on crop yield and nutrient use efficiency.

1.6 ACKNOWLEDGEMENTS

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microtomography facility. We are grateful to Mike Marsh and the staff at Object Research Systems for providing a license to Dragonfly software and for the technical support in reconstructing and interpreting microCT images. Thank you also to the Davis R Users group for statistical and coding consultation, and to Tad Doane and Alex Barbour for laboratory support. This work was made possible by funding from the California Department of Food and Agriculture Fertilizer Research and Education Program (16-0662-SA-0), the Almond Board of California (17-ParikhS-COC-01), and the United States Department of Agriculture (USDA), National Institute of Food and Agriculture (NIFA) through Hatch Formula Funding (CA 2076-H) and multistate regional project (W-3045). ALS is supported by the Director, Office of Science, Office of Basic Energy Science, of the US Department of Energy under contract no. DE-AC02-05CH11231. Additionally, this research was supported by the UC Davis Dissertation Year Fellowship, a Henry A. Jastro Graduate Research Award, the Beatrice Oberly and S. Atwood McKeehan Fellowship, and the Foundation for Food and Agriculture Research Fellowship.

Chapter 2: Three-year field trials with seven biochars reveal minor changes in chemical properties of two agricultural soils but no impact on yield[*]

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Danielle L. Gelardi,[1] Patricia A. Lazicki, [1] Michelle M Leinfelder-Miles,[2] Kate M. Scow,[1] Daniel J. Geisseler,[1] Sanjai J. Parikh[1]

[1] Department of Land, Air and Water Resources, University of California, Davis, 1 Shields Ave, Davis CA 95616, USA

[2]University of California Cooperative Extension, San Joaquin County, UC Division of Agriculture and Natural Resources, 2101 E. Earhart Ave., Ste. 200, Stockton, CA 95206, USA

ABSTRACT

Although many studies have demonstrated that biochar can deliver agronomic benefits such as increased soil water retention, increased fertility, and increased yield, these experiments are frequently small-scale and short-term. Furthermore, biochar has been observed to have the greatest benefits on crop growth in marginal soils, such as those low in fertility, coarse textured, contaminated, highly acidic, or receiving limited inputs of fertilizer and irrigation water. The objective of this study was to determine the impact of biochars on processing tomato production in two fertile soils in a Mediterranean climate. Seven biochars produced from different feedstocks at different temperatures were screened in a short-term growth chamber trial. The high electrical conductivity (EC) and pH of almond shell biochar produced at 800 °C (AS800) prevented the growth of romaine lettuce, and all replicates died. The remaining six biochars, on average, increased lettuce yield by 31%. These same seven biochars were amended to a silt loam and sandy loam in three-year field trials, at two application rates in conjunction with two synthetic fertilizer rates. No biochar had a significant effect on processing tomato yield, crop ripening, or plant nitrogen (N) uptake at any rate in any year in any location. Minor increases in soil pH, EC, and mineral N concentration were observed in years 2 and 3, though effects were not consistent across biochars, locations, and years. The results of this study demonstrate that short-term laboratory experiments are not sufficient to make conclusions about field-scale agriculture. Results also indicate that biochar may confer limited agronomic benefits in fertile soils in Mediterranean climates. While there were no tangible agricultural improvements in this study, biochar may deliver benefits not captured in conventional agronomic measures, such as increased soil health or climate change mitigation. Work is ongoing to measure these ecological and societal effects.

KEYWORDS

Biochar, long-term field experiment, Mediterranean climate, fertility, agronomy

HIGHLIGHTS

- **Biochar benefits measured in growth chamber trials were not observed at field-scale**
- **Biochars did not increase crop yield in two fertile soils in 3-year field trials**
- **Minor and inconsistent increases in pH, EC, and soil mineral N were observed**
- **Biochar may be better suited to deliver agronomic benefits in marginal soils**
- **No negative effects of biochar amendments were observed**

2.1 INTRODUCTION

The use of biochar, the solid material created through the thermochemical conversion of biomass in an oxygen limited environment,[3] has been proposed as a solution to many agricultural challenges.[69] During pyrolysis, agricultural waste products can be converted to a renewable fuel known as syngas, and carbon (C) that would otherwise be released during biomass decomposition can be stored as biochar, a recalcitrant form of C.[70] This process has clear waste management benefits, and has been demonstrated to reduce greenhouse gases in multiple life cycle assessments.[70–72] Furthermore, biochar has been reported to deliver a suite of agronomic benefits when added to agricultural soils, including increased soil fertility,[73] increased soil water content,[10] and shifts in the soil chemical or microbial environment.[74,75] These benefits are often reported to increase crop yield, though results are inconsistent and vary widely. While many studies demonstrate increased yield following biochar addition,[74,76,77] others show little to no effect,[11,12,78] and in some rare cases, negative effects have been reported.[79] The efficacy of biochar to deliver agronomic outcomes is dependent on variables such as feedstock, production method, and production temperature, as well as soil, climate, and cropping conditions. These variables have commonly led authors to conclude that location- and material- specific investigation is required to determine if a particular biochar may deliver agronomic benefits in a particular system.[14,15,80]

Improvements in crop yield from biochar addition are frequently hypothesized to be the result of increased soil fertility, though biochar is not specifically a fertilizing material. While there may be short-term yield gains from the release of biochar-bound nutrients,[81] or slight, temporal gains from the weathering of endogenous biochar nutrients,[11] it is widely accepted that biochar should be used in conjunction with synthetic fertilizer, compost, or manure.[9,50,82–84] When applied to soils, biochar may enhance soil fertility by increasing cation exchange capacity (CEC), as negatively charged biochar surfaces adsorb to cations such as magnesium (Mg^{2+}), potassium (K^+), and calcium (Ca^{2+}).[85,86] Biochar has also been observed to covalently bond with ammonium (NH_4^+).[6] While a chemical affinity between biochar and nitrate (NO_3^-) is uncommon due to electrostatic repulsion,[87] biochar pores may physically entrap nitrate, making it more available for plant uptake.[8,42,50] As most biochars are alkaline, a shift in pH via a liming effect can also improve soil fertility by reducing aluminum toxicity or increasing phosphorous availability in soils of low pH.[7,88] Within studies that report a biochar-associated increase in soil fertility, the effect on crop yield is mixed, with some demonstrating increased yield,[74,76,85] minor or temporary increases,[78,89] soil-texture specific increases,[86,90,91] or no effect on yield.[73,92] Still other studies report no effect of biochar on soil fertility at all.[93,94]

The influence of biochar on soil water dynamics may also play a role in increasing crop yields, though results appear largely dependent on soil texture. A recent meta-analysis concluded that biochar substantially increased soil water content at field capacity and permanent wilting point in coarse textured soils only.[95] Multiple authors have concluded that, overall, sandy soils have a greater response to biochar addition than do finer textured soils.[10,95] Despite these observed trends, biochar has been reported to improve soil water dynamics even in fine textured soils. In field trials, biochar was observed to reduce maize crop water stress and increase yield in a silt loam,[96] prevent soybean crop loss in years of reduced precipitation in a sandy clay loam,[97] and increase wheat yield and quality under multiple deficit irrigation regimes in a silty clay loam.[98] By contrast, one study demonstrated that biochar-associated water savings in a clay soil were not substantial enough to reduce crop water stress or lead to increased maize yields.[99] Other authors have reported little to no effect, or transient effects, of biochar on soil water dynamics at field scale.[12,78,93]

The conditions in which biochar appears to deliver the most consistent agronomic benefits are those in which soils require conditioning or remediation for the successful growth of crops. A global meta-analysis concluded that biochar boosts yields in the tropics by 25%, but overall has no effect on yield in temperate latitudes.[80] Arable tropical soils are typically characterized by acidity, low fertility, and receive limited fertilizer inputs, and therefore may have the most to gain from the addition of biochar. Though the liming effect of biochar is widely reported,[15] it has been observed that up to 50 tons of biochar per hectare may be required to match the fertility benefits of just 3 tons per hectare of dolomite.[100] Biochar has also been observed to improve yields in saline and sodic soils, through the sorption of sodium (Na^+) or by releasing non-sodium base cations to decrease exchangeable sodium percentage.[101–103] Similarly, biochar can immobilize heavy metals or organic pollutants, thereby increasing yields and decreasing the concentration of contaminants in crop biomass.[104,105] Collectively, this research suggests biochar has a promising role in remediating or conditioning soils that may otherwise pose challenges for agricultural production. However, there appear to be fewer agronomic benefits from applying biochar to temperate and fertile cropping systems.[80]

An additional challenge to determining if biochar may deliver agronomic benefits is a lack of field-scale experiments. One literature review concluded that, of nearly 800 studies evaluated, approximately 25% were conducted in the field.[14] Of those field studies, more than 50% were in plots less than 20 m^2 and under investigation for one year or less. This review highlights the limitations in biochar research, which pose obvious challenges to extrapolating results to production-scale agriculture. Indeed, it has been observed that laboratory results do not necessarily scale, as in Jones et al. (2012), where the short-term effects of biochar on soil and plant growth reported from laboratory studies were not observed in a three-year field trial using the same soil and biochar. Fortunately, there have been a number of large-scale field trials spanning 3 or more planting seasons published in recent years: Hale et al., 2020; Jin et al., 2019; Kätterer et al., 2019; Liu et al., 2019; Madari et al., 2017; McDonald et al., 2019; Nan et al., 2020; Oladele, 2019; Pandit et al., 2018; Sadowska et al., 2020; and Sánchez-Monedero et al., 2019. While multiple studies demonstrated the potential of biochar to remediate or condition low quality agricultural soils,[88,99,107] benefits have also been observed in fertile soils,[74] though these are frequently limited in size or duration.[73,75,78,89,97] Inconsistencies emphasize the need for increased field-scale, long-term, and location- and material-specific research to inform the use and regulation of biochar in working lands.

To fills numerous gaps in the literature, the overarching aim of our study was to elucidate the effects of biochar in a Mediterranean climate, through three-year field experiments conducted in two texturally distinct but fertile soils. A silt loam and sandy loam were chosen, each with a “Grade 1- Excellent” score in the California Revised Storie Index for agricultural suitability.[108] Seven biochars were applied at two rates, in conjunction with two synthetic nitrogen (N) fertilizer rates (Table 2.1). The first objective was to determine to what degree biochar affects processing tomato yield and plant N accumulation, as well as soil mineral N concentration, pH, electrical conductivity (EC), and moisture. The second objective was to evaluate the fertilizer rate, soil texture, and biochar production parameters and application rate which may optimize potential benefits. The final objective was to link results with preliminary laboratory trials, to determine if short-term effects observed in the laboratory were observable at the field scale and across time. To our knowledge, this study provides the first multi-year, multi-site, multi-scale data about the agronomic impact of biochar for cropping systems in California. It is particularly novel in that it tests seven distinct biochars at multiple application rates, combined with multiple fertilizer rates, in two different locations. Results are intended to support policymakers and land managers in making decisions about the use of biochar for California, and in global locations with similar climates, soils, and cropping systems.

2.1 MATERIALS AND METHODS

2.1.1 Biochar selection and characterization

Seven biochars from four commercial suppliers were obtained from the following feedstocks and produced at the following temperatures: almond shell at 500 and 800 °C (AS500, AS800), coconut shell at 650 °C (CS650), softwood at 500, 650, and 800 °C (SW500, SW650, SW800), and an additional softwood biochar produced at 500 °C inoculated with a microbial formula (SW500-I). Biochars were chosen based on commercial availability and/or relevance of the feedstock to regional waste management issues. A variety of biochar treatments was included to provide a gradient of feedstocks and production temperatures for field trials. Unless otherwise stated, biochars were sieved to 2 mm and characterized using procedures recommended by the International Biochar Initiative (IBI, 2015): pH and EC were measured at a 1:20 biochar to 18.2 MΩ-cm water (Barnstead nanopore, Thermo Fisher) dilution (w:v) after solutions were shaken for 90 minutes; total C, N, hydrogen, and oxygen were measured using a dry combustion-elemental analyzer (Costech ECS4010); and moisture, volatile, and ash content were measured as a percent of total dry weight through sequential increases in furnace temperature (105, 750, and 950 °C, respectively). Particle size distribution was measured by laser diffraction (Coulter LS230). CEC was measured using a combination of the modified ammonium acetate compulsory displacement method[51] and the rapid saturation method:[52,53] 0.25 g of biochar was leached under vacuum (-20 to -40 kPa) with 18.2 MΩ-cm water (Barnstead nanopore, Thermo Fisher). Leachate was stored and analyzed for dissolved organic carbon (DOC) through combustion (Shimadzu TOC-V). Biochar samples were then washed with 1 M sodium acetate (pH 8.2) until the EC of the elute was the same as the eluant. Samples were rinsed three times with 10 ml of 2-proponal, then dried under vacuum for 10 minutes. To displace Na^+ ions, biochars were washed with 1 M ammonium acetate using the same volume as was required for sodium acetate. Leachate was collected and analyzed for Na^+ concentration through atomic absorption spectroscopy (Perkin Elmer AAnalyst 800). Specific surface area was determined by Micromeritics'

Particle Testing Authority (https://www.particletesting.com/) from CO_2 adsorption isotherms according to the Brunauer, Emmet, Teller (BET) method.[54]

2.2.2 Growth chamber trials

To screen biochars for their effect on plant growth, romaine lettuce (*Lactuca sativa*) was grown in 4.5 kg of Hanford Sandy Loam (HSL) completely mixed with 2% (w/w) AS500, AS800, CS650, SW500, SW500-I, SW650, SW800, a raw, unpyrolyzed almond shell (AS), or a soil-only control (NO), in four replicates. Romaine was chosen for its short growing period and its small size. HSL was chosen for continuity between growth chamber and field trials. The pH and EC of each soil and biochar mixture was taken at time 0, using a 1:2 soil to water ratio (w/v) after 15 minutes on the shaker and 60 minutes equilibration.[62] The growth chamber was illuminated for 12 h per day and kept at 22 ± 1 °C. Lettuce was transplanted into pots 20 days after seeding. In three separate fertilizing events, each pot received 400 mg N kg^{-1} (as NH_4NO_3), 100 mg P kg^{-1} (as KH_2PO_4) and 200 mg K kg^{-1} (as KH_2PO_4 and K_2SO_4). Pots were watered to 50% of water holding capacity every 2-3 days. All aboveground biomass was harvested 45 days after transplanting. Plants were weighed, oven dried at 60 °C, and ground to a fine powder. Milled lettuce samples were analyzed for total C and N using a dry combustion-elemental analyzer (Costech ECS4010).

2.2.3 Field site and management

Identically designed trials, approximately 0.5 hectares each, were established in two California locations: (1) Davis (Yolo County), in a Yolo Silt Loam (YSiL): Fine-silty, mixed, superactive, nonacid, thermic Mollic Xerofluvent,[109] and (2) Parlier (Fresno County), in a Hanford sandy loam (HSL): Coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthent.[110] Field sites were chosen within the heavily-farmed Central Valley to provide agricultural soils with contrasting textures. Collectively, these soils represent over 260,000 hectares of arable land in California.[58] Each trial was designed as a randomized complete block, with three blocks and one replicate per block of the following combinations of treatments, in plots measuring 4.6 m wide (3 beds) and 6.1 m long: One of seven biochars (AS500,

AS800, CS650, SW500, SW500-I, SW650, SW800), a raw, unpyrolyzed almond shell (AS), or a soil-only control (NO). Treatments were subsurface banded at one of two rates (low: 2.3 t ha^{-1} or high: 4.6 t ha^{-1}), in conjunction with one of two fertilizer rates in split plots (low: 168 kg N ha^{-1} or high: 252 kg N ha^{-1}) (Table 1.1). Biochars were amended to soils in a single application event in October 2017, by hand application into trenches 25-30 cm in depth. Trenches were created and left open following the installation of subsurface drip tape. One subsurface drip line was buried at the center of each bed, and remained in place for the duration of the three-year trials. Biochar-filled trenches were immediately closed, burying the concentrated biochar at the center of the bed. This application technique places the biochar directly above the drip tape and within the rooting zone of the plant, in order to collocate it with irrigation and fertigation. It also allows the simulation of high application rates in the rooting zone (approximately 22.8 and 45.6 t ha^{-1}) while using less biochar in the field overall. A visual schematic of this application method is provided in Santos-Medellin et al. (2021).

Fields were managed under processing tomato (*Solanum lycopersicum*) production using common practices[112] for three consecutive growing seasons from 2018 to 2020. Precipitation and temperature data for each location during each growing season can be found in the supplementary information (SI) (Table 2.S1) Tomatoes were transplanted in late April or early May each year, except in 2018 in Parlier, where planting was delayed until early June due to challenges in field preparation. Tomatoes were transplanted in one row per 1.5 m wide bed. Tomatoes were irrigated to 100% of evapotranspirative demand as determined by a Tule Evapotranspiration Tower (www.tuletechnologies.com/). Urea-ammonium-nitrate 32 (UAN-32) was fertigated through the drip tape in five different events throughout the growing season, to a total of 168 or 252 kg N ha^{-1}. Fertilizer rates were selected at the low and high ends of the recommended range for processing tomatoes.[112] Potassium thiosulfate was applied at a rate of 39.2 kg K ha^{-1} 83 days after planting. Broadly, Dual Magnum, Treflan, and/or Round-Up were used to treat weeds. Advise 4, Coragen, Platinum, and/or Admire were used for pest control. The quantity and timing of pesticide application varied by season and location, following common regional practices.[112]

Table 2.1 Experimental matrix for three-year field trials in two locations

Treatment ID	Feedstock	Temperature (°C)
NO	No biochar (control)	n/a
AS	Raw almond shell	n/a
AS500	Almond shell	500
AS800	Almond shell	800
CS650	Coconut shell	650
SW500	Softwood	500
SW500-I	Softwood (inoculated)	500
SW650	Softwood	650
SW800	Softwood	800
Fertilizer rate	(kg N hectare^{-1})	
Low	168	
High	252	
Biochar application rate	(tonnes hectare^{-1})	
Low	2.3 (subsurface banded, to simulate 22.8 in the root zone)	
High	4.6 (subsurface banded, to simulate 45.6 in the root zone)	

2.2.4 Plant sampling and analysis

Plants were harvested at the end of August, except in 2018 in Parlier, when harvest was delayed until October due to the late planting. All aboveground biomass was harvested from three plants in the center of each plot. Red fruit, green fruit, and vines were separated and weighed, and a subsample of each was kept for analysis. Fruit was blended, freeze dried, and ground, while vines were oven dried at 60 °C and ground. All powdered plant tissues were analyzed for total C and N using a dry combustion-elemental analyzer (Costech ECS4010). Tomato yields are reported in terms of fresh weight, with red fruit weight reported as marketable yield, and red + green fruit reported as total yield.

2.2.5 Soil sampling and analysis

Prior to establishing field trials, baseline soil samples were taken from each location down to 30 cm in September 2017. Samples were kept on ice until they could be transferred to a 4 °C refrigerator, after which they were sieved to 4 mm and analyzed within one week. NO_3^- and NH_4^+ were extracted with a 1:5 soil to 0.5 M potassium sulfate solution dilution (w/v) and measured colorimetrically according to Doane and Horwath (2003) and Verdouw et al. (1978), respectively, on a spectrophotometer (Shimadzu

UV-1280). The following analyses were performed on air dried soils. Total C was measured using a dry combustion-elemental analyzer (Costech ECS4010). Extractable P was measured using the Olsen sodium bicarbonate extraction.[61] Concentrations of K^+, Ca^{2+}, Mg^{2+}, and Na^+ were measured by extracting 4 g of soil with 40 ml of 1 M ammonium acetate on a shaker for 30 minutes. Nutrient concentrations of filtered extracts were determined through atomic absorption spectroscopy (Perkin Elmer AAnalyst 800). The pH and EC of soils with and without biochar were measured via 1:2 soil to 18.2 MΩ-cm water (Barnstead nanopore, Thermo Fisher) dilution (w:v), after 15 minutes on the shaker and 60 minutes at rest [62]. Soil texture analysis was performed by the Analytical Lab at the University of California, Davis (Davis, CA, USA) using the hydrometer method.[63] Soil moisture content was reported as the difference in soil weight before and after 24 h in a 105 °C oven.

During the three-year field trials, soil sampling was performed directly after harvest each fall. Because the drip tape remained buried 25-30 cm below the soil surface for the duration of the experiment, probes were taken 13-18 cm on either side of the bed's center. Each sample was composited from three Giddings probe samples taken to 90 cm and subsequently separated into three depths: 0-30, 30-60, and 60-90 cm. A total depth of 90 cm was chosen to investigate the effects of biochar deeper into the soil profile than is conventionally explored. For ease of discussion, and because biochar had the greatest effect from 0-30 cm, only that depth is presented here. Data concerning 30-60 and 60-90 cm can be found in SI (Figures 2.S1 and 2.S2). Samples were kept on ice until they could be transferred to a 4 °C refrigerator, after which they were sieved to 4 mm and analyzed within one week as described above.

2.2.6 Statistical analyses

The trials at Davis and Parlier were analyzed separately to detect the effect of biochar within each location. All data were analyzed as a randomized complete block design with split plots using mixed models and four-way analysis of variance (ANOVA) in the lme4 and Tidyverse packages in R.[64,65,113] Blocks, split plots, and subplots were considered random effects, with all treatment factors (biochar type, biochar rate, fertilizer rate, and year) considered fixed effects. Two separate models were built for each response variable. The first included each individual biochar as well as the unamended control. The second averaged all biochar treatments together, to test the overall effect of adding biochar compared to the unamended control. Both sets of models tested treatment factors individually and the interactions between them. All effects with p-values < 0.05 were considered statistically significant. P-values were generated using the emmeans package in R and corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method.[66] Scatter plots were generated in R using the ggplot2 package.[67] and are visualized as the mean, with error bars representing the 95% confidence interval of the mean.

2.3 RESULTS

2.3.1 Baseline soil characterization

Samples taken prior to the establishment of the three-year field trials demonstrated each site had fertile soils (Table 2.2). Both HSL and YSiL contained substantial levels of Ca^{2+}, Mg^{2+}, and K^+, though YSiL had more than double the quantity of each, and 1% total C compared to only 0.37% in the HSL. Both soils were high in NO_3^- and had a soil pH slightly above neutral. HSL is a much coarser soil, with 58.7% sand and 12.0% clay, compared to 24.0% sand and 32.7% clay in YSiL.

Table 2.2 Select physical and chemical properties of Hanford Sandy Loam (HSL) and Yolo Silt Loam (YSiL) from 0 to 30 cm (n = 3) ± standard error of the means. Samples were taken prior to the establishment of the field trial in September 2017 to measure baseline fertility

	HSL	YSiL
Total C (%)	0.37 ± 0.009	1 ± 0.02
NH_4^+-N (mg kg^{-1})	0.74 ± 0.1	1.02 ± 0.1
NO_3^--N (mg kg^{-1})	34.5 ± 0.5	40.4 ± 1.1
Ca^{2+} (mg kg^{-1})	943.4 ± 11.6	2191.3 ± 7.2
Mg^{2+} (mg kg^{-1})	58.1 ± 1.6	508.5 ± 11.6

K^+ (mg kg^{-1})	55.9 ± 1.0	360.1 ± 0.7
Na^+ (mg kg^{-1})	118.1 ± 2.3	146.6 ± 0.7
Olsen P (mg kg^{-1})	9.2 ± 0.1	9.8 ± 0.2
pH	7.30 ± 0.1	7.31 ± 0.1
EC (µS cm^{-1})	427.3 ± 2.8	269.3 ± 1.9
Sand (%)	58.7 ± 1.4	24.0 ± 0.9
Clay (%)	12.0 ± 0.9	32.7 ± 0.5

EC = electrical conductivity

2.3.2 Biochar characterization

Biochars exhibited a broad range of chemical and physical properties depending on their production temperature and feedstock (Table 2.3). Generally, increased production temperature was associated with higher ash concentration, pH, EC, and surface area, and decreased C, hydrogen, and DOC concentration. These trends are consistent with those of a recent meta-analysis on temperature and biochar properties.[16] All biochars contained less than 1% N, spanning from SW800 at 0.13% to CS650 at 0.79%. Overall, AS800 possessed the most unique properties, with the lowest C content at 35.3%, the highest ash content at 55.4%, the highest EC at 27.2 mS cm^{-1}, and a pH of 10.13. Contrary to trends observed in the literature regarding high temperature biochars,[16] AS800 had the highest oxygen to carbon (O/C) ratio at 0.56, and the second highest CEC at 53.77 cmolc kg^{-1}. The elevated O content of AS800 suggests it may have been oxidized through exposure to air immediately after pyrolysis (i.e. post pyrolysis oxidation).

Table 2.3 Select chemical and physical biochar properties (n=3) ± standard error of the means

	AS500	AS800	CS650	SW500	SW500-I	SW650	SW800
Carbon (%)	65.8 ± 0.45	35.33 ± 0.25	71.23 ± 0.73	70.89 ± 0.25	63.49 ± 0.33	78.32 ± 0.41	41.76 ± 0.47
Nitrogen (%)	0.76 ± 0.01	0.55 ± 0.02	0.79 ± 0.04	0.13 ± 0.03	0.69 ± 0.01	0.29 ± 0.01	0.13 ± 0.03
Oxygen (%)	17.11 ± 0.75	26.44 ± 0.75	13.66 ± 0.64	17.07 ± 0.58	20.11 ± 0.23	10.18 ± 0.16	15.3 ± 0.88
Hydrogen (%)	3.05 ± 0.04	1.83 ± 0.02	3.23 ± 0.06	3.76 ± 0.01	3.79 ± 0.03	2.92 ± 0.07	1.48 ± 0.05
O/C ratio	0.19 ± 0.01	0.56 ± 0.01	0.15 ± 0.01	0.18 ± 0.01	0.24 ± 0	0.1 ± 0	0.27 ± 0.01
H/C ratio	0.55 ± 0.01	0.62 ± 0.01	0.54 ± 0.01	0.63 ± 0	0.71 ± 0.01	0.44 ± 0.01	0.42 ± 0.02
Volatile (%)	30.74 ± 2.67	28.17 ± 0.5	32.14 ± 0.36	37.99 ± 0.86	38.83 ± 1.21	26.87 ± 0.29	21.67 ± 0.17

Ash (%)	19.01 ± 0.99	55.35 ± 0.78	5.28 ± 0.15	4.48 ± 0.06	9.21 ± 0.53	4.45 ± 0.29	31.45 ± 1.21
pH	9.34 ± 0.02	10.13 ± 0.01	7.77 ± 0.02	7.85 ± 0.02	10.43 ± 0.01	8.03 ± 0.03	10.29 ± 0.01
EC (mS cm^{-1})	3.17 ± 0.01	27.2 ± 0.12	0.28 ± 0	2.54 ± 0.02	2.05 ± 0.02	0.12 ± 0	2.71 ± 0.01
DOC (mg kg^{-1})	38322.1 ± 1776.6	1055.9 ± 52.9	644.5 ± 77.1	43776.2 ± 1103.8	32171.2 ± 934.8	423.4 ± 50.6	475.2 ± 66.9
CEC (cmolc kg^{-1})	24.02 ± 0.57	52.74 ± 0.81	26.82 ± 1.06	16.46 ± 0.39	34.13 ± 0.18	21.65 ± 0.43	60.83 ± 0.75
Mean particle size (µm)	464	269.8	609.1	493.6	241.1	212.3	139.4
Med. particle size (µm)	590.6	334.8	931.2	763.5	312.8	446.3	171.2
Surface Area (m^2 g^{-1})	54.7	188.2	233.6	93.5	152.6	305.6	363.6

EC = electrical conductivity; DOC = dissolved organic carbon; CEC = cation exchange capacity

2.3.3 Growth chamber trials

There was a main effect of biochar on soil pH and EC at time 0 (prior to transplanting), as well as on lettuce yield and lettuce N concentration (Table 2.4). When averaged across all biochars, biochar increased soil pH compared to the control from 6.50 to 8.07 ($p = 0.04$). AS800 increased soil pH to 10.45, or 3.95 units. Biochar's effect on EC was more variable, and not statistically significant when averaged across all biochars. However, AS800 similarly increased EC the most of all tested biochars, from 181 to 5392 µs cm^{-1} ($p < 0.001$). Soil amended with AS800 did not support the growth of romaine lettuce, and transplants from each of the four AS800 replicates died. As such, AS800 is not included in the following results. Averaged across all remaining biochars, biochar increased lettuce yield by 17.6 g, or 31.13 %, compared to the control ($p = 0.046$). The effect of individual biochars were not significant compared to the control, due to high variability within treatments. Only SW500 significantly increased plant N compared to the control, from 2.98 to 3.56% ($p = 0.008$). The raw, unpyrolyzed almond shell (AS) decreased plant N from 2.98 to 0.97% ($p < 0.001$).

Table 2.4 Results from a growth chamber experiment in which a sandy loam was amended with 0% (NO) or 2% (w/w) of the following treatments: AS, AS500, AS800, CS650, SW500, SW500-I, SW650, SW800 (n=4). In the upper panel, the estimated means are reported with asterisks indicating significance levels (˙p<0.10, *p<0.05, **p<0.01, ***p<0.001). P-values refer to comparisons between treatments and the control and were corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method. All bolded values indicate results with p-values <0.05. In the lower panel, F-statistics and significance levels are reported from ANOVAs for the main effect of biochar.

	Soil pH	Soil EC (µS cm^{-1})	Lettuce yield (g)	Lettuce N (%)
NO	6.5	181	56.6	2.98

AS		6.51	302	37.4	**0.97*** **
AS500		**8.39*** **	**535***	86.1	3.31
AS800		**10.45*** **	**5393*** **	na	na
CS650		6.54	219	79.9	3.04
SW500		**8.06*** **	481 ˙	69.3	**3.56** **
SW500-I		**8.1*** **	351	71.5	3.33
SW650		**6.69*** **	191	79.9	2.92
SW800		**8.23*** **	**533***	76.5	2.69 ˙
All biochars		**8.07** **	1101	**74.2***	3.14
Biochar	F	**3929*** **	**590.38*** **	**3.178***	**52.153*** **

2.3.4 Field trials: Tomato yield and plant N accumulation

Biochar did not have a significant effect on marketable yield, or the percentage of tomatoes determined marketable (ripe yield divided by total yield, hereby referred to as the marketable ratio) in either location, at either application rate, in any year (Table 2.5, Figure 2.1). This was true when biochars were averaged together and when analyzed separately. Fertilizer rate did not result in differences in marketable yield or ratio in any year in either location. The primary controls on marketable yield were year and location. When sites were analyzed together, yields were higher in Davis than in Parlier in years 2 ($p = 0.009$) and year 3 ($p = 0.008$). Yields were substantially lower in 2020 in both locations (each $p < 0.001$).

Averaged across all three years in Davis, the high fertilizer rate led to an increase in aboveground biomass N (N in fruit + vines) from 245 kg N ha^{-1} at the low rate, to 304 kg N ha^{-1} ($p = 0.023$) This effect was not detected in Parlier. Biochar had no effect on aboveground biomass N in either location, at either application rate, in any year (Table 2.5, Figure 2.2). Means for each treatment and significance levels for treatments vs. the controls can be found in SI (Table 2.S2).

Table 2.5 F statistics of treatment factors (biochar, fertilizer rate (Fert), year, and biochar application rate (nested within biochar, as Biochar:CharRate)) and their interactions on processing tomato marketable yield, marketable ratio, and aboveground biomass N (Plant N) in Davis and Parlier field trials. Asterisks indicate significance levels (˙p<0.10, *p<0.05, **p<0.01, ***p<0.001), and bolded values indicate results with p-values <0.05.

Davis	Parlier

	Marketable Yield (t ha^{-1})	Marketable Ratio	Plant N (kg ha^{-1})	Marketable Yield (t ha^{-1})	Marketable Ratio	Plant N (kg ha^{-1})
Biochar	0.4792	0.587	0.501	0.4	1.079	0.834
Fert	0.4	18.435 ·	**42.868***	0.0001	1.1595	3.554
Year	**290.273*****	**307.871*****	**119.838*****	**165.748*****	**122.035*****	**53.584*****
Biochar*CharRate	0.693	0.391	1.275	0.384	0.487	0.522
Biochar*Fert	0.953	0.7622	0.633	0.291	0.608	0.487
Biochar*Year	0.81	0.941	0.443	0.502	**1.709***	1.206
Fert*Year	**3.447***	**4.823****	1.44	0.226	1.974	1.192
Biochar*Fert*Year	1.253	1.586	0.771	0.9325	**2.141****	0.483

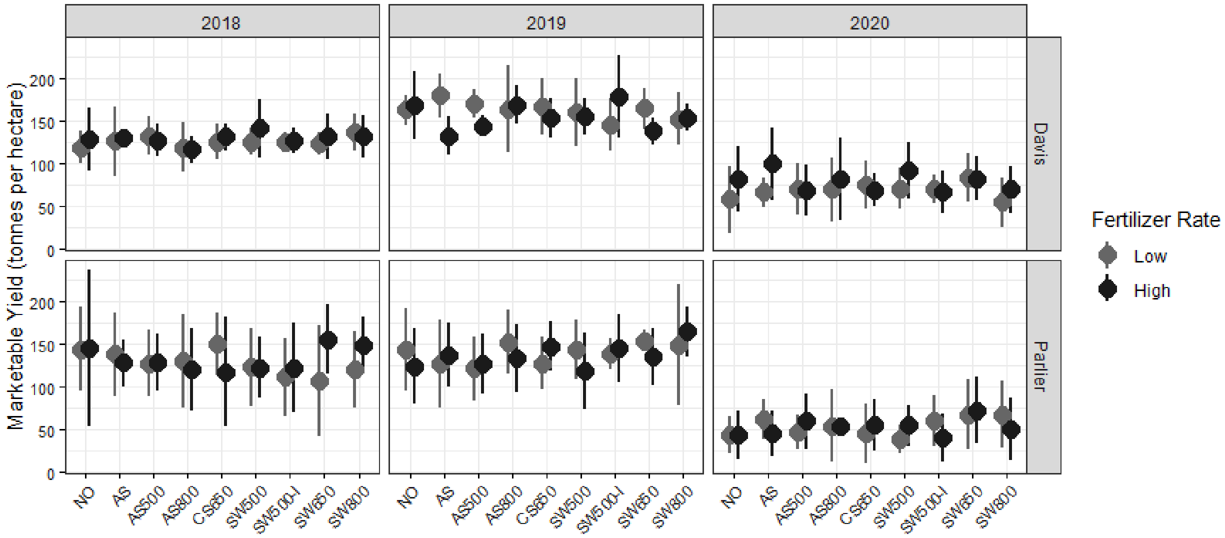

Figure 2.1 Marketable yield in a three-year processing tomato field trial by biochar, year, location, and fertilizer rate (Low = 168 kg N ha^{-1}; H = 252 kg N ha^{-1}). Results are averaged over the level of biochar rate (n = 3 per rate) as it was not significant in any models tested. Error bars represent the 95% confidence intervals of the means (n = 6).

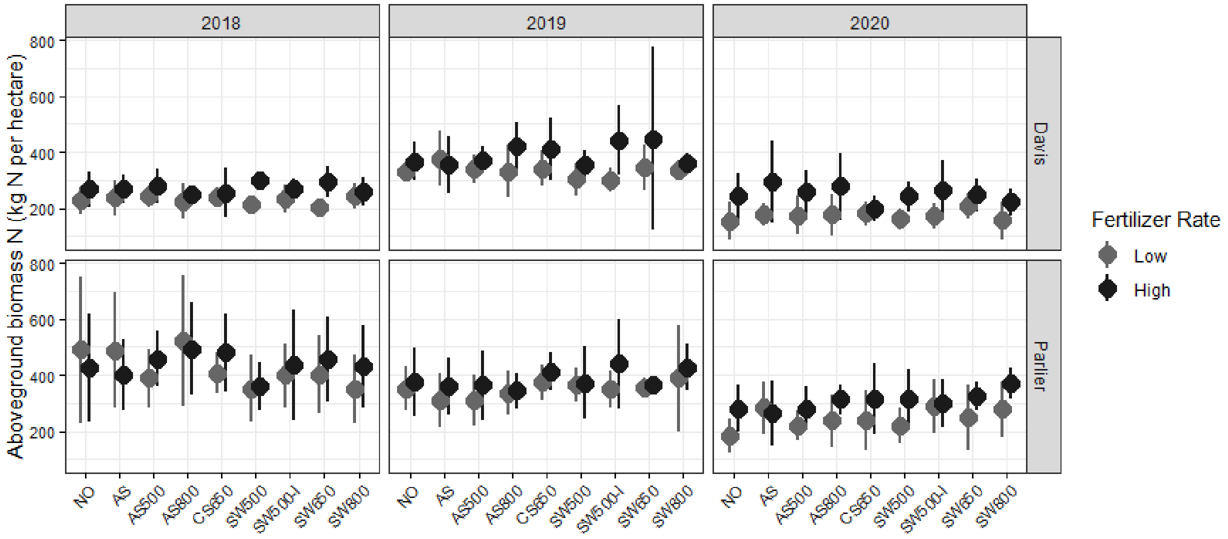

Figure 2.2 Aboveground biomass (fruit + vine) nitrogen (N) in a three-year processing tomato field trial by biochar, year, location, and fertilizer rate (Low = 168 kg N ha^{-1}; H = 252 kg N ha^{-1}). Results are averaged over the level of biochar rate (n=3 per rate) as it was not significant in any models tested. Error bars represent the 95% confidence intervals of the means (n = 6).

2.3.5 Field trials: Soil pH

Fertilizer and biochar rate explained little variation in pH models and were not statistically significant factors (Table 2.6). As such, the following results are averaged over those levels. In Davis, there was no detected effect of biochar on soil pH in any year (Figure 2.3). In Parlier, there was a main effect of biochar and year. The effect of biochar in Parlier was greatest in year 2, when biochar (averaged together) raised the soil pH from the control at 7.35 to 7.50 ($p = 0.044$). AS800 had the largest impact in year 2, raising pH to 7.79 ($p < 0.001$). By year 3, the effect of AS800 and of all biochars averaged together had diminished, and were not significant at $p = 0.09$ and 0.106, respectively. Means for each treatment and significance levels for treatments vs. the controls can be found in SI (Table 2.S3).

Table 2.6 F statistics of treatment factors (biochar, fertilizer rate (Fert), year, and biochar application rate (nested within biochar, as Biochar:CharRate)) and their interactions on soil pH, electrical conductivity (EC), mineral nitrogen (N) and moisture in Davis and Parlier field trials. Asterisks indicate significance levels (˙$p<0.10$, *$p<0.05$, **$p<0.01$, ***$p<0.001$), and bolded values indicate results with p-values <0.05.

	Davis	Parlier

	pH	EC (µS cm^{-1})	Mineral N (kg ha^{-1})	Moisture (%)	pH	EC (µS cm^{-1})	Mineral N (kg ha^{-1})	Moisture (%)
Biochar	1.788 ·	**2.542***	1.49	0.94	**6.329*****	1.784 ·	0.947	0.948
Fert	0.0512	2.637	3.385	1.759	0.012	**9.251****	4.117 ·	0.172
Year	**14.386*****	0.039	**10.127*****	**5.253****	**73.063*****	**43.487*****	**112.044*****	**61.725*****
Biochar* CharRate	1.182	1.615	0.671	0.785	0.976	0.775	0.186	1.207
Biochar* Fert	1.37	**2.305***	**0.657**	0.834	0.433	1.399	0.687	0.392
Biochar* Year	0.71	**1.873***	1.678 ·	1.124	1.452	0.856	1.215	0.769
Fert*Year	**6.358****	**3.48***	0.456	**3.838***	**14.156*****	2.426 ·	1.878	**3.694***
Biochar* Fert*Year	1.242	1.377	0.607	0.631	0.528	0.686	0.784	0.556

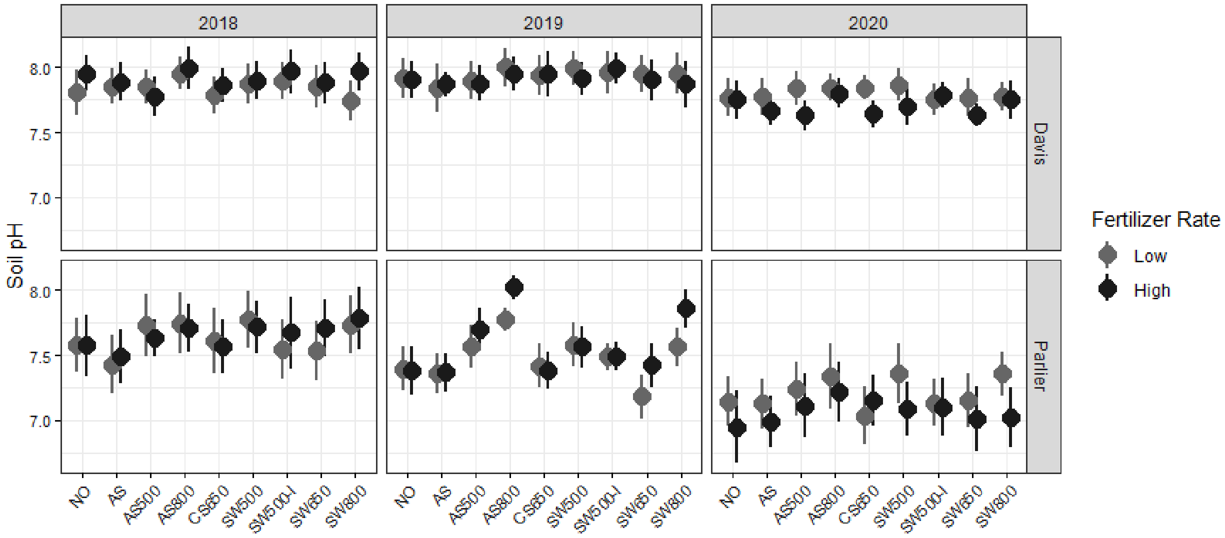

Figure 2.3 Soil pH in a three-year processing tomato field trial by biochar, year, location, and fertilizer rate (Low = 168 kg N ha^{-1}; High = 252 kg N ha^{-1}). Results are averaged over the level of biochar rate (n = 3 per rate) as it was not significant in any models tested. Error bars represent the 95% confidence intervals of the means (n = 6).

2.3.6 Field trials: Soil EC

In Davis, there was a main effect of biochar on soil EC, as well as significant interactions between biochar and year, and biochar and fertilizer rate (Table 2.6). The effect of biochar was strongest in year 3, and when averaged across fertilizer rate and biochar rate, AS800 increased soil EC from 142 to 200 µS cm^{-1} (p = 0.063), AS to 192 (p = 0.081), and SW650 to 190 (p = 0.02) (Figure 2.4). When averaged across year and biochar rate, biochar had a greater effect in Davis when combined with the high fertilizer rate, with AS, AS500, and AS800 each raising EC by 45.7, 42.4, and 43 µS cm^{-1}, respectively (p = 0.031, 0.057, and 0.051). In Parlier, there was a main effect of biochar on soil EC, though not statistically significant (p = 0.087). Similar to Davis, individual effects were only detected in year 3, with a trend towards increased EC in the cases of AS and AS800, from 146 µS cm^{-1} to 183 and 181 µS cm^{-1}, respectively (not significant at p = 0.055 and 0.091). There was no additive effect between fertilizer rate and biochar detected in Parlier.

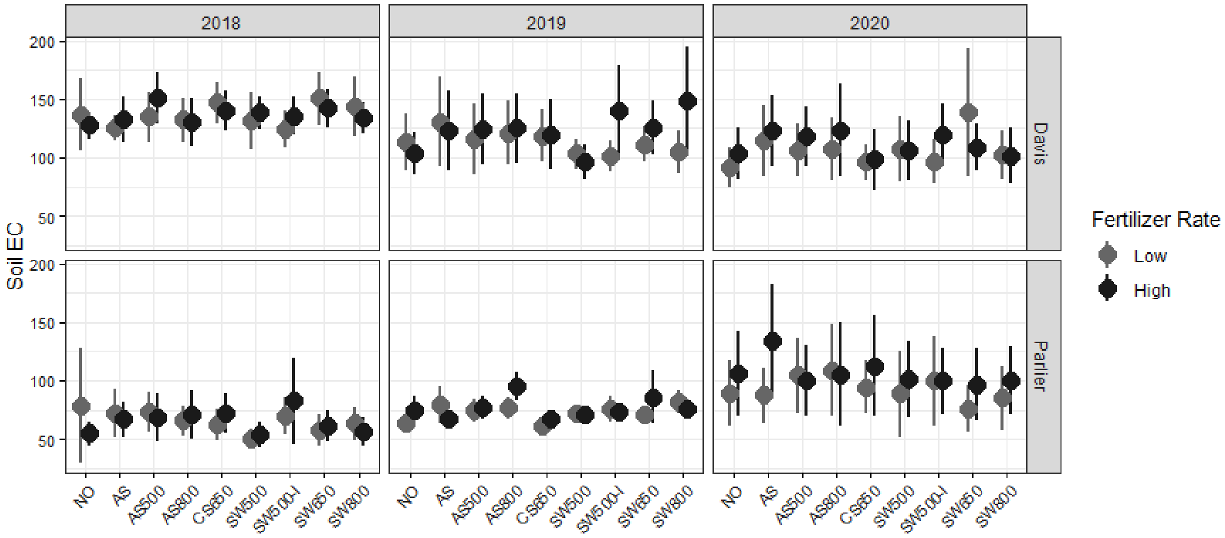

Figure 2.4 Soil electrical conductivity (EC) in a three-year processing tomato field trial by biochar, year, location, and fertilizer rate (L= low, or 168 kg N ha^{-1}; H = high, or 252 kg N ha^{-1}). Results are averaged over the level of biochar rate (n = 3 per rate) as it was not significant in any models tested. Error bars represent the 95% confidence intervals of the means (n = 6).

2.3.7 *Field trials: Soil mineral nitrogen and moisture*

When averaged across all biochars, there was an increase in the concentration of mineral N (NH_4^+-N and NO_3^--N combined) in Davis in year 3, from 42.9 to 59.1 kg N ha^{-1} (p = 0.012). When averaged across biochar rate and fertilizer rate, the following treatments increased mineral N in Davis in year 3: AS to 72.6 kg N ha^{-1} (p= 0.004), AS800 to 70.6 kg N ha^{-1} (p = 0.009), and SW650 to 70.1 kg N ha^{-1} (p = 0.011). In Parlier, when averaged across all biochars at both rates and fertilizer rates, there was a trend towards increased N in year 3 from 63.3 to 73.7 kg N ha^{-1}, though the effect was not significant (p = 0.075). No other effects of biochar on mineral N were detected in Parlier in any year (Figure 2.5). In both locations, in all years at both rates, biochar had no effect on postharvest soil moisture content.

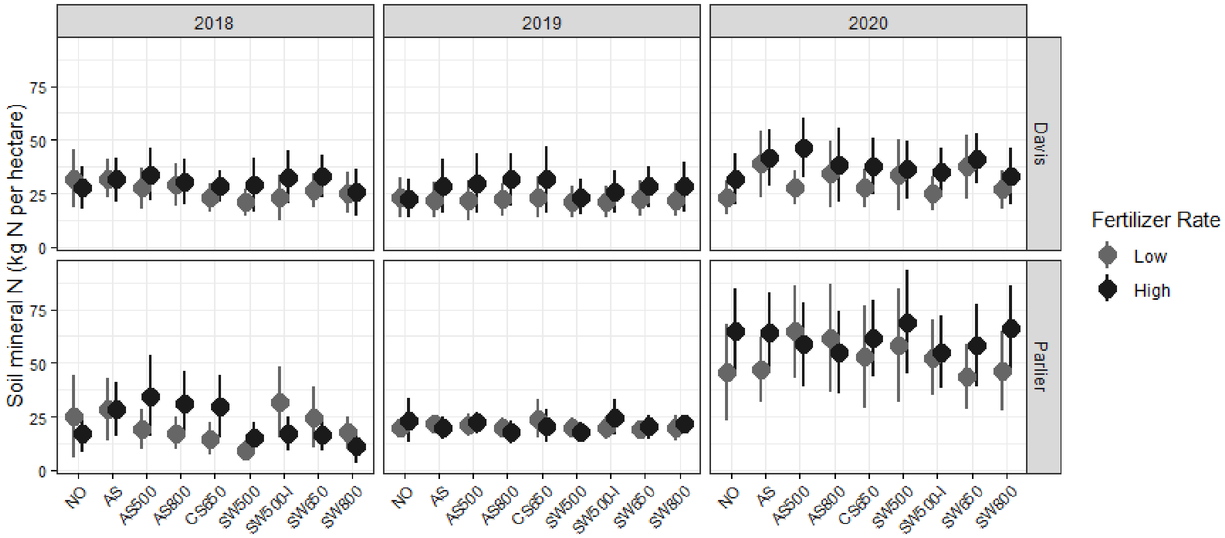

Figure 2.5 Soil mineral nitrogen (NH_4^+-N and NO_3^--N combined) in a three-year processing tomato field trial by biochar, year, location, and fertilizer rate (L= low, or 168 kg N ha^{-1}; H = high, or 252 kg N ha^{-1}). Results are averaged over the level of biochar rate (n = 3 per rate) as it was not significant in any models tested. Error bars represent the 95% confidence intervals of the means (n = 6).

2.4 DISCUSSION

2.4.1 *Biochar alters the soil chemical environment but does not influence yield*

This three-year field trial was designed to test the effect of biochar amended to contrasting soil textures on crop yield and soil fertility, as the biochar aged and against natural variation over time. Results showed a clear impact of time: processing tomato yields were significantly lower in year 3 in both locations, though this was not observed elsewhere in Yolo and Fresno counties.[114] Year 3 yield reductions in this study were likely the result of having grown the same crop in the same location for three years without tillage or crop rotation. Though bulk density was not measured, it was observed that, by year 3, soils were more difficult to sample due to compaction from repeated harvest, bed shaping, and Giddings probe activities. Location also played a substantial role in crop yield, with Davis supporting higher yields in two of the three growing seasons. This was to be expected, as Davis had substantially higher fertility (Table 2.2).

Against natural variation, biochar had an impact on soil pH, EC, and mineral N concentration, though results were not consistent across location and time. Differences between the effects of biochar on the soil chemical environment at each location may be partly explained by soil texture. In the coarser soils of Parlier, biochar raised soil pH in year 2, and to a lesser extent in year 3. This effect was greatest with AS800, which itself was the highest pH biochar, as is common with those produced at higher temperatures.[16] In Davis, biochar did not impact pH, perhaps due to the higher buffering capacity common in finer textured soils. Surprisingly, the reverse trend was observed for soil EC and mineral N, with effects detected in Davis but not in Parlier. In the finer textured soils of Davis, AS, AS800, and SW650 each increased soil EC and mineral N in year 3. It is possible that, due to the coarse soils of Parlier, any salts or N weathered from the biochar were leached through the profile. The most consistent response variable measured was soil moisture, which was not affected by biochar in any set of experimental conditions. Despite the effect of biochar on the soil chemical environment, biochar did not have an effect on crop yield, fruit ripening, or aboveground biomass N in any year in any location, as observed in multiple other field trials.[73,78]

The impact of biochar on soil chemical properties in this study may have been due to biochar weathering, from biochar increasing the retention of ions from fertilizers and those native in the soil, or a combination of each. Effects on pH and EC were smallest in year 1, which suggests that year 2 and 3 results were due to biochar weathering. The weathering of biochar and release of endogenous nutrients was also observed in a California field trial in a silt loam soil and identical climate, only in the second year of a four year study.[11] The increase in mineral N suggests potential binding, either through direct—possibly covalent—bonding with ammonium,[6] through a cation bridging reaction with nitrate,[18] or by physically entrapping nitrate within biochar pores.[50,84] Regardless of the mechanism, the result was not substantial enough to influence processing tomato yield, ripening, or plant N uptake. The lack of crop response to the increased N fertilizer rate demonstrates that the tomatoes were not N limited to begin with, and therefore had little to gain from the addition of biochar where N was concerned. These results are consistent with the many studies which also suggest biochar has limited potential in increasing yield when added to fertile agricultural soils.[73,75,78,80,89,97]

2.4.2 Biochar across scales- results from the laboratory are not observed in the field

The growth chamber experiment involved a different crop and a different biochar application rate and method, and thus direct comparisons cannot be made to the field trials in this study. However, the observed differences add to examples in the literature that indicate results from small-scale, single-season laboratory studies are not sufficient to make decisions about biochar for production-scale agriculture.[12,14] On average, biochar increased lettuce yields by 31% in the growth chamber. A similar effect was completely absent in the field trials with processing tomatoes using the same biochars and one of the same soils (HSL). Additionally, AS800 did not support the growth of lettuce in the growth chamber, likely due to its exceptionally high pH and EC. Although AS800 raised pH and EC in the field trials, the resulting levels were within a normal range for crop production and did not reduce yield. The difference in the effect of AS800 is likely due to time. While AS800 resided in the soil for only 2 months in the growth chamber, it had seven months to reside in the soil before the first crop of processing tomatoes was transplanted. Winter rains during this period likely leached soluble salts bound to the biochar at the time of amendment to the soil. The discrepancy in results from multiple scales emphasizes the need for longer-term studies, as biochar will behave differently over time.[14]

Furthermore, AS500, AS800, and SW500 were observed to substantially decrease ammonium leaching, and to a lesser extent nitrate leaching, when amended to HSL in soil column studies in previous work. Of these three biochars, only AS800 increased soil mineral N in field trials, and under no experimental conditions did they affect plant N uptake. In the same column study, AS500 and SW500 were observed to substantially decrease saturated hydraulic conductivity (K_{sat}) in HSL and YSiL, while AS800 increased K_{sat} in YSiL. While water retention properties cannot be derived from K_{sat} , a water conductivity property, K_{sat} is frequently used to describe biochar's potential to improve soil water dynamics for agriculture. In this instance, K_{sat} results observed in the lab were not linked to increased water retention in the field. The discrepancy is possibly in part due to the presence of crops at the field-scale, which likely depleted soil moisture prior to sampling. This highlights yet another difference between laboratory and field scale experiments.

2.4.3 Biochar in fertile soils yield few benefits but no harm observed

As biochars in this study delivered few agronomic benefits for the two fertile agricultural soils in temperate Mediterranean climates, it is difficult to make conclusions about the biochar feedstocks, production parameters, and application rates which may optimize benefits. Additionally, the results of this study do not allow conclusions to be made about the soil textures or fertilizer rates best suited to be combined with biochar application. However, the significant influence on soil EC, pH, and mineral N may suggest these biochars could improve crop production in less fertile or more acidic soils. Importantly, this agronomic study demonstrates that adding seven biochars at two rates did not result in any negative effects on processing tomatoes or soil in the responses measured. This information is critical for growers, land managers, and policymakers interested in amending soils with biochar. For growers considering the economics of biochar amendments, there may be little incentive to adding biochar to fertile soils. However, biochar is increasingly being evaluated as a C offset strategy in policy environments.[115,116] While there were no tangible agronomic benefits from adding biochar to the soils in this study, there may be soil health or climate change mitigation benefits.[117,118] These benefits could potentially be delivered without agronomic consequence, especially in cases where the cost of biochar application is offset through cost-share or incentive programs.

Work is ongoing to measure the effect of these biochars on soil microbial communities and C and N cycling in these same field studies, which may demonstrate effects not covered in conventional agronomic measurements. This agronomic study demonstrates that biochar may be added to agricultural soils for any number of goals, without reducing processing tomato yield in the process. Research should be undertaken on crops which may respond differently to the addition of biochar. Furthermore, the tendency of biochar to raise soil EC may be of greater concern in areas with high baseline salinity. Finally, care should be taken to test biochars prior to their incorporation into the soil for contaminants and ecotoxicological effects, in order to safeguard farmworker and environmental health.[119,120]

2.5 CONCLUSIONS

In this three-year field trial in a temperate Mediterranean climate, biochar was not observed to increase processing tomato yield, fruit ripening, or N uptake in two irrigated and fertilized soils with high baseline fertility and a neutral pH. However, there were increases in soil mineral N, EC, and pH, though inconsistent across time, location, and specific biochars. This may indicate that biochar could have a greater impact on crop production in soils that are acidic, limited in fertility, or do not receive regular fertilizer inputs. Research is ongoing to determine the impact of these biochars on parameters outside the usual agronomic measures, such as microbial community composition and climate change mitigation potential. While biochar may deliver limited agronomic benefits in temperate, fertile cropping systems, it is possible it can be added to soils for other ecological or societal benefits while bearing no negative effect on yield. That there was no positive effect on yield in this study, however, should inform the implementation of cost-share and incentive programs that offset the economic burden to growers. Furthermore, the discrepancy in results from growth chamber experiments, where biochar was observed to increase crop yield, and field trials, highlights the importance of field-scale data for investigating the use of biochar in production agriculture. Data from this multi-scale, multi-site, and multi-year study contribute to the knowledge about the potential of biochar for agronomic outcomes in fertile, Mediterranean cropping systems, and can be used by land managers and policymakers to inform the use and regulation of biochar for amendment to working lands.

2.6 ACKNOWLEDGEMENTS

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Chapter 3: If biochar does not influence yield in two agricultural soils, what does it do? Soil health measurements from a 3-year field trial

Danielle L. Gelardi,[1] Daniel Rath, [1] Alexander Barbour,[1] Kate M. Scow,[1] Daniel J. Geisseler,[1] Sanjai J. Parikh[1]

[1] Department of Land, Air and Water Resources, University of California, Davis, 1 Shields Ave, Davis CA 95616, USA

ABSTRACT

Biochar is commonly purported to deliver agricultural benefits such as increased crop yield or crop quality. However, there is growing evidence to suggest that the effect of biochar may be greatest in marginal soils which require conditioning for the successful growth of crops. The objective of this study was to investigate the effect of biochar in fertile soils in a Mediterranean climate. In three-year processing tomato field trials, in which three biochars were amended to two soil textures, biochar was not observed to influence yield. To determine the impacts of biochar on parameters not typically captured in conventional agronomic measurements, a soil health assessment was conducted 2.5 years after biochar was amended to the soils. In both the fertile silt loam, and the more nutrient-limited sandy loam, biochars had a variable but positive effect on pH, EC, soil potassium concentration, water stable aggregation, and permanganate oxidizable carbon. There was no effect on soil moisture or potentially mineralizable nitrogen or carbon. Effects were largest in plots amended with almond shell biochars compared to those with softwood biochar. In the silt loam, the effects of biochar on the soil chemical and physical environment were not substantial enough to influence the microbial community, and there was no change in microbial biomass or phospholipid fatty acid (PLFA) community composition. In the sandy loam, there was a strong microbial response, with almond shell biochars associated with a slight increase in total biomass, an increase in the ratio of fungal to bacteria PLFAs, and reductions in multiple PLFA ratios typically interpreted as indicators of environmental stress. Results of this study demonstrate that biochar may deliver soil health benefits in agricultural soils in a Mediterranean climate, though increased soil health may not confer increased agricultural production within a three-year time period. Furthermore, soil

health benefits were not consistent across soil texture and biochar type. Evaluations of biochar for soil health objectives must therefore be constrained by the specific parameters of individual biochars and landscapes.

3.1. INTRODUCTION

There has been much investigation into whether biochar, or pyrolyzed biomass, can deliver tangible agricultural benefits when added to the soil. Many authors report improved yields,[74,76,77] increased soil fertility,[85,91] or increased soil water retention[96,97] as a result of using biochar in cropping systems, while others report minor, temporal, or no effects.[11,12,73,78,92,93] Differences in performance can be linked to differences in biochar production parameters and feedstocks,[16,121] and perhaps more importantly, to differences in the soil itself.[10,86,90,95] Biochar has been observed to deliver yield benefits most consistently in soils which require conditioning for the successful growth of crops,[80,122] such as soils that are saline or sodic,[101–103] contaminated,[104,105] highly acidic,[15] or low in fertility.[80] However, in fertile soils, temperate climates, and in cropping systems with regular inputs of irrigation and fertilizer, biochar often delivers fewer agronomic improvements.[73,75,78,80,89]

The purported benefits of adding biochar to soil are not limited to yield improvements, however, as biochar has also been observed to influence parameters that constitute the ever-evolving notion of soil health.[117,123,124] While there is much debate over the exact definition[125–127] and optimal suite of measurements[128–134] for soil health, there is a growing consensus it should be evaluated within specific contexts and for specific functions, in lieu of being appraised as a one-size-fits-all ideal.[135] There is also a general agreement it should be assessed through a combination of physical, chemical, and biological indicators.[136] Physical indicators of soil health frequently focus on the size and stability of soil aggregates, as increased aggregation may confer benefits such as resistance to erosion, improved water conductivity, and the ability to store and protect soil carbon (C).[137–139] Soil chemical parameters are most commonly measured in soil health assays, and include pH, electrical conductivity (EC), and a suite of fertility measurements.[127,136] Biological indicators of soil health include total microbial biomass, microbial community composition measured through phospholipid fatty acid (PLFA) analysis, and proxies for microbial activity, such as CO_2 respiration during soil incubation.[133,136] Underlying these physical, chemical, and microbial metrics are the quantifications of soil C in its various fractions, which dominate our current understanding of soil health. This includes measurements of dissolved organic C (DOC), potentially mineralizable C (PMC), permanganate oxidizable C (POXC), microbial C, and total C.[136]

An increase in soil C is often used to infer benefits such as increased fertility or soil water storage. This in turn is used to describe a soil that has been made "healthier." While increased soil C and improved soil health may deliver multifaceted ecological benefits, neither have been consistently linked with increased crop quality or productivity.[140–142] This highlights a challenge in soil health research, as "health" cannot be divorced from the function that soil is expected to perform, or the inherent qualities of the soil and landscape it is measured within. Increased fertility and soil water storage may confer "health" in the context of croplands, but not in the context of a forest soil, or for the function of aquifer recharge. Scale is also an important consideration. Increasing C in a soil with 0.3% organic matter may have a greater impact than the same increase in a soil with 3.0% organic matter. Both increases may be irrelevant depending on the desired ecological function of that soil. The pursuit of soil health indicators that can be used across systems and management practices is essential to develop a common scientific language.[126] However, interpretations of soil health indicators should always be location and function specific.[125] Furthermore, conclusions about the effect of management practices on soil health, such as the addition of biochar, should not be overstated,[143] and should be limited to the specific conditions in which results were observed.

Biochar has been observed to impact many of the indicators included in soil health assessments. To fully understand the ecological benefits and consequences of amending biochar to soil, it is critical these effects be reported in addition to traditional agronomic measures. The influence of biochar on soil C has been widely investigated. As biochar itself is primarily comprised of C,[4] it is unsurprising that many authors report increased total C following biochar addition.[75,77,118,144] Simply put, adding C to the soil increases C in the soil. Due to the difficulty in methods, few authors distinguish between added biochar C and secondary soil C formation or preservation that may occur due to the addition of biochar. While biochar is commonly cited as a source of recalcitrant C, biochar stability varies as a function of its chemistry, with lower oxygen (O) to C ratios (O/C) linked with greater stability.[145] One meta-analysis estimates that 3% of biochar C has a mean residence time (MRT) of only 108 days.[146] The rapid utilization of the labile fraction of biochar C has been measured through increased PMC across multiple conditions,[147–149] though CO_2 evolution typically slows as biochar weathers. Biochar has also been shown to increase soil C indirectly, through increased aggregation and therefore C protection,[117] or through negative priming of soil organic matter.[146] These results were not consistent across soil textures and biochar types, further emphasizing the need for location and material-specific research.

Biochar has been demonstrated to impact soil health with respect to physical, chemical and biological functions. Multiple authors have observed biochar to influence physical indicators of soil health, through increases in aggregate size or stability.[117,150,151] The effects of biochar on soil chemical indicators vary widely,[74,76,85,86,90,91,93,94] though there appears to be a more consistent liming effect of many biochars on soil pH. [7,15,88,100] Biochar's impact on the soil physical and chemical environment may lead to shifts in the microbial environment as well.[152,153] Biochar has been demonstrated to increase microbial biomass and activity,[118] and to shift community composition towards consortia more effective at utilizing recalcitrant C and less sensitive to environmental stressors such as nutrient or water shortage (increased ratios of gram-positive to gram-negative bacteria (G+/G-) and fungal to bacterial (F/B) PLFA[154])[155]. The effect of biochar on other microbial stress indicators such as ratios of saturated to monounsaturated PLFA (S/U) and cyclopropyl 17:0 or 19:0 PLFAs to their precursors (cy17/pre and cy19/pre, respectively)[156] are less widely studied, though some authors have observed little to no effect.[157,158] As with other effects, the microbial response to biochar appears dependent on a suite of biochar properties, such as pH, nutrient content, and labile C, as well as the physiochemical properties of the soil.[148,155,159] Furthermore, results may not persist over time,[160] may be overridden by management practices,[161] and do not necessarily confer higher soil functioning in the context of agriculture, such as the ability to support increased yields or water retention.[93]

In this study, the effect of biochar on soil health is evaluated within agricultural lands, for the ecosystem service of producing crops. Processing tomatoes were grown in two fertile soils of contrasting texture in a Mediterranean climate for three years. Prior to crop production, soils were amended with almond shell biochars produced at 500 and 800 °C, or a softwood biochar produced at 500 °C. The objectives of this experiment were: 1) To determine if biochar amendments influence crop yields in agricultural soils receiving adequate irrigation and fertilizer for crop needs. Our hypothesis was that biochar would not influence yield; 2) To determine if biochar influences the chemical, physical, and biological parameters that constitute soil health. Our hypothesis was that biochars would increase overall soil health, and that the impacts would be greater in the coarser, less fertile sandy loam compared to the silt loam; 3) To identify the biochar feedstock and production parameters associated with changes in chemical, physical, and biological soil health parameters. This study is novel in that it investigates the influence of multiple biochars in two agricultural soils across three-year field trials, and reports both agronomic and soil health effects. This data is essential for advancing our understanding of the benefits and consequences of adding biochar to working lands, and can be used to inform decisions about biochar made by growers, land managers, and policymakers.

3.2. METHODS

3.2.1 Biochar selection and characterization

Three biochars from two commercial companies were obtained from the following feedstocks and produced at the following temperatures: almond shell at 500 and 800 °C (AS500, AS800) softwood at 500 °C (SW500). Biochars were chosen from regionally relevant feedstocks and to provide a temperature and feedstock gradient. Unless otherwise stated, biochars were sieved to 2 mm and characterized using procedures recommended by the International Biochar Initiative (IBI, 2015): pH and EC were measured at a 1:20 biochar to 18.2 MΩ-cm water (Barnstead nanopore, Thermo Fisher) (w:v) dilution after solutions were shaken for 90 minutes; total C, nitrogen (N), hydrogen, and oxygen (O) were measured using a dry combustion-elemental analyzer (Costech ECS4010); and moisture, volatile, and ash content were measured as a percent of total dry weight through sequential increases in furnace temperature (105, 750, and 950 °C, respectively). Particle size distribution was measured by laser diffraction (Coulter LS230). CEC was measured using a combination of the modified ammonium acetate compulsory displacement method[51] and the rapid saturation method:[52,53] 0.25 g of biochar was leached with 18.2 MΩ-cm water under vacuum (-20 to -40 kPa). Leachate was stored and analyzed for DOC through combustion (Shimadzu TOC-V). Biochar samples were then washed with 1 M sodium acetate (pH 8.2) until the EC of the elute was the same as the eluant. Samples were rinsed three times with 10 ml of 2-proponal, then dried under vacuum for 10 minutes. To displace sodium (Na^+) ions, biochars were washed with 1 M ammonium acetate using the same volume as was required for sodium acetate. Leachate was collected and analyzed for Na^+ concentration through atomic absorption spectroscopy (Perkin Elmer AAnalyst 800). Specific surface area was determined by Micromeritics' Particle Testing Authority (https://www.particletesting.com/) from CO_2 adsorption isotherms according to the Brunauer, Emmet, Teller (BET) method.[54]

3.2.2 Field site and management

Identical field trials, approximately 0.5 hectares each, were established in two California locations: (a) Davis (Yolo County), in a Yolo Silt Loam (YSiL: Fine-silty, mixed, superactive, nonacid, thermic Mollic Xerofluvent), and (b) Parlier (Fresno County), in a Hanford sandy loam (HSL: Coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthent). Field sites were chosen within the heavily-farmed Central Valley in California to provide agricultural soils with textural distinctions. Collectively, these soils represent over 260,000 hectares of arable land in California.[58] Each site was designed as a randomized complete block, with three blocks and one replicate per block of the following treatments, in plots measuring 4.6 m wide (3 beds) and 6.1 m long: One of three biochars (AS500, AS800, SW500) or a soil-only control (NO). Treatments were subsurface banded by hand at a rate of 4.6 t ha^{-1} once in October 2017 into trenches 25-30 cm in depth. Trenches were created and left open following the application of subsurface drip tape. Biochar-filled trenches were immediately closed, burying the concentrated biochar at the center of the bed. This application technique places the biochar directly above the drip tape and within the rooting zone of the plant, in order to collocate it with irrigation and fertigation. It also allows the simulation of high application rates in the rooting zone (approximately 45.6 t ha^{-1}) while using less biochar in the field overall. A visual schematic of this application method is provided in Santos-Medellin et al. (2021). Precipitation and temperature data for each year biochar resided in the soil is reported in Table 3.1.

Table 3.1 Climate data (total precipitation and mean air temperature) for each year that biochar resided in the soil in Davis and Parlier field trials [162]

	Davis		Parlier	
	Total precip (cm)	Average air temp (°C)	Total precip (cm)	Average air temp (°C)
2018	35.2	16.1	19.2	17.5
2019	80.2	16.0	26.8	17.3
2020	15.6	16.7	14.9	17.4

Fields were managed under processing tomato (*Solanum lycopersicum*) production for three consecutive growing seasons between 2018 and 2020. Tomatoes were transplanted in late April or early May each year, except in 2018 in Parlier, where planting was delayed until early June due to challenges in field preparation. Tomatoes were transplanted in one row per 1.5 m wide bed. One subsurface drip line was buried at the center of each bed, and remained there for the duration of the three-year trials. Tomatoes were irrigated to 100% of evapotranspirative demand as determined by a Tule Evapotranspiration Tower (https://www.tuletechnologies.com/). Urea-ammonium-nitrate 32 (UAN-32) was fertigated through the drip tape in five different events throughout the growing season to a total of 252 kg N ha^{-1}. Potassium thiosulfate was applied at a rate of 39.2 kg K ha^{-1} 83 days after planting. Broadly, Dual Magnum, Treflan, and/or Round-Up were used to treat weeds. Advise 4, Coragen, Platinum, and/or Admire were used for pest control. The quantity and timing of pesticide application varied by season and location, following common regional practices.

3.2.3 Processing tomato yield

Processing tomatoes were harvested from three plants at the center of each plot at the end of August, except in 2018 in Parlier, where harvest was delayed until October. Marketable yield, or the total of red and ripening fruit, is reported by fresh weight in tonnes per hectare.

3.2.4 Soil sampling and analysis

Soil sampling was performed in April 2020, approximately 2.5 years after biochar was first amended and after two complete seasons of processing tomato trials. Samples were taken prior to transplanting tomatoes for the third growing season. Each sample was hand augured to 30 cm and composited from five subsamples per plot. Samples were taken carefully from the center of the bed so as not to puncture the subsurface tape directly below. Soils were kept on ice until they could be transferred to a 4 °C refrigerator, after which they were sieved to 4 mm and analyzed within one week.

Total C and N were measured using a dry combustion-elemental analyzer (Costech ECS4010). The pH and EC of soils were measured via 1:2 soil to 18.2 MΩ-cm water (w:v) dilution, after shaking for 15 minutes and equilibration for 60 minutes.[62] Dissolved organic carbon was extracted from soils with 0.5 M K_2SO_4 after shaking for 30 minutes and analyzed through combustion (Shimadzu TOC-V). Soil texture analysis was performed by the Analytical Lab at the University of California, Davis (Davis, CA, USA) via the hydrometer method.[63] PLFA analysis was performed on freeze dried soils by Microbial ID, Inc. (Newark, DE USA) using the Buyer/Sasser method (2012).[163] The remaining analyses were performed by the Soil Health Laboratory at Oregon State University (Corvallis, OR, USA). Water stable aggregates (WSA) are reported as the percentage of 0.25 - 2.00 mm aggregates that remained on a sieve after 5 minutes of simulated rainfall from the Cornell Sprinkle Infiltrometer.[164] Active C, hereafter referred to as POXC, is reported as the readily oxidizable C via potassium permanganate reduction.[164] Potentially mineralizable C (PMC) is reported as the CO_2 evolved after 24 and 96 hours from incubations with soil wetted to 50% water filled pore space and incubated at 23 °C.[164] Potentially mineralizable nitrogen (PMN) was measured as the increase in NO_3-N during 28-day soil incubations at 50% water-filled pore space at 23 ºC.[164] Nitrate nitrogen was measured using a 2 M KCl extraction. Soil elemental content was extracted with a Mehlich-3 solution and measured via inductively coupled plasma optical emission spectroscopy (ICP-OES; Agilent 5110).[164]

3.2.5 Statistical analysis

Davis and Parlier data were analyzed separately to detect the effect of biochar within each location. All data were analyzed as a randomized complete block design with one-way analysis of variance (ANOVA) in the lme4 and Tidyverse packages in R.[64,65,113] Blocks were considered random effects and biochar considered a fixed effect. Two separate models were built for each response variable. The first included each individual biochar as well as the unamended control. The second averaged all biochar treatments together, to test the overall effect of adding biochar compared to the unamended control. For analysis of results, all effects with p-values < 0.05 were considered significant, though results under the 0.1 threshold are discussed to demonstrate effects with marginal significance. P-values were generated using the emmeans package in R[66] and corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method. Boxplots were generated in R using the ggplot2 package[67] and visualized with the median as the middle bar, and the first and third quartiles as the boxes' lower and upper limits, respectively. Box whiskers represent the highest and lowest values within 1.5 times the inter-quartile range.

Phospholipid fatty acids were grouped using the markers outlined in Bossio and Scow (1998).[165] Data were normalized and canonical correspondence analysis (CCA) was used to determine the distribution of microbial community compositions along environmental gradients. A Monte Carlo permutation (n=999) was used to determine the significance of environmental factors to the distribution of samples using the vegan package in R.[166] Environmental factors were fit onto the CCA ordination to determine which factors were most closely associated with the separation between various treatments.[166]

3.3. RESULTS

3.3.1 Biochar and soil characterization

Soil texture analysis revealed the YSiL in Davis to have 24 (± 0.9)% sand and 32.7 (± 0.5)% clay, while the HSL in Parlier had 58.7 (± 1.4)% sand and 12 (± 0.9)% clay. Biochars exhibited a broad range of chemical and physical properties depending on their production temperature and feedstock (Table 3.2). Consistent with a recent meta-analysis on production temperature and biochar properties, the higher temperature AS800 was associated with increased ash content, pH, EC, and surface area, and decreased C, hydrogen, and DOC.[16] Contrary to trends observed in the same meta-analysis, AS800 had the highest O/C ratio at 0.56 and the highest CEC at 53.77 cmolc kg^{-1}.[16] The unusual O content of AS800 suggests it may have been oxidized through exposure to air immediately after pyrolysis while still hot. All biochars contained less than 1% N, spanning from SW500 at 0.13% to AS500 at 0.76%. Overall, AS800 was the most distinct biochar, with the lowest C content at 35.3%, the highest ash content at 55.4%, the highest EC at 27.2 mS cm^{-1}, the highest pH of 10.13, and the smallest mean and median particle sizes at 269.8 and 334.8 µm, respectively.

Table 3.2 Select chemical and physical biochar properties (n=3) ± standard error of the means

	AS500	AS800	SW500
Carbon (%)	65.8 ± 0.45	35.33 ± 0.25	70.89 ± 0.25
Nitrogen (%)	0.76 ± 0.01	0.55 ± 0.02	0.13 ± 0.03
Oxygen (%)	17.11 ± 0.75	26.44 ± 0.75	17.07 ± 0.58
Hydrogen (%)	3.05 ± 0.04	1.83 ± 0.02	3.76 ± 0.01
Molar O/C ratio	0.19 ± 0.01	0.56 ± 0.01	0.18 ± 0.01
Molar H/C ratio	0.55 ± 0.01	0.62 ± 0.01	0.63 ± 0
Volatile (%)	30.74 ± 2.67	28.17 ± 0.5	37.99 ± 0.86
Ash (%)	19.01 ± 0.99	55.35 ± 0.78	4.48 ± 0.06
pH	9.34 ± 0.02	10.13 ± 0.01	7.85 ± 0.02
EC (mS cm^{-1})	3.17 ± 0.01	27.2 ± 0.12	2.54 ± 0.02
DOC (mg kg^{-1})	38322.1 ± 1776.6	1055.9 ± 52.9	43776.2 ± 1103.8
CEC (cmolc kg^{-1})	24.02 ± 0.57	52.74 ± 0.81	16.46 ± 0.39
Mean particle size (µm)	464	269.8	493.6
Median particle size (µm)	590.6	334.8	763.5
Surface Area (m^2 g^{-1})	54.7	188.2	93.5

EC = electrical conductivity; DOC = dissolved organic carbon; CEC = cation exchange capacity

3.3.2 Processing tomato yield

Estimated means and p-values for all response variables are included in supplementary information (SI) (Table 3.S1). Biochar had negligible effect on the marketable yield of processing tomatoes in both Davis and Parlier (Table 3.3). Though it appears AS500 and AS800 may have reduced yield in Davis in years two and three (Figure 3.1), within treatment variability was large, and no statistically significant effects were detected. When analyzed between years, yields in 2020 were significantly lower than in 2018 or 2019 in both Parlier (p = 0.003, < 0.001, respectively) and in Davis (both p-values < 0.001).

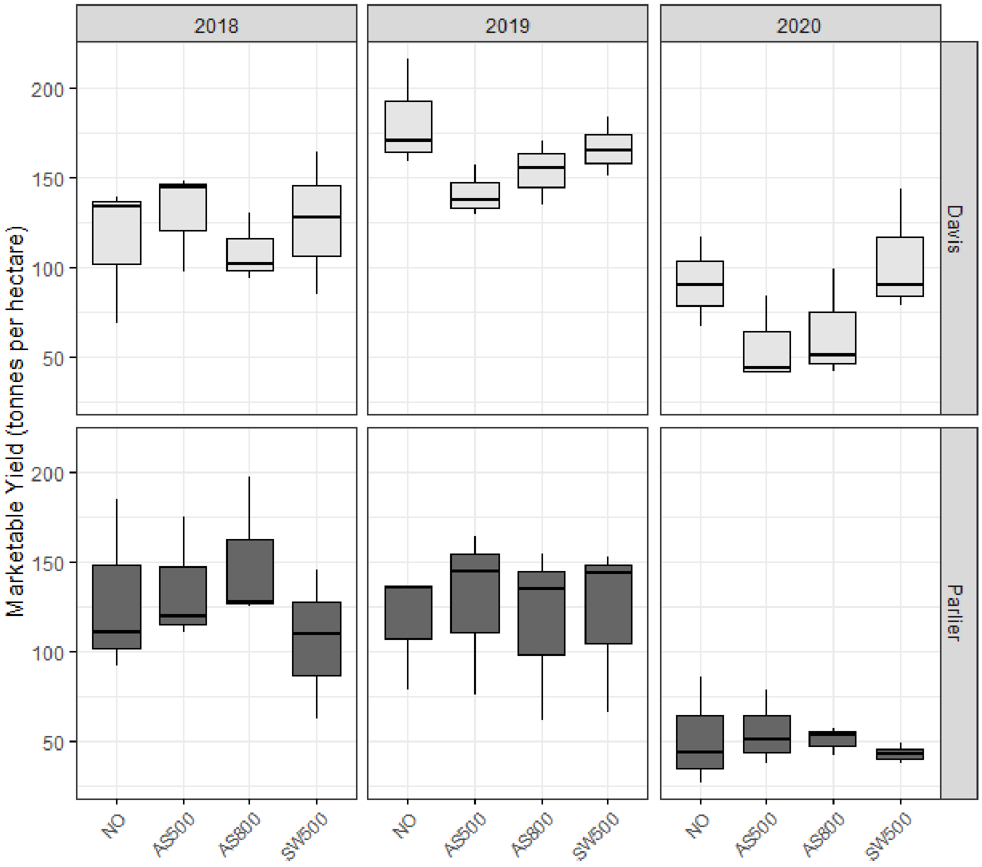

Figure 3.1 Marketable yield in a three-year processing tomato field trial by biochar, year, and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3).

Table 3.3 F statistics and p-values from ANOVAs of the effect of biochar on yield and soil health indicators 2.5 years after amendment, in Davis and Parlier field trials (n = 3). Bolded values indicate results with p-values <0.05.

	Davis		Parlier	
	F	p	F	p
Marketable Yield (t ha^{-1})	0.724	0.545	0.214	0.886
Total carbon (%)	3.282	0.079	1.263	0.368
PMC-24 h (µg g^{-1} day^{-1})	1.213	0.366	1.911	0.206
PMC-96 h (µg g^{-1} day^{-1})	0.497	0.698	1.344	0.327
POXC (mg kg^{-1})	**4.841**	**0.033**	**9.788**	**0.01**
DOC (mg kg^{-1})	0.169	0.915	2.098	0.202
Total nitrogen (%)	0.647	0.613	1	0.45
PMN (mg kg^{-1} day^{-1})	1.062	0.418	1.348	0.326
pH	**11.785**	**0.003**	1.503	0.286
EC (µS cm^{-1})	0.38	0.771	0.809	0.524
Ca (mg kg^{-1})	2.673	0.1184	0.828	0.967
Cu (mg kg^{-1})	1.501	0.307	0.102	0.956
Fe (mg kg^{-1})	1.957	0.222	3.571	0.086
K (mg kg^{-1})	0.832	0.513	3.689	0.062
Mg (mg kg^{-1})	**17.682**	**0.002**	0.342	0.797
Mn (mg kg^{-1})	2.367	0.17	0.57	0.655
P (mg kg^{-1})	0.625	0.624	1.54	0.298
Zn (mg kg^{-1})	0.338	0.799	0.497	0.698
Water stable aggregates (%)	0.452	0.723	**5.64**	**0.035**
Moisture (%)	**6.158**	**0.029**	1.401	0.312
PLFA Biomass (nmol g^{-1})	0.226	0.8774	2.999	0.095
Cy17/pre PLFA ratio	2.276	0.157	**8.157**	**0.0154**
Cy19/pre PLFA ratio	0.817	0.53	**8.412**	**0.007**
F/B PLFA Ratio	0.803	0.527	2.935	0.121
G+/G- PLFA Ratio	0.327	0.807	1.866	0.236
S/U PLFA ratio	0.979	0.463	**4.762**	**0.035**

PMC = potentially mineralizable carbon; POXC = permanganate oxidizable carbon; DOC = dissolved organic carbon; PMN = potentially mineralizable nitrogen; EC = electrical conductivity; PLFA = phospholipid fatty acid; PLFA ratios designated as follows: Cy17/pre = cyclopropyl 17:0 to precursors; Cy19/pre = cyclopropyl 19:0 to precursors; F/B = fungal to bacterial; G+/G- = gram-positive to gram-negative bacteria; S/U = saturated to monounsaturated

3.3.3 Soil carbon and nitrogen

YSiL in Davis had more than 3x the total C than HSL in Parlier (1.06% compared to 0.28% (p = 0.001)) (Figure 3.2). Biochar had a marginally significant effect on total C in Davis two and a half years after amendment to the soil (p = 0.079). When each biochar was compared to the control, only AS500 increased total C in Davis, from 1.06 to 1.20% ($p = 0.063$). Similar increases in total C were not observed in Parlier. There was no effect of biochar in either location on DOC or PMC at 24 or 96 h (Table 3.3). In Davis, adding biochar increased POXC from the control at 65.0 mg kg^{-1} as follows: AS500 to 89.4 mg kg^{-1} (not significant at $p = 0.533$), AS800 to 122.9 mg kg^{-1} ($p = 0.054$) and SW500 to 122.1 mg kg^{-1} ($p = 0.056$) (Figure 3.2). Averaged across all biochars, biochar significantly increased POXC by 46.5 mg kg^{-1}, or a total of 71.5% ($p = 0.022$). In Parlier, POXC was increased from the control at 76.6 mg kg^{-1} as follows: AS500 to 90.2 mg kg^{-1} ($p = 0.018$), AS800 to 86.9 mg kg^{-1} ($p = 0.059$), and SW500 to 93.3 mg kg^{-1} ($p = 0.007$). Averaged across all biochars, POXC was significantly increased in Parlier by 13.6 mg kg^{-1}, or 17.8% ($p = 0.002$). Davis had more than 3x the total soil N than Parlier, at 0.103% compared to 0.03%. There was no effect of biochar on total N or PMN in either location.

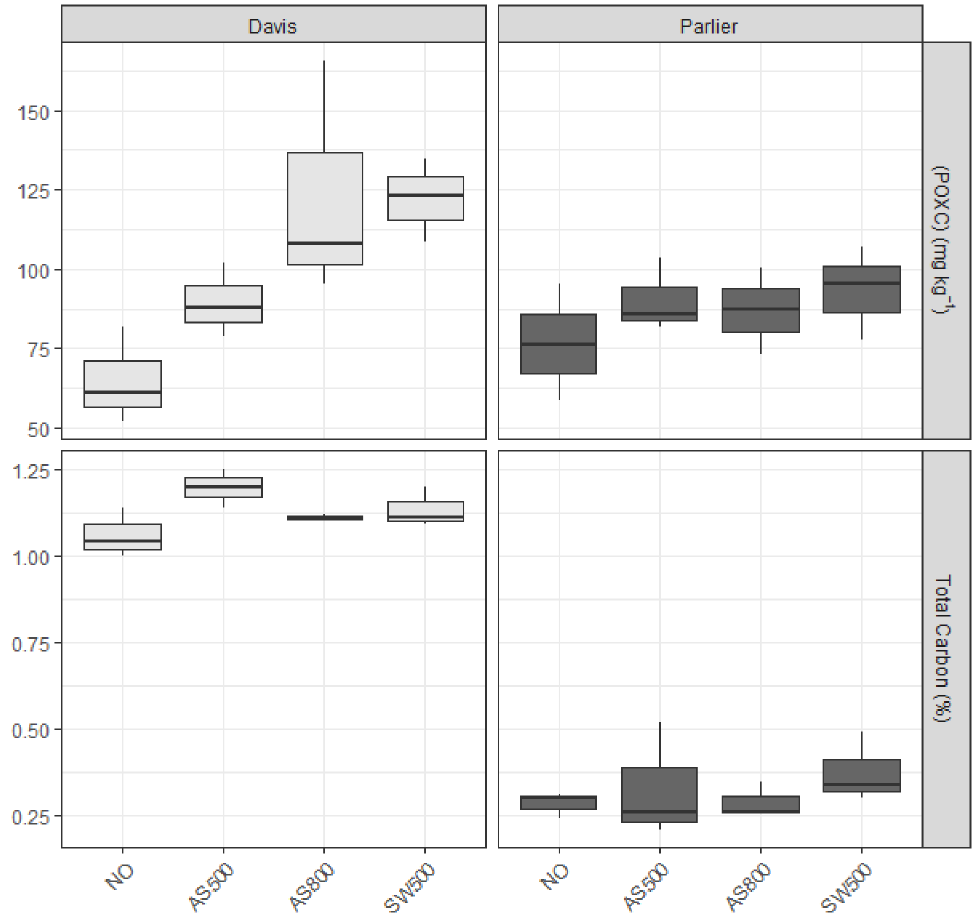

Figure 3.2 Permanganate oxidizable carbon (POXC) and total carbon in soils 2.5 years after biochar amendment, from a three-year processing tomato field trial, by biochar and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3).

3.3.4 Chemical indicators of soil health: pH, EC, fertility

Two and half years after its amendment to the soil, AS800 increased soil pH in Davis from 7.73 to 8.03 (p = 0.014) (Figure 3.3). While pH increases were observed across biochars and locations, no other statistically significant effects were detected. Likewise, AS500 and AS800 appeared to increase EC in Parlier, though the effects were not significant.

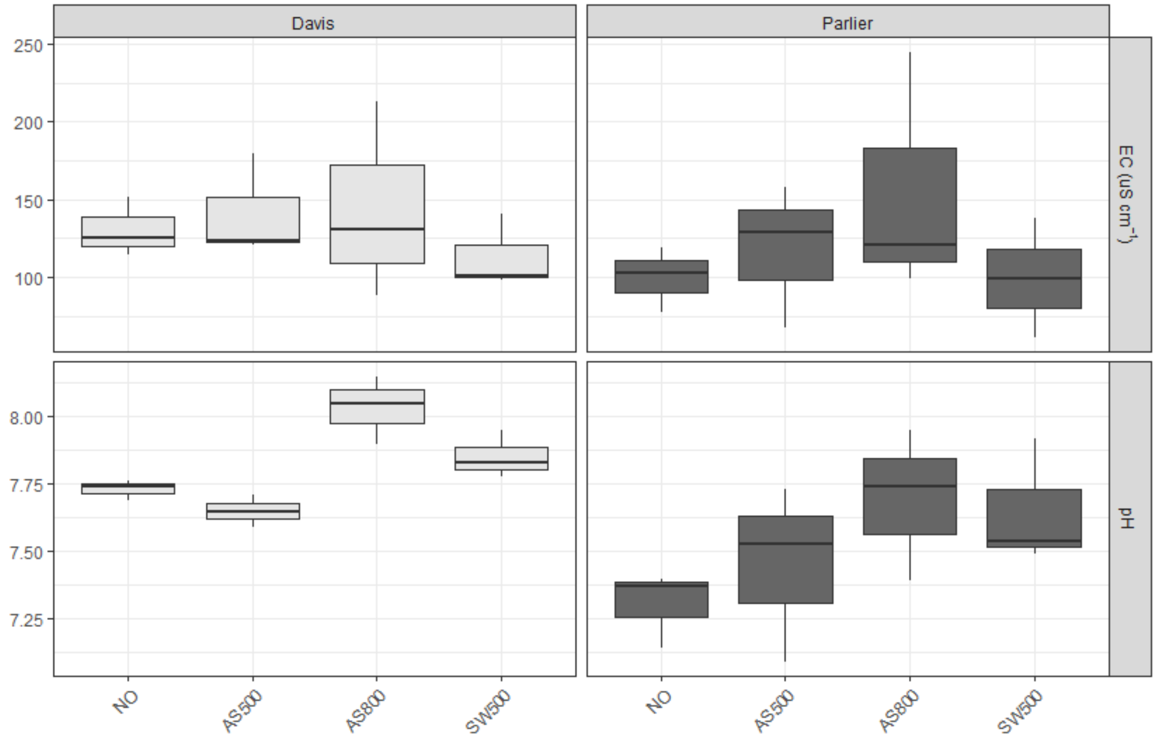

Figure 3.3 Soil electrical conductivity (EC) and pH 2.5 years after biochar amendment from a three-year processing tomato field trial, by biochar and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3).

YSiL in Davis contained at least double the calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), and phosphorous (P) than HSL in Parlier, or every nutrient measured except for zinc (Zn) (Table 3.S1). The effects of biochar were minor and inconsistent. When averaged across biochars in Davis, soil Ca was reduced from 1608.0 mg kg^{-1} by 6.5% ($p = 0.02$) and Mg from 1480.9 mg kg^{-1} by 8.3% ($p < 0.007$). Similar decreases were not observed for other nutrients or in Parlier. In Parlier, almond shell biochars appeared to increase soil K, though results were not statistically significant (Figure 3.4). This effect was greatest for AS800, which increased K from 25.3 to 89.9 mg kg^{-1} ($p = 0.075$).

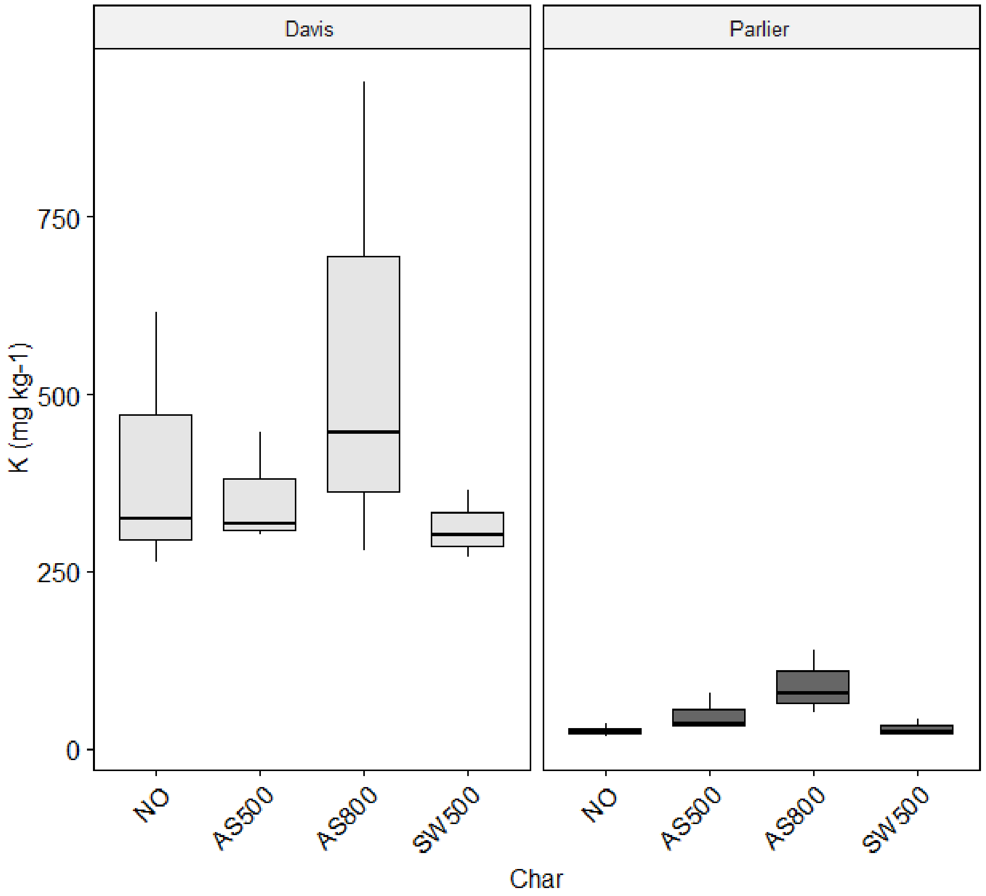

Figure 3.4 Soil potassium (K) 2.5 years after biochar amendment from a three-year processing tomato field trial, by biochar and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3).

3.3.5 Physical indicators of soil health: Water stable aggregates and soil moisture content

There was a main effect of biochar on WSA in Parlier ($p = 0.035$) though, due to variation within each treatment, the effects of individual biochars were not significant. AS500 appeared to increase WSA in Parlier from 28.1 to 42.0% ($p = 0.1$) and AS800 to 40.4% ($p = 0.151$). While increases in WSA were observed across biochars and locations, no statistically significant effects were detected (Figure 3.5). The effect of biochar on moisture content at the time of sampling was inconsistent. In Davis, there was a main effect of biochar on soil moisture ($p = 0.029$), primarily due to AS800, which increased soil moisture from 15.6% to 18.6% ($p = 0.051$). Averaged across treatments in Parlier, biochar appeared to decrease soil moisture, from 16.2% to 11.4% ($p = 0.069$).

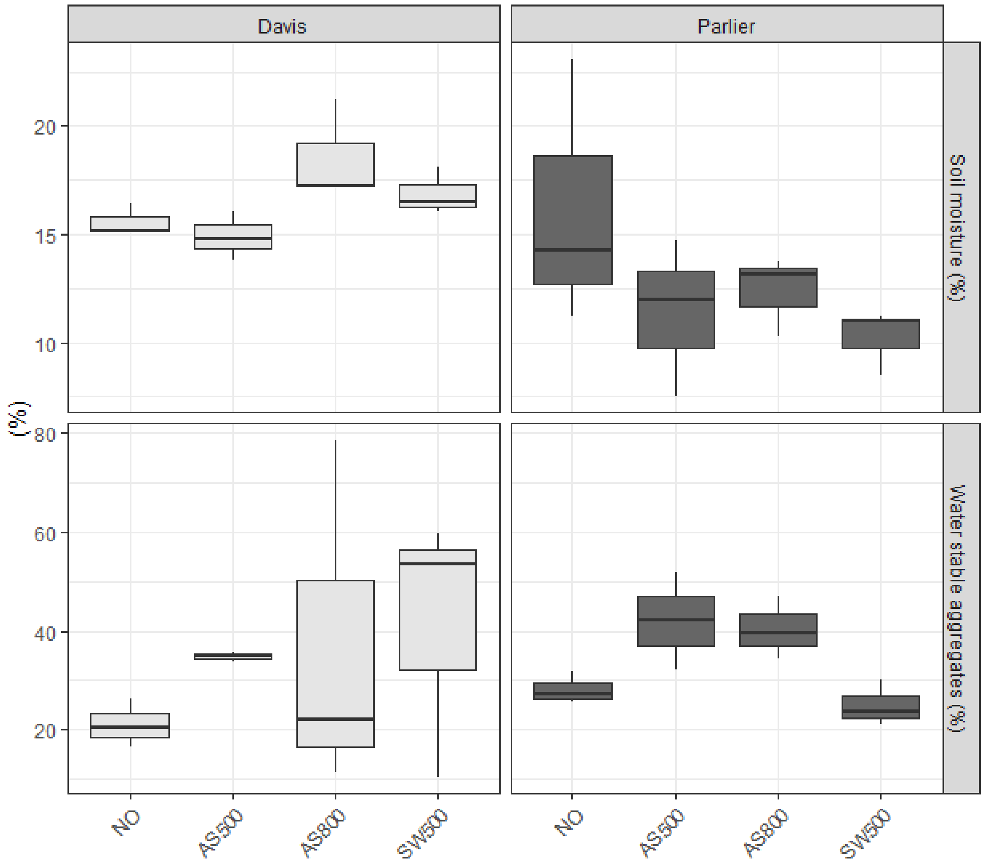

Figure 3.5 3Moisture and water stable aggregates from soils 2.5 years after biochar amendment, from a three-year processing tomato field trial, by biochar and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3).

3.3.6 Microbial indicators of soil health: Biomass and community composition

YSiL in Davis contained nearly double the PLFA biomass than Parlier, or 67.5 compared to 34.6 nmol g^{-1} (Figure 3.6). Biochar had no effect on PLFA biomass in Davis, and a marginally significant effect in Parlier ($p = 0.095$) (Table 3.S1). Due to variation within treatments, no individual biochar raised PLFA biomass compared to the control. Averaged across biochars, however, there was a marginally significant increase in PLFA biomass of 6.23 nmol g^{-1} in Parlier ($p = 0.078$).

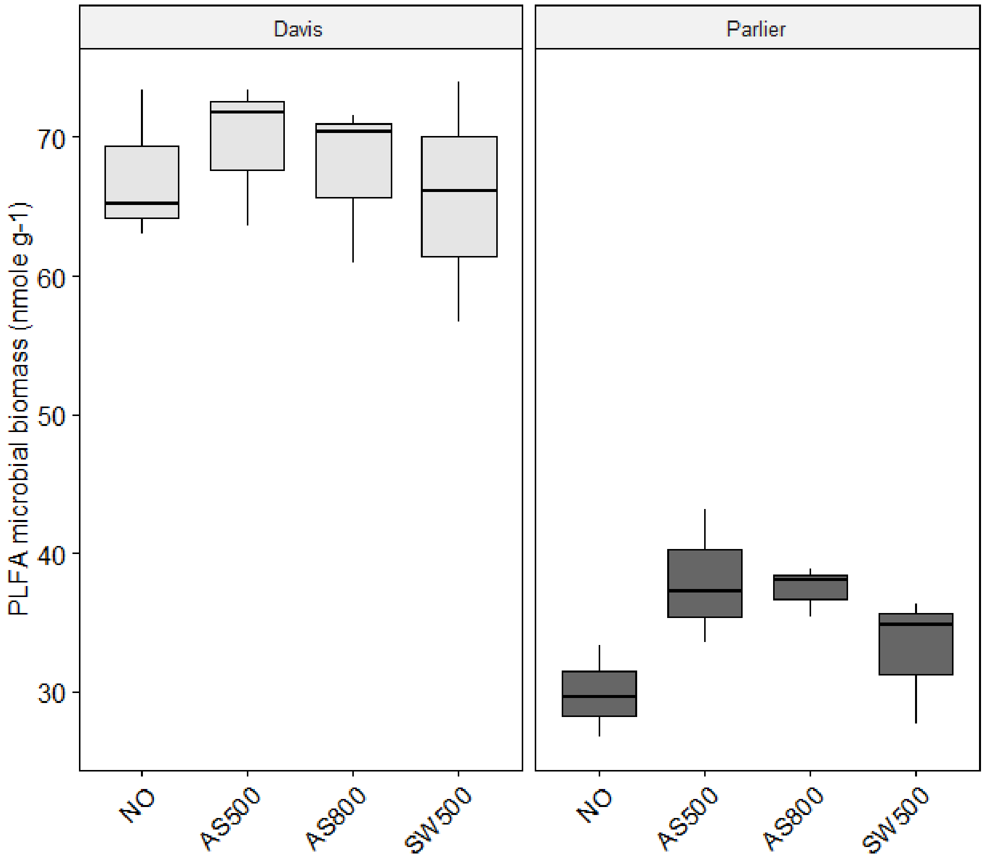

Figure 3.6 Phospholipid fatty acid (PLFA) biomass from soils 2.5 years after biochar amendment, in a three-year processing tomato field trial, by biochar and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3).

Canonical correspondence analysis (CCA) provided more detail for how the overall community composition differed between Davis and Parlier, and how each community responded to the addition of biochar. When both locations were analyzed together, the first two CCA axes explained 37.6% and 18.3% of the variation in composition (Figure 3.S1). Based on the Monte Carlo permutation test, location was a significant factor in community composition (p = 0.001) and biochar was not (p = 0.216). Community composition was clustered separately between the two field sites and arrayed along vectors of nearly every environmental variable measured. When each location was analyzed separately, no effect of biochar on community composition was detected in Davis (p = 0.124) and communities were not clustered separately from one another (CCA not shown). In Parlier, biochar had a marginally significant effect on community composition (p = 0.052). The first two CCA axes explained 43.2% and 11.2 % of the variation in composition (Figure 3.7). The community composition in AS500 and AS800 clustered separately from the control, arrayed along vectors of WSA, followed by pH, K, and POXC.

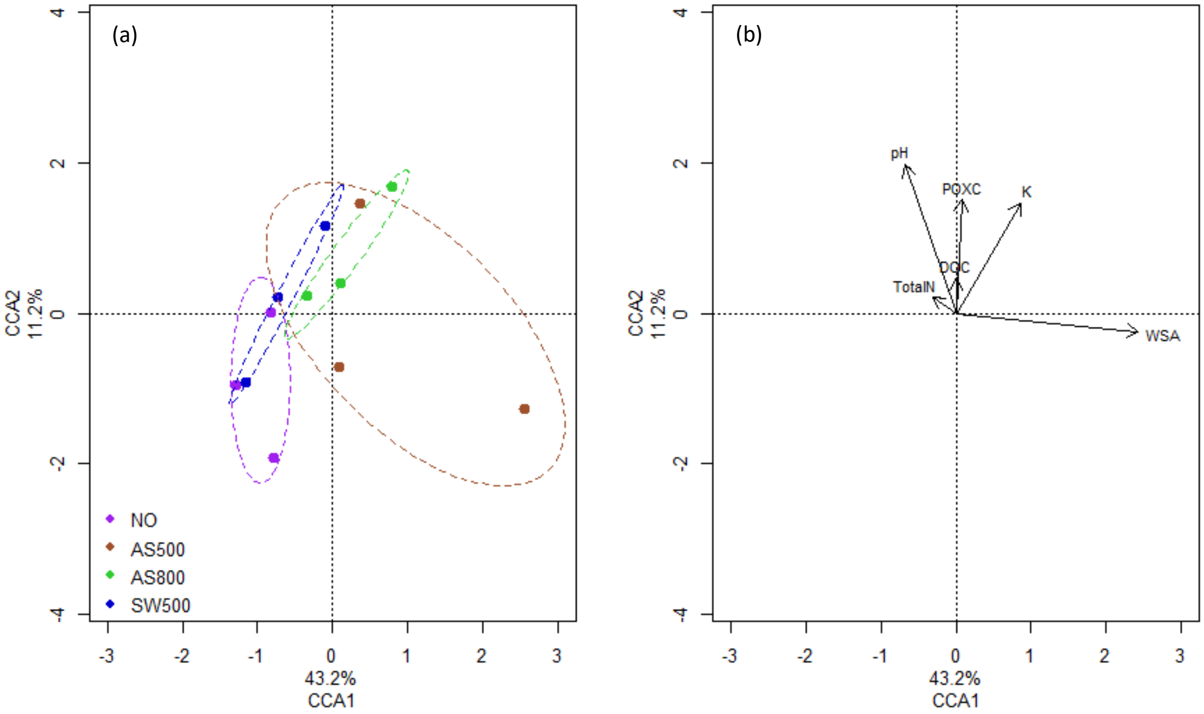

Figure 3.7 The impact of (a) biochar and (b) environmental variables on soil microbial community composition 2.5 years after biochar was amended to the soil in three-year processing tomato field trials in Parlier. In the legend, color represents biochar treatments. Arrows represent the vectors for key environmental variables.

Biochar had no effect on select PLFA ratios in Davis (Figure 3.8). In Parlier, AS500 and AS800 reduced cy17/pre, cy19/pre and S/U. AS500 and AS800 appeared to reduce G+/G- and increase F/B, though the effects were not significant (p = 0.236 and 0.121, respectively). The effect of SW500 on PLFA ratios was minor and not statistically significant for any ratio in either location.

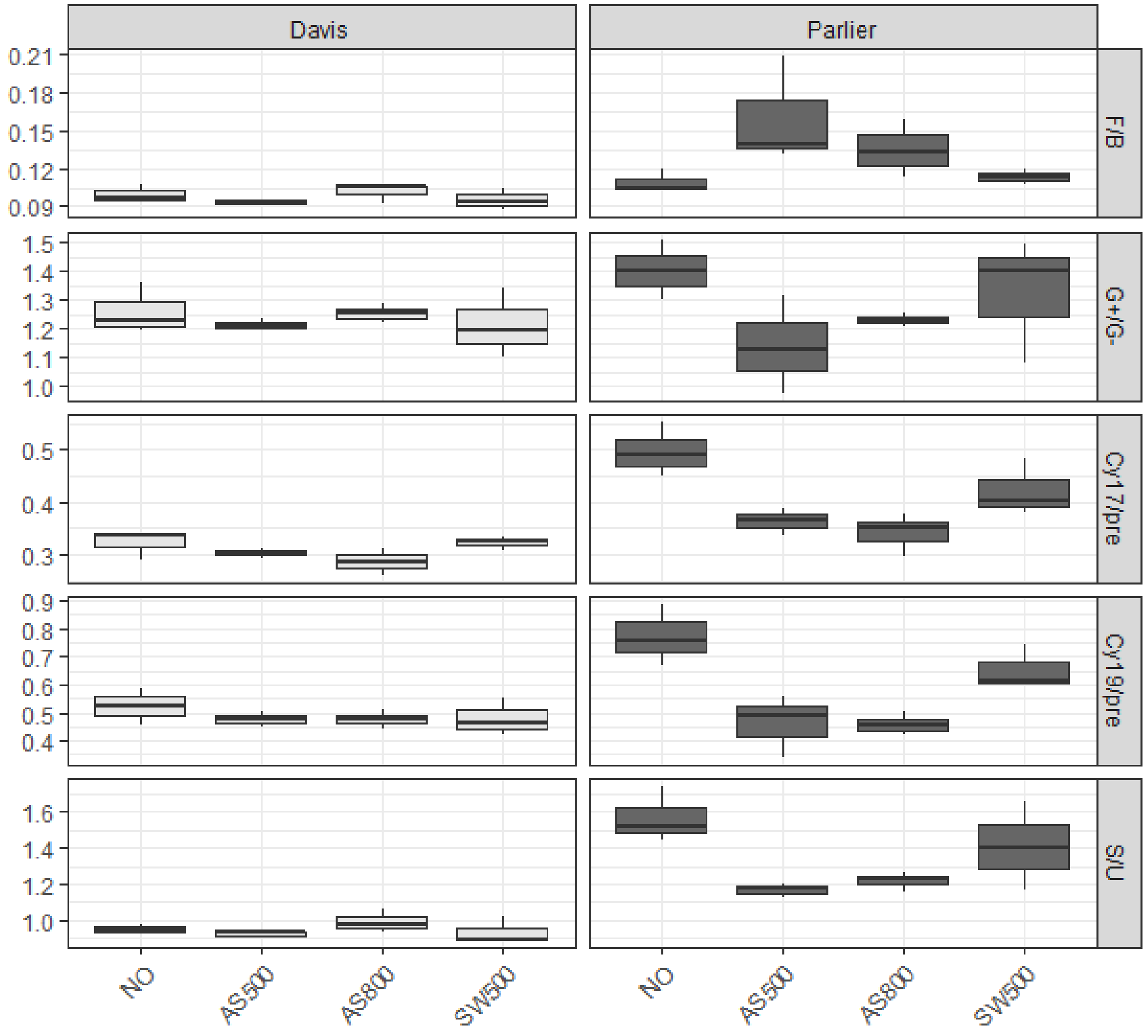

Figure 3.8 Ratios of select phospholipid fatty acids (PLFAs) from soils 2.5 years after biochar amendment, from a three-year processing tomato field trial, by biochar and location. Box plots show medians with the middle bars and the first and third quartiles with the boxes' lower and upper limits, respectively. The ends of each whisker represent the highest and lowest values within 1.5 times the inter-quartile range (n = 3). F/B = fungal to bacterial; Cy17/pre = cyclopropyl 17:0 to precursors; Cy19/pre = cyclopropyl 19:0 to precursors; G+/G- = gram-positive to gram-negative bacteria; S/U = saturated to monounsaturated

3.4 DISCUSSION

3.4.1 Yield and indicators of soil health differ substantially between locations

The effect of biochar was analyzed within each location separately, though in combined models location was significant at a level of $p < 0.001$ for nearly every response variable tested. While the YSiL of Davis and the HSL of Parlier are each classified as entisols in a thermic soil temperature regime and xeric soil moisture regime,[109,110] the soils are substantially different within those categories. YSiL is comprised of mixed sedimentary, volcanic, and metamorphic parent materials deposited by alluvial transport.[109] These features have contributed to the development of a fine textured and fertile soil. By contrast, HSL is composed of glacial outwash from a predominantly granitic parent material,[110] which has weathered into a much coarser and less fertile soil. In addition, the climate of Davis is more favorable for crop production. In each of the three-year field trials, Davis had cooler temperatures and received substantially more precipitation.[162] Given these differences, it is unsurprising that soils in Davis (with or without biochar amendment) appeared to have greater soil health by nearly every indicator measured: more than three times as much total C and N, and more than double the quantity of Ca, Cu, Fe, K, Mg, Mn, P, PMC at 24 and 96 h, and microbial biomass.

Processing tomato yield from years 2 and 3 were also substantially higher in Davis than in Parlier, though it is not possible to link these yields to soil health status alone. The soil forming factors of climate and parent material in Davis have endowed it with an intrinsically “healthier” profile, and may support higher yields regardless of health promoting or degrading management practices. The inherent differences in YSiL and HSL highlight the challenges in measuring and comparing soil health across climates and soil textures, and emphasize the need for regionally specific investigations. Against the intrinsic differences in each soil in this study, and in the context of an irrigated and fertilized cropping system, biochar delivered negligible benefits for processing tomato yield, and perhaps, in the case of almond shell biochars (AS500 and AS800) even a slight negative effect in years 2 and 3 in Davis.

3.4.2 Biochar induces minor and inconsistent shifts in the soil chemical and physical environment

All biochars in this study had a liming effect in each location, though results varied in statistical significance. In both the HSL and YSiL, AS800, which was the highest pH biochar, raised soil pH most substantially, even 2.5 years after amendment to the soil. This is consistent with other observations of increased pH in field trials 2-3 years after biochar incorporation.[75,85] The effect on fertility was mixed between locations, though the behavior of biochar appeared to be more consistently linked to its feedstock than its production temperature. Biochars derived from nut shells have been observed to increase soil K.[11,167] In particular, almond shell ash has been reported to contain 18-36% K, and described as an untapped resource for K recovery for fertilizer.[168] In Parlier, both AS500 and AS800 appeared to increase K and EC. This effect was not observed in Davis, where, surprisingly, AS500 and AS800 had no effect on K, but slightly decreased Mg and Ca. This is in opposition to a field study in a nearly identical soil and climate, in which walnut shell biochar led to an increase in K and Ca two years after amendment to the soil.[11] While it is possible this reduction in soil nutrient concentration explains the slight reduction in yield observed in Davis in years 2 and 3, levels of Mg and Ca in the soil remained substantial even after losses, and were not likely to have affected crop production.

All biochars appeared to increase the concentration of water stable aggregates in both soils (except SW500 in HSL), though variation within each treatment was high and statistically significant results were not detected. Two proposed mechanisms for increased aggregate stability are an increase in multivalent cations which bridge organic colloids and clays, or the increased presence of bacterial mucilages and fungal hyphae.[169] It is difficult to conclude that either of these occurred in this study. In Parlier, there was an increase in F/B and a slight increase in EC (though no increase in divalent cations was detected), which may have supported increased aggregate stability. In Davis, no effect on microbial communities or cation release can explain increased WSA. A third hypothesis is that the biochar-associated increase in POXC in each location lead to increased aggregate stability. POXC has indeed been correlated with increased soil structural stability.[170] As POXC is converted to CO_2 during the oxidation process, however, it is difficult to investigate the underlying mechanisms.

3.4.3 Biochar increases POXC but not other soil C fractions

POXC is purported to represent the organic matter fraction readily available for consumption by microbes, and has been determined to be more sensitive to management practices relative to other soil C fractions.[171] Indeed, POXC was the only C fraction measured with a substantial response to biochar addition. Averaged across treatments, biochar nearly doubled POXC in Davis, and increased it 17.8% in Parlier. Despite the positive correlation between POXC and PMC observed elsewhere,[172] no effects on PMC were detected in this study. That increases in PMC and DOC were not detected 2.5 years after biochar amendment to the soil suggests that much of the labile biochar C had already weathered by the time of sampling.[146–149] Additionally, it has been observed that the correlation between POXC and PMC is weakest in soils with low soil organic matter,[172] as was reported in a study from similar climates and soil textures as those in this experiment. POXC has been determined to be comprised of a relatively processed pool of soil C, and positively correlated with microbial biomass.[171] It is possible that increased POXC in Parlier was the result of the increased microbial biomass and F/B, though this cannot explain POXC in Davis.

3.4.3 Microbial response to biochar is greater in Parlier than in Davis

There was no effect of biochar in Davis on any microbial metric measured, including PLFA biomass, community composition, or the ratio of select PLFAs typically used to indicate shifts in soil health or microbial stress. In Parlier, the microbial effects of biochar were consistent by biochar feedstock rather than production temperature, with SW500 having little effect compared to AS500 and AS800. Consistent with a recent meta-analysis, AS500 and AS800 biochar increased F/B,[155] a ratio known to be sensitive to pH change and C chemistry.[152] Contrary to results from this same meta-analysis, G+/G- in this study trended lower as the result of biochar addition. Biochar frequently increases G+/G-, as G+ bacteria is more effective at utilizing recalcitrant C.[155] While biochars represent an input of recalcitrant, POXC in this study also increased. It is possible that HSL in Parlier was so C limited prior to biochar amendment, that the formation of POXC served to increase the biomass of G- bacteria despite the presence of recalcitrant biochar C. Cy17/pre, cy19/pre, and S/U each decreased as the result of AS500 and AS800 addition as well. Reductions in these ratios are typically interpreted as a reduction in microbial nutrient and water stress,[156] indicating that AS500 and AS800 may have improved the soil environment for microbial communities. This effect was not observed in Davis, where each of these ratios were substantially lower than those in Parlier to begin with. This signals that the microbial community in Davis was already benefitting from a “healthier” environment and was not impacted by the small shifts induced by the addition of these biochars.

4.4 Soils with lower intrinsic health may have more to gain from addition of biochar

Results from our study highlight the challenge of scale in soil health research. By many indicators, Davis was a healthier soil than Parlier and stood less to gain from the addition of biochar, for the ecological function of processing tomato production. The effects of biochar on the soil chemical or physical environment in Davis did not appear to register with the microbial community, as measured by PLFA, microbial biomass, or PMC. The microbial communities in the coarser and more nutrient limited soils of Parlier had a substantial response to biochar addition. However, in neither scenario did the chemical, physical, or microbial effects result in increased yields.

3.5 CONCLUSIONS

The overarching objective of this study was to measure the effect of biochar on agronomic and soil health indicators in three-year field trials, in two contrasting soil textures in a Mediterranean climate. Our hypothesis that biochar would not influence processing tomato yield was confirmed. Biochar had negligible impact on yield, despite the observed increases in permanganate oxidizable C, water stable aggregation, soil potassium concentration, and pH. This is in agreement with results reported elsewhere, which indicate biochar may deliver limited benefits for crop production in fertile agricultural soils. However, the impact on soil chemical and physical parameters may be interpreted as an increase in overall soil health. Our hypothesis that biochar would have a greater effect on soil health indicators in the coarser, more nutrient limited soils of Parlier, was also confirmed. In Parlier, the effects of biochar led to increased microbial biomass, decreased evidence of microbial nutrient and water stress, and shifts in community composition towards a higher ratio of fungi to bacteria. Among the materials tested, almond shell biochars produced at 500 and 800 °C had the most substantial effects. These biochars increased K and pH in Parlier, perhaps relieving nutrient stress and increasing microbial biomass and soil fungi, which in turn may have contributed to the increased water stable aggregation and POXC. By contrast, biochar associated shifts in the soil chemical and physical environment in the fine textured and more fertile soils of Davis were not substantial enough to influence the microbial community or the crop.

Our study suggests that biochars produced from almond shell, or those with high ash, pH, and K, may have a role to play in improving the chemical, physical, and biological parameters of soil health, particularly in sandy soils with limited C and nutrient concentrations. However, results underscore that increased soil health does not necessarily confer increased soil function within a three-year timeframe, for the purpose of producing crops. While increased soil health has not reliably been linked to increased agricultural productivity, it is believed to confer other ecological benefits. More research is needed to understand how biochar may affect these landscapes for objectives such as increased C sequestration or greenhouse gas release, over time and under a changing climate.

3.6 ACKNOWLEDGEMENTS

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An emerging environmental concern: Biochar-induced dust emissions and their potentially toxic properties*

Danielle Leigh Gelardi,[1] Chongyang Li,[1] Sanjai J. Parikh,[1]
[1]University of California Davis, Land, Air and Water Resources, One Shields Ave. Davis, CA, 95616

ABSTRACT

Amending soils with biochar is increasingly proposed as a solution to many pressing agricultural and environmental challenges. Biochar, created by thermochemical conversion of biomass in an oxygen-limited environment, has several purported benefits, including remediation of contaminated soils, increased crop yields, reduced fertilizer demands, increased plant available water, and mitigation of climate change. Due to these potential benefits, biochar-related research has flourished in the past decade, though there remains a critically understudied area of research regarding biochar's potential impact on human health. Because biochar characteristically has low bulk density and high porosity, the material is susceptible to atmospheric release via natural or mechanical soil disturbance. The specific risks of biochar inhalation have not been elucidated; however, recent publications have demonstrated that biochar can increase soil dust emissions of particles < 10 μm (PM_{10}) or possess elevated levels of toxic chemicals. These data should not be interpreted to suggest that all biochars are problematic, but rather to highlight an important and overlooked field of study, and to stress the need to critically assess parameters for biochar production and management strategies that safeguard human health. Here the literature on biochar-related dust emissions and potentially toxic properties (PTPs) is reviewed in order to summarize what is known, highlight areas for future study, and aggregate solutions to minimize potential harm.

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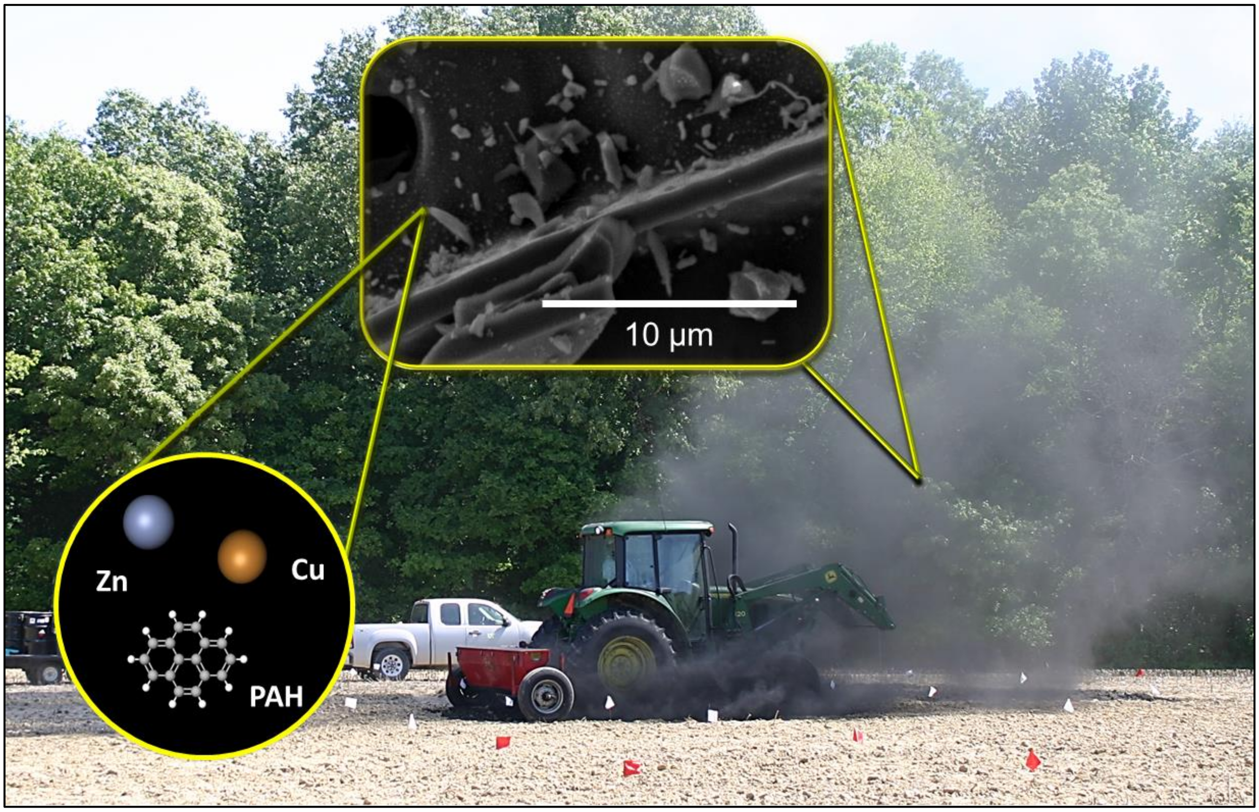
GRAPHICAL ABSTRACT



KEYWORDS

Biochar, Soil, Dust, Toxicity, Human Health

HIGHLIGHTS

- Biochar can increase soil dust emissions or possess elevated levels of pollutants.
- Despite exponential growth of biochar studies, health risks are rarely explored.
- Studies regarding dust, biochar contaminants, and toxicity were reviewed.
- Strategies to minimize harm during production and application were synthesized.

4.1 INTRODUCTION

The use of biochar, a carbonaceous material created from the thermochemical conversion of biomass in an oxygen-limited environment,[3] as an agricultural soil amendment is an ever-growing topic of interest, eliciting the attention of scientists, policymakers, and growers alike. The number of published biochar studies continues to increase at a near exponential rate, from one publication per annum in the early 2000s, to over 2,100 in 2018 (Figure 4.1a) (Web of Science). Policymakers have also taken notice, resulting in biochar included as a negative emission technology in the 2018 Intergovernmental Panel on Climate Change (IPCC) Special Report.[115] As scientific and policy interest in biochar grows, so too does the size of the biochar market. Since 2009, over 650 patent applications mentioning "biochar" have been filed with the United States Patent and Trademark Office, over half of which were filed between 2016 and 2018 (Figure 4.1b) (US Patent and Trademark Office).

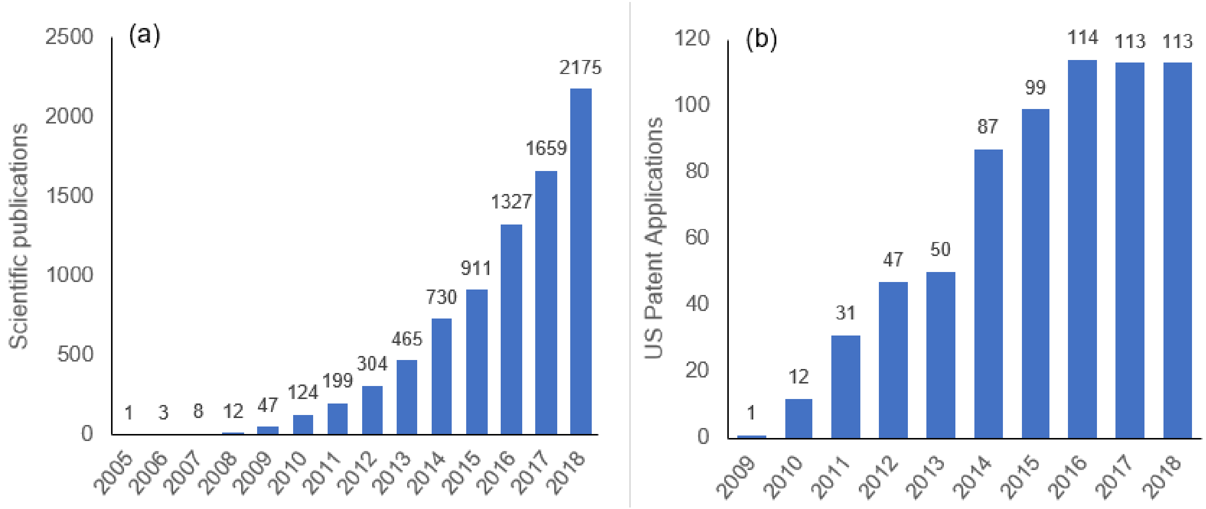


Figure 4.1 The increased interest in biochar demonstrated through (a) the number of scientific publications per year with "biochar" listed in available fields and (b) the number of published US patent applications

While interest in biochar is evident, many questions remain about the efficacy of biochar use as a soil amendment. Biochar has a number of purported agronomic benefits, including increased water holding capacity,[174,175] increased soil carbon stocks,[81] reduced nutrient leaching,[176–178] enhanced microbial activity,[179] decreased greenhouse gas emissions,[180] and the remediation of soil contaminants.[181] Despite the proliferation of biochar studies, research continues to show inconsistent results on the ability of biochar to deliver these benefits, due to differences in biochar feedstock, production methods, soil properties, climate, and cropping systems.[14,80] Meta-analyses and literature reviews have demonstrated that biochar is most likely to deliver agricultural benefits if its production and use is well parameterized for specific outcomes in specific conditions.[15,80,182] This is true not only for agronomic benefits but for climate change mitigation benefits as well. Life cycle assessments (LCAs) have repeatedly shown biochar production and use to reduce current greenhouse gas (GHG) emissions if systems are optimized to minimize biochar transportation, energy inputs, and the use of non-waste biomass products.[70–72,183,184] Two of these LCAs also conclude that biochar-related air pollution may contribute to a larger negative effect over its whole life cycle due to potential adverse human health impacts.[70,71] Authors caution that these issues must be addressed before biochar production and use becomes common practice.

While investigation into the agronomic potential of biochar use is well underway, the potential air quality and human health consequences remain critically understudied.[185] Biochar is typically characterized by a low bulk density, high surface area, and variable particle size distribution.[4] While these qualities can provide benefits such as water and nutrient retention, they also render biochar susceptible to its release into the atmosphere as the result of natural or mechanical disturbance. In agricultural settings, this airborne release can occur during biochar application to the soil, or after it has been incorporated as the result of natural wind-driven erosion or through mechanical tillage events. It is well documented that agricultural dust is a major contributor to airborne particulate matter less than 10 µm in diameter (PM_{10}), particularly in intensively farmed regions.[186–188] Two recent studies have concluded that soils amended with biochar have the potential to generate significantly more PM_{10} than those without.[189,190]

PM_{10} exposure is a public safety concern as it can bypass the body's particulate interception mechanisms and penetrate deep into the airways. PM_{10} inhalation has been associated with increased chronic respiratory symptoms and the worsening of lung and heart disease.[191] Exposure to both the organic and inorganic components from agricultural PM_{10} have been linked with these adverse health effects in farmworkers.[192–194] While there are chemical, physical, and end-use distinctions between biochar and other carbonaceous materials such as coal, there are many chemical and physical similarities.[69] These similarities, and what is well known about the linkages between coal inhalation and chronic heart, kidney, and respiratory disease,[195–199] call for further investigation into airborne emissions from biochar-amended soils.

With the growing interest in biochar as a soil amendment comes an imperative to better understand potential consequences for air quality, and how these might affect agricultural workers and neighboring farm communities. While the physical size of biochar-related PM_{10} is itself a serious concern, the organic and inorganic chemical constituents of biochar may also present a human health risk. The primary aim of this review is to highlight the emerging environmental concern of biochar-induced dust emissions by evaluating the limited literature currently available. In addition, solutions to minimize potential harm during biochar production and application are synthesized, and areas for future investigation are suggested.

4.2 LITERATURE REVIEW APPROACH

Web of Science was searched using “biochar AND dust OR toxicity OR health.” Studies regarding materials similar to biochar, such as hydrochar, soot, and carbon nanotubes, were excluded, as were studies concerning aquatic environments and waste water treatment systems. There are few studies regarding biochar-induced dust emissions due to the emerging nature of this field, though all available publications concerning this topic were included. Publications regarding biochar polycyclic aromatic hydrocarbons (PAHs), the ability of biochar to bind to soil contaminants, and the ecotoxicological effect of biochar, however, are increasingly available. While authors were careful to include a representative sample of these works, with an emphasis on review papers, recent publications, and studies which investigated multiple biochar production parameters and multiple contaminants, the list of studies included here is not exhaustive. The purpose of this review is not to provide a quantitative assessment, but rather to highlight an emerging environmental concern. As such, a selection of publications was included which contribute to the overall objectives of summarizing the current state of knowledge and highlighting areas for future study.

4.3 BIOCHAR AND DUST EMISSIONS

In a series of wind tunnel experiments designed to simulate natural erosion processes, Ravi et al. (2016) demonstrated a significant increase in PM_{10} emission in a sand, sandy loam, and silt loam amended with a pine biochar produced by slow pyrolysis at 300 °C, compared to the unamended controls.[190] PM_{10} emissions were generally higher in all soils at all biochar application rates at all wind velocities. Authors hypothesize this to be the result of fine biochar particles becoming airborne, and the eventual abrasion of larger biochar particles into those with diameters less than 10 µm. The latter mechanism is explained through a phenomenon known as saltation bombardment, in which soil particles too large for airborne emission move across the soil surface and erode less stable particles (Figure 4.2). This hypothesis suggests that fine biochars, or coarse biochars in sandy soils, may contribute to the highest rates of biochar-induced PM_{10} emissions. This may have far reaching implications for the use of biochar as a soil amendment, as many studies show highest levels of nutrient and water retention in coarse textured soils.[15]

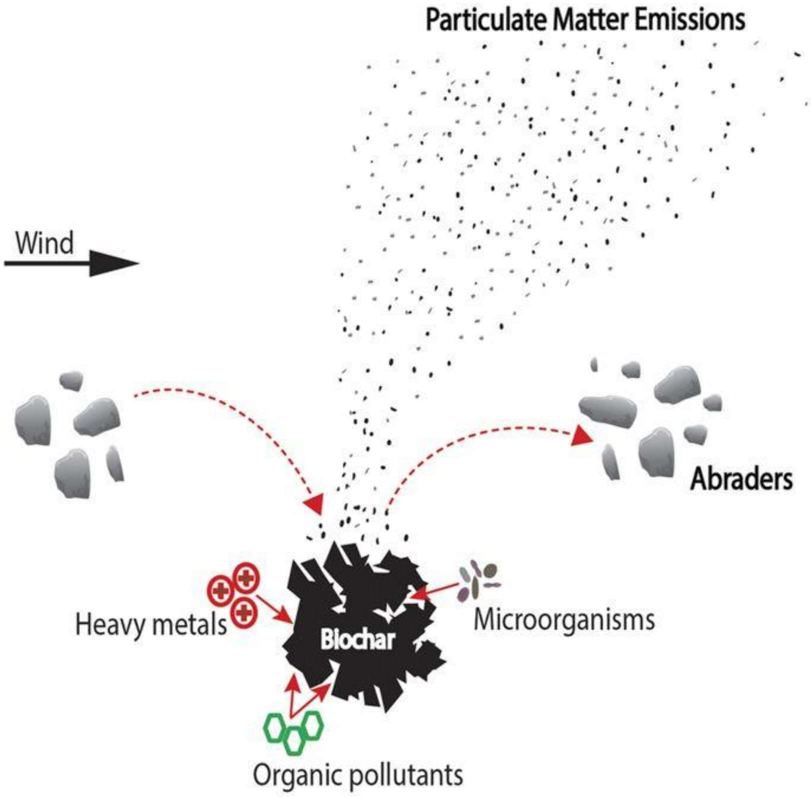


Figure 4.2 A conceptual model of particulate matter emissions from biochar-amended soils. Reproduced from Ravi, S., Sharratt, B.S., Li, J., Olshevski, S., Meng, Z., Zhang, J., 2016. Particulate matter emissions from biochar-amended soils as a potential tradeoff to the negative emission potential. Sci. Rep. 6, 1–7. https://doi.org/10.1038/srep35984

The mechanisms proposed by Ravi et al. (2016) assume the increased PM_{10} to be comprised of biochar itself, though authors do not analyze PM_{10} for its individual soil or biochar constituents. Li et al. (2018) similarly demonstrated an increase in PM_{10} from biochar-amended soils, though the increase was not universal for all biochars tested.[189] In this study, mechanical tillage in a silt loam and sandy loam was simulated and PM_{10} emissions, as well as the quantity of biochar in the $PM_{10,}$ was measured. In soils amended with a walnut shell biochar produced through gasification at 900 °C (WS900), dust emission increased with increasing biochar amendment rate, and was higher in the silt loam than in the sandy loam. Interestingly, however, concentrations of biochar in the PM_{10} did not increase with increased application of WS900. This indicates that the presence of WS900 induced soil particles themselves to be released into the atmosphere. A chemical analysis of all biochars used in the study showed that WS900 had the highest concentration of K^+ and Na^+, monovalent cations known to have a dispersive effect on soil particles. It is hypothesized that this dispersive effect lead to aggregate instability and colloid mobilization, thus making the amended soil more susceptible to dust emission. This biochar-induced colloid dispersibility is consistent with the findings of other researchers.[200]

Together these studies indicate that biochar soil amendments have the potential to increase PM_{10} emissions during natural and mechanical soil disturbance. As previously described, toxicity of PM_{10} is not only attributed to its chemical composition but also its size, and the inhalation of PM_{10} materials is associated with respiratory and heart ailments.[191] Despite the potential magnitude of this emerging environmental hazard, and the rise in biochar-related publications (Figure 4.1), few studies (n = 5) have been conducted on biochar-induced dust emissions and the associated risks (Table 4.1). More research is needed to better understand the mechanisms by which an increase in dust emission occurs, and which combinations of soil and biochar physical and chemical properties are most likely to lead to hazardous outcomes. It is important to highlight that the work of Ravi et al. (2016) and Li et al. (2018) investigates only the short-term residence of biochar in soil, and that both studies were conducted in laboratory settings. Additional research, particularly that conducted at field scale, is required to evaluate how dust emissions may change as biochar forms physio-chemical complexes within the soil. Nevertheless, these studies, as well as those concerning concentrations of PTPs in biochar particulate matter (Table 4.1), serve as a cautionary note to land managers and policymakers, particularly within intensively farmed regions.

Table 4.1. Summary of publications regarding biochar-induced dust emissions

Primary finding	Suggested mechanism	Source
Increase in PM_{10} in biochar-amended soils	PM_{10} comprised of biochar: fine biochar particles become airborne; larger particles are abraded into finer particles	Ravi et al., 2016
Increase in PM_{10} in biochar-amended soils	PM_{10} comprised of soil: elevated levels of monovalent ions from biochar cause dispersal of soil particles	Li et al., 2018
Biochar produced from moist rice husk generated: 1.2-1.6x more PM; 2.1-2.8x more PM-bound PAHs, than biochar from dried rice husk	PM and PAHs generally formed through incomplete combustion of volatiles; incomplete combustion worsened in the presence of moisture	Dunnigan et al., 2018
PAHs in PM 5.4x higher under low (200 mL/min) inert gas flow rate compared to high (800 mL/min)	Longer residence time of volatiles: enhanced secondary reactions to form PAHs; enhanced collisions among PAHs and PM	Ko et al., 2018
Less than 0.75% of biochar PAHs released into simulated lung fluids	PAHs physically entrapped within biochar microporosity, resulting in strong desorption hysteresis	Liu et al., 2019

Abbreviations: PM_{10}, particulate matter less than 10 µm in diameter; PM, particulate matter; PAHs, polycyclic aromatic hydrocarbons

4.4 BIOCHAR AS A POTENTIAL SOURCE OF TOXIC COMPOUNDS

Research has shown that carbon black, a material similar to biochar, exhibits increasing toxicity to the cells of humans and mice with decreasing size.[204,205] Table 4.2 provides a selection of studies which also demonstrate cytotoxicity or phytotoxicity as the result of direct contact with biochar, under some or all experimental conditions. As in the carbon black studies, Sigmund et al. (2017b) hypothesize the cytotoxic effect to be the result of the fine particulate nature of biochar. While this suggests that the size of biochar-related PM_{10} is itself a serious threat to human health, the chemical constituents in PM_{10} can offer their own unique hazards.

PAHs, for example, are known to form during the pyrolysis of biomass, with biochar PAH concentration heavily dependent on production methods, feedstock, and temperature.[206–208] While some biochars contain PAH concentrations well below environmental quality standards,[206,209,210] others have values well beyond.[206,211–214] High PAH concentration in biochars has been linked with mortality of crustaceans (*D. magna*),[212] inhibition of urease enzyme activity,[215] *Salmonella*/microsomal mutagenicity,[216] and inhibition of *V. fischeri* luminescence.[217]

Biochars analyzed by Hale et al. (2012) indicate that slow pyrolysis at high temperature (550-900 ˚C) is likely to minimize PAH content, while those produced through fast pyrolysis and gasification may have the highest levels. This is consistent with the findings of other researchers, who have described a process called pyrosynthesis, in which gaseous hydrocarbon radicals are generated under high temperatures (> 500 ˚C) via cracking of organic material.[218] These radicals then undergo a series of biomolecular reactions to form polyaromatic rings. High temperatures can also facilitate the fusing of lighter molecular weight PAHs into heavier, more toxic PAHs, which can more easily condense back into the biochar. PAH formation under high temperatures can be minimized through the use of slow pyrolysis, as lighter PAHs have time to volatilize from the system,[219] and by increasing the flow of carrier gases during biochar production.[202,208,220] The gasification process, which involves an additional oxidative step, has also been shown to lead to high PAH yields, as oxygen is vital to form certain PAH precursors.[221]

Though PAHs can pose a serious threat to human health, a recent study has shown little to no release of PAHs from biochar in simulated lung fluids, indicating that biochar PAHs may not be readily bioavailable through inhalation pathways.[203] Additionally, the concentration and toxicity of PAHs has been shown to decrease as biochar ages.[222,223]

Other native toxicants formed during biochar production may include heavy metals, volatile organic compounds (VOCs), dioxins, furans, and PCBs. Heavy metals occur naturally in biomass feedstocks and are concentrated in biochar through the production process.[210] As with PAHs, many studies demonstrate biochars to have metal concentrations well below most environmental quality standards.[209,210,212,224] Biochar copper and zinc levels, however, have been observed to have phytotoxic effects in cucumber, cress, and sorghum.[225] Similarly, high levels of VOCs have been detected in biochar and observed to cause phytotoxicity in cress.[226] In contrast, observed levels of total dioxins, PCBs and furans in biochar are often very low (up to several pg g^{-1}), with bioavailable fractions below analytical detection limit.[206,227]

Table 4.2 Selection of publications on biochar-related toxicological impacts and suggested mechanisms

Toxicological impact	Suggested mechanism	Source
Phytotoxicity	Exposure to: **1.** PAHs; **2.** Volatile organic compounds; **3.** PAHs and/or HM; **4.** Volatile fatty acids and/or nitrogen-containing organic compounds; **5.** High pH, EC, and/or ammonia gas production; **6.** High pH, EC, and/or HM	**1.** Oleszczuk et al., 2014; **2.** Buss and Mašek, 2014; **3.** Li et al., 2015; **4.** Rombolà et al., 2015; **5.** Amaro et al., 2016; **6.** Visioli et al., 2016
Cytotoxicity	Exposure to: **1.** PAHs; **2.** PAHs; **3.** Unknown; **4.** $PM_{2.5}$ bound to cell surface; **5.** Low molecular weight aromatic compounds; **6.** Exposure to compounds in biochar mobile matter	**1.** Oleszczuk et al., 2013; **2.** Gondek et al., 2017; **3.** Mierzwa-Hersztek et al., 2017; **4.** Sigmund et al., 2017b; **5.** Wang et al., 2017; **6.** Yang et al., 2019
Additional adverse effects: **1.** Mutagenesis; **2.** Earthworm avoidance; **3.** Urease inhibition	Exposure to: **1.** PAHs; **2.** High pH, EC, and/or ammonia gas production; **3.** PAHs, HM, and/or oxidative reactions with biochar free radicals	**1.** Anjum et al., 2014; **2.** Amaro et al., 2016; **3.** Liu et al., 2018

Abbreviations: PAHs, polycyclic aromatic hydrocarbons; HM, heavy metals; EC, electrical conductivity; $PM_{2.5}$, particulate matter less than 2.5 µm in diameter

4.5 BIOCHAR-BOUND POLLUTANTS

A growing number of researchers are examining not only pollutants formed as the result of biochar production, but those bound to biochar as well. Biochar is a sink for a broad range of soil pollutants. Negatively charged sites on biochars can facilitate electrostatic affinity for positively charged heavy metals, for example, making it effective at binding lead, chromium, cadmium, nickel, copper, and zinc in soil.[181,236–241] The high aromaticity, large surface area, and microporosity of biochar have also been shown to make it an effective agent at immobilizing organic pollutants, including compounds in pesticides[237,241,242] and pharmaceuticals,[241,243] as well as other harmful pollutants such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs),[244] polychlorinated biphenyls (PCBs),[245,246] and PAHs.[247,248] A more comprehensive list of studies regarding heavy metal and organic contaminant sorption to biochar prior to 2013 was detailed in a review paper by X. Zhang et al. (2013).

While the immobilization of pollutants may reduce their bioavailability, leaching, and volatilization from the soil,[181] it is troubling from the perspective of dust emissions, as biochar-bound pollutants may also be released into the atmosphere and made available for human inhalation. Together, these pollutants represent neurotoxins, carcinogens, mutagens, and reproductive toxins, many of which become acutely hazardous through inhalation. At present, there is a dearth of research examining the potential for biochar-bound substances to become airborne. There is an urgent need for investigation into this topic, particularly in locations where biochar is used expressly for soil remediation purposes.

4.6 PROPOSED REGULATIONS

The United States has not yet adopted regulatory standards for biochar contaminant levels, though maximum threshold values for a limited number of toxicants have been established in frameworks proposed by the European Biochar Certificate[249] and the International Biochar Initiative Guidelines[3] (Table 4.3). Differences in these standards have led to inconsistencies in both scientific and legislative literature. There is a pressing need for a unified regulatory framework, which would facilitate communication in academic fields and in the emerging biochar market.

Table 4.3 Maximum threshold values of heavy metals/metalloids and organic compounds for biochars.

Elements or compounds	European Biochar Certificate		International Biochar Initiative
	Basic Grade	Premium Grade	
As (mg kg^{-1})	n.a.	n.a.	13-100[†]
Cd (mg kg^{-1})	1.5	1	1.4-39[†]
Cr (mg kg^{-1})	90	80	93-1200[†]
Co (mg kg^{-1})	n.a.	n.a.	34-100[†]
Cu (mg kg^{-1})	100	100	143-1500[†]
Hg (mg kg^{-1})	1	1	0.8-17[†]
Mo (mg kg^{-1})	n.a.	n.a.	5-75[†]
Ni (mg kg^{-1})	50	30	47-600[†]
Pb (mg kg^{-1})	150	120	121-300[†]
Se (mg kg^{-1})	n.a.	n.a.	2-36[†]
Zn (mg kg^{-1})	400	400	416-2800[†]
PAHs (mg kg^{-1})	12	4	6-20[†]
PCBs (mg kg^{-1})	0.2 (I-TEQ)	n.a.	0.2-0.5[†]
Dioxins (ng kg^{-1})	20 (I-TEQ)	n.a.	9
Furans (ng kg^{-1})	20 (I-TEQ)	n.a.	9

Abbreviations: PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; n.a., not available.

[†] The maximum allowed threshold values have a range because they are from a number of jurisdictions including EU, Australia, Canada, USA and Quebec.

An additional challenge presented by EBC and IBI criteria is that threshold values represent ‘total’ concentrations, measured through robust acid digestion for heavy metals, or by exhaustive solvent extraction for organics. These methods tend to overestimate the fraction of ‘bioavailable’ toxicants and therefore the ecotoxicological effects. More research is needed on how toxicants may be released from biochar over time and made available to the human respiratory system. This field of study would assist in refining the conceptual definition of the ‘bioavailable’ toxicants in biochar and contribute to safer, more consistent regulatory standards. Finally, attempts should be made to investigate additional unknown, but potentially hazardous toxicants, carcinogens, or endocrine-disruptors in the biochar matrix using non-target analysis techniques, in order to expand regulations to include additional biochar-related risks.

4.7 STRATEGIES TO MITIGATE POTENTIAL HARM

To our knowledge, no research has been conducted to compare strategies to minimize biochar-induced dust emissions and the associated risks, though common-sense suggestions and best practices can be found throughout biochar literature. Major (2010) summarizes various biochar application methods and recommends combining biochar amendment with other on-farm processes to reduce costs and to minimize the potential for dust emissions.[250] Suggestions include adding biochar to compost, liquid fertilizer, or lime. To reduce dust emissions, recommendations for applying biochar with high moisture content or in liquid slurries are common, as are warnings to avoid application on windy days.[233,249,251] While most biochar field trials utilize a broadcasting application technique (Figure 4.3a), Major (2010) suggests that subsurface banding (Figure 4.3b) may have the greatest potential to reduce wind and rain-driven biochar losses. To date, very few studies have utilized this technique.[252] Regardless of application method, the use of appropriate respirators, eye protection, gloves, long sleeves and pants is recommended for farm operators and workers while handling biochar.[253]

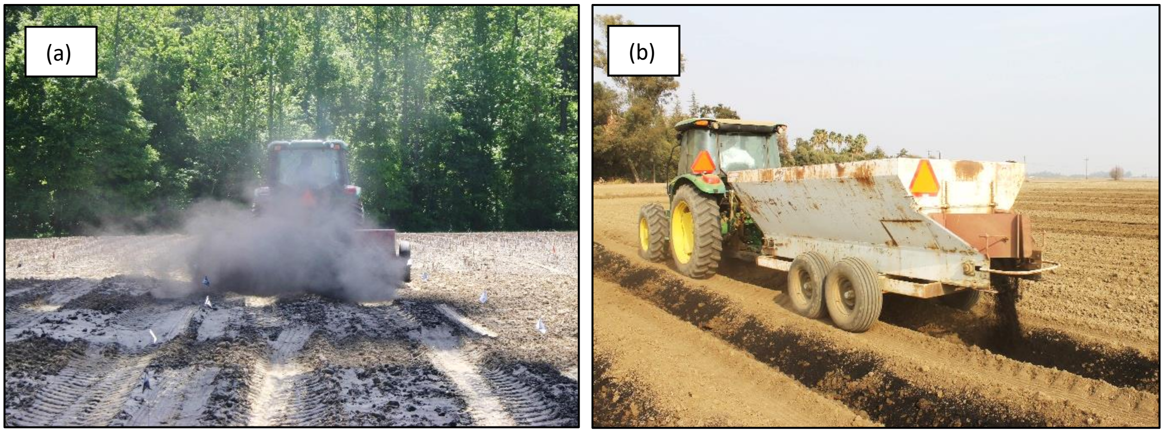


Figure 4.3 Biochar applied to a field using (a) a broadcasting technique of a dry biochar and (b) subsurface banding of a biochar at 40% moisture content. Photo credit for 4.3a to Brian Kozlowski at the University of Tennessee.

The above strategies address the one-time health hazard presented by the application of biochar, but do not address the risk of continued dust emission after biochar has been incorporated. The work of Ravi et al. (2016) and Li et al. (2018) demonstrate this to be a potentially serious concern, though it is unclear if increased residence time of biochar in soil would increase or decrease health risks. While biochar may become unavailable for airborne emission through mineral and organic complexation and aggregation, it may also have increased time to form complexes with soil pollutants, rendering toxicants susceptible to atmospheric emission as well. Subsurface banding may have a role in reducing biochar-induced PM_{10} emissions, as it buries biochar deep below the soil surface and places it at the rooting zone of the plant rather than throughout the bulk soil. Additionally, research indicates that increasing soil water content can exponentially reduce dust emissions.[187,189] Therefore, it can be concluded that mechanical tillage activities should not be undertaken when biochar-amended soil is dry. Tilling wet soil can lead to compaction and clodding, however, and so special attention should be paid to regionally-specific ideal moisture conditions.

Li et al. (2018) demonstrate that a high concentration of monovalent ions has the potential to disperse soil particles and increase dust emissions, while the findings of Ravi et al. (2016) indicate that particle size distribution combined with soil texture are determining factors for dust emissions. These properties should be considered before choosing a biochar and incorporating it into the soil, as should the levels of potentially toxic elements.

During the biochar production process, steps can be taken to create a safer, more effective soil amendment. As heavy metals and metalloids are concentrated in biochar through pyrolysis,[210] the use of treated feedstocks such as Chromated Copper Arsenate (CCA)-pressure treated wood should be avoided, along with materials from construction and demolition, and feedstocks of unknown origin. Research suggests that slow pyrolysis may minimize biochar PAH content compared to gasification, and that increased residence time[206] and carrier gas flow[202,208,220] can offset PAH formation under high temperatures. There may also exist simple pre- and post- production modifications that reduce levels of PTPs. Studies indicate that drying feedstock biomass prior to pyrolysis may reduce production-related PM_{10} emissions, as well PM-bound PAHs, as the presence of moisture encourages the incomplete combustion of volatile compounds formed during pyrolysis.[201] Research has also demonstrated that biochars can be dried at temperatures between 100 and 300 °C, effectively removing PAHs through thermal desorption within 24 hours.[254] Efforts have also been made to improve the physical properties of biochar during its production. An increasingly popular technique is to pelletize biochars to increase resistance to abrasion.[255] Addition of binders during pelletization, such as lignin and $Ca(OH)_2$, can further enhance the mechanical strength of biochars.[256] With increased mechanical strength and abrasion resistance, biochar may emit less dust compared to those that have not been compressed.

4.8 CONCLUDING REMARKS

Perhaps the most salient conclusion that can be drawn from the limited literature on biochar-induced dust emissions and their PTPs is the importance of knowing the physical and chemical properties of biochar prior to amendment in the soil. Regulators and biochar producers have a great responsibility to work with land managers and growers to ensure the safe and effective use of this increasingly popular soil amendment. Despite the proliferation of biochar studies, a disproportionately small fraction investigate biochar-induced dust emissions, PTPs, and ecotoxicity. As interest in biochar use rapidly grows, it is imperative to address the gaps in knowledge concerning the potential impact on human health. Areas for future investigation include the mechanisms by which biochar may increase PM_{10} emissions, and the soil and biochar properties most likely to lead to hazardous outcomes. Future research is also required on the chemical composition of biochar-induced PM_{10}, in order to determine the concentrations of biochar and biochar-bound pollutants potentially available for human inhalation. As research into these areas expands, it is also necessary to investigate strategies to reduce potential harm during biochar production and incorporation of biochar into the soil, and to create clear, unified environmental quality standards across regions and disciplines.

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APPENDIX 1: SUPPLEMENTARY INFORMATION FOR CHAPTER 2

Table 2.S1: Total precipitation and average air temperature data for Davis and Parlier during each of the three growing seasons (CIMIS, 2021)

		Davis		Parlier	
		Total precip (cm)	Average air temp (°C)	Total precip (cm)	Average air temp (°C)
2018	April	1.32	15	1.54	17
	May	0.58	18.4	0	20.5
	June	0.03	22.1	0	24.7
	July	0.08	24	0	29
	August	0.11	21.7	0.01	26
	Growing season total/avg	**2.12**	**20.24**	**1.55**	**23.44**
	Annual total/avg	**35.2**	**16.1**	**19.2**	**17.5**
2019	April	0.49	16.8	0.04	18.3
	May	7.34	16.7	5.42	18.2
	June	0.06	23.1	0	25.6
	July	0.02	22.8	0	27.2
	August	0.03	23.7	0	27.2
	Growing season total/avg	**7.94**	**20.62**	**5.46**	**23.30**
	Annual total/avg	**80.2**	**16.0**	**26.8**	**17.3**
2020	April	3.02	16	2.98	16.9
	May	0.76	19.7	0.83	21.5
	June	0.21	22.6	0	24.9
	July	0	22.7	0	27.1
	August	0	24.5	0	27.6
	Growing season total/avg	**3.99**	**21.10**	**3.81**	**23.60**
	Annual total/avg	**15.6**	**16.7**	**14.9**	**17.4**

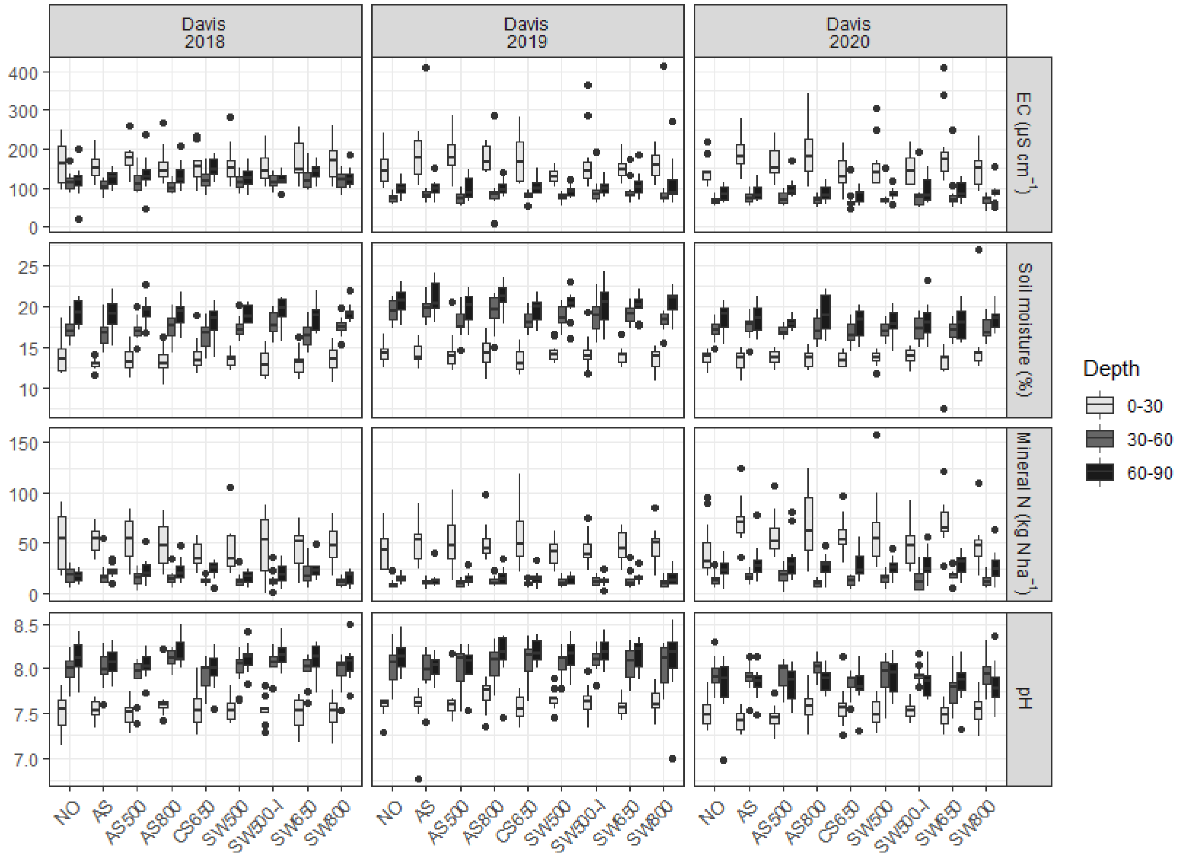

Figure 2.S1 Soil electrical conductivity (EC), moisture, mineral N, and pH in Davis during a three-year processing tomato field trial by biochar, year, and depth. Results are averaged over the level of biochar rate (n = 3 per each of two rates) and fertilizer rate (n = 3 per each of two rates). Box plots are visualized with the median as the middle bar, and the first and third quartiles as the boxes' lower and upper limits, respectively. Box whiskers represent the highest and lowest values within 1.5 times the inter-quartile range. Outliers beyond that range are represented as points.

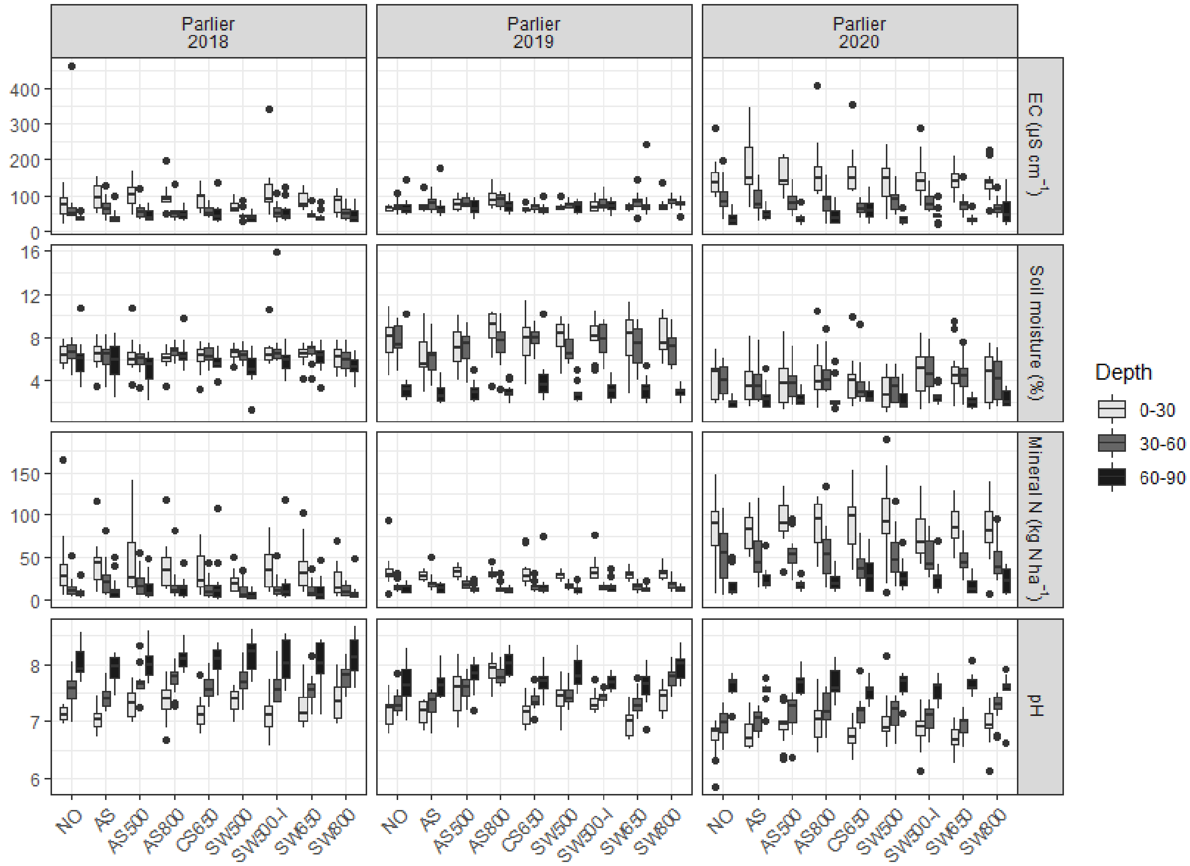

Figure 2.S2 Soil electrical conductivity (EC), moisture, mineral N, and pH in Parlier during a three-year processing tomato field trial by biochar, year, and depth. Results are averaged over the level of biochar rate (n = 3 per each of two rates) and fertilizer rate (n = 3 per each of two rates). Box plots are visualized with the median as the middle bar, and the first and third quartiles as the boxes' lower and upper limits, respectively. Box whiskers represent the highest and lowest values within 1.5 times the inter-quartile range. Outliers beyond that range are represented as points.

Table 2.S2: Effects of biochar on marketable yield, marketable ratio, and aboveground biomass nitrogen uptake (Plant N) from a three-year field trial in which a silt loam (Davis) and a sandy loam (Parlier) were amended with the following treatments: AS, AS500, AS800, CS650, SW500, SW500-I, SW650, SW800. In the upper panel, the estimated means are averaged over fertilizer and biochar rates, and reported with asterisks indicating significance levels (˙p<0.10, *p<0.05, **p<0.01, ***p<0.001). P-values refer to comparisons between treatments and the control and were corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method. All bolded values indicate results with p-values <0.05.

	Davis			Parlier		
	Marketable Yield (t ha^{-1})	Marketable Ratio	Plant N (kg ha^{-1})	Marketable Yield (t ha^{-1})	Marketable Ratio	Plant N (kg ha^{-1})
	2018					
NO	123.9	0.82	246	144.7	0.72	459
AS	128.1	0.81	253	133.2	0.66	451
AS500	130	0.81	262	128	0.67	423
AS800	118	0.82	235	125	0.59	507
CS650	128.3	0.84	247	133.8	0.66	444
SW500	133.6	0.83	255	122.6	0.75	355
SW500-I	126.2	0.81	251	116.9	0.63	418
SW650	127.9	0.84	250	131.4	0.66	430
SW800	134.8	0.86	251	134.6	0.76	391
All biochars	128.4	0.83	250	127.5	0.67	424
	2019					
NO	165.9	0.86	349	134.2	0.92	363
AS	156.1	0.81	366	132.2	0.92	335
AS500	156.7	0.84	356	124	0.92	336
AS800	166.4	0.85	376	142.9	0.93	340
CS650	160.3	0.82	375	137.5	0.89	393
SW500	157.6	0.86	329	130.9	0.89	368
SW500-I	162.1	0.85	372	142.2	0.91	393
SW650	151.5	0.86	395	144.9	0.9	361
SW800	153.4	0.86	347	157.1	0.94	409
All biochars	158.3	0.85	346	139.9	0.91	371
	2020					
NO	69.9	0.97	198	43.7	0.91	232
AS	82.9	0.97	236	53.5	0.87	272
AS500	69.1	0.97	216	53.3	0.95	250
AS800	75.7	0.97	226	54	0.94	275
CS650	72.2	0.98	190	49.7	0.8	275
SW500	81.7	0.99	201	46.6	0.94	268
SW500-I	68.8	0.96	218	50.3	0.8	294
SW650	83.1	0.98	227	70.1	0.89	287
SW800	62.2	0.97	191	58.6	0.87	323
All biochars	73.3	0.97	210	54.7	0.88	282

Table 2.S3: Effects of biochar on soil pH, electrical conductivity (EC), mineral nitrogen (N), and moisture from a three-year field trial in which a silt loam (Davis) and a sandy loam (Parlier) were amended with the following treatments: AS, AS500, AS800, CS650, SW500, SW500-I, SW650, SW800. In the upper panel, the estimated means are averaged over fertilizer and biochar rates, and reported with asterisks indicating significance levels (˙p<0.10, *p<0.05, **p<0.01, ***p<0.001). P-values refer to comparisons between treatments and the control and were corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method. All bolded values indicate results with p-values <0.05.

	Davis				Parlier			
	pH	EC (µS cm^{-1})	Mineral N (kg ha^{-1})	Moisture (%)	pH	EC (µS cm^{-1})	Mineral N (kg ha^{-1})	Moisture (%)
	2018							
NO	7.53	163	53.1	13.8	7.33	118	46.6	10.13
AS	7.55	156	53.7	12.9	7.29	127	48	9.68
AS500	7.5	176	52.8	13.4	7.41	140	49.6	9.84
AS800	7.63	157	49.6	13.4	7.49	128	45.2	9.66
CS650	7.54	157	39.2	13.9	7.34	124	35.9	10.01
SW500	7.54	162	44.4	13.5	7.45	116	32.8	9.99
SW500-I	7.54	154	48.8	13	7.34	135	44	9.84
SW650	7.5	172	45	13.2	7.38	129	41.2	9.77
SW800	7.5	169	48.5	13.4	7.44	125	35.3	9.74
All biochars	7.54	164	46.9	13.4	7.41	128	40.6	9.84
	2019							
NO	7.58	151	42.9	14.2	7.37	108	38.7	11.14
AS	7.56	176	49.9	14.2	7.35	123	38.8	10.28
AS500	7.61	186	51.6	14.3	7.56	133	42.3	10.72
AS800	7.7	175	51.2	14.3	**7.79*** **	135	40.9	11.43
CS650	7.56	172	56.3	13.4	7.35	117	45.2	10.52
SW500	7.65	130	40.5	14.3	7.53	100	34.5	11.14
SW500-I	7.64	169	43.9	14.2	7.48	121	39.9	11.17
SW650	7.56	153	45.6	14	7.28	110	37.9	10.94
SW800	7.63	162	48	13.5	7.51	118	40	10.81
All biochars	7.62	164	48.1	14	**7.5***	119	40.1	10.96
	2020							
NO	7.5	142	42.9	13.6	7.09	146	63.3	8.92
AS	7.42	192 ˙	**72.6****	13.3	7.09	183 ˙	76.9	8.6
AS500	7.45	164	58.4	13.7	7.18	160	76.3	8.79
AS800	7.59	190 ˙	**70.6****	13.6	7.29 ˙	181 ˙	79.1	9.04
CS650	7.58	139	56.7	13.5	7.16	154	75.2	8.73
SW500	7.5	157	62.8	13.7	7.26	149	79.5	8.31
SW500-I	7.53	149	46.4	13.9	7.19	149	62.4	9.41
SW650	7.48	**200***	**70.1****	13	7.08	170	78.9	8.9
SW800	7.53	146	47.7	15	7.24	141	64.4	9.79
All biochars	7.52	163	**59.1***	13.8	7.2 ˙	158	73.7 ˙	8.99

APPENDIX 2: SUPPLEMENTARY INFORMATION FOR CHAPTER 3

Table 3.S1: The effect of biochar on soil health indicators 2.5 years after biochar amendment, in Davis and Parlier field trials by specific biochar (n =3), and by all biochars within each location averaged together. Estimated means are reported with asterisks indicating significance levels (˙p<0.10, *p<0.05, **p<0.01, ***p<0.001). P-values refer to comparisons between treatments (AS500, AS800, SW500) and the control (NO), and were corrected for multiple comparisons using Tukey's honestly significant difference (HSD) method. All bolded values indicate results with p-values <0.05.

	Davis					Parlier				
	NO	AS500	AS800	SW500	All biochars	NO	AS500	AS800	SW500	All biochars
Total carbon (%)	1.06	1.2 ˙	1.11	1.13	1.15 ˙	0.28	0.33	0.29	0.37	0.33
PMC-24 h (μg g^{-1} day^{-1})	41.8	26.3	31.1	31	29.8 ˙	20.3	23.1	28.4	20.8	24.1
PMC-96 h (μg g^{-1} day^{-1})	19.2	16.9	16.2	18.4	17.2	11.8	13.2	15.3	11.9	13.5
POXC (mg kg^{-1})	65	89.4	122.9 ˙	122.1 ˙	**111.5***	76.6	**90.2***	86.9 ˙	**93.3****	**90.2****
DOC (mg kg^{-1})	11.7	10.7	10.9	11	10.9	7.46	8.83	10.01	7.71	8.8
Total nitrogen (%)	0.103	0.11	0.107	0.103	0.107	0.03	0.03	0.033	0.03	0.031
PMN (mg kg^{-1} day^{-1})	0.544	0.551	0.542	0.759	0.617	0.503	0.61	0.667	0.51	0.596
pH	7.73	7.65	**8.03***	7.85	7.84	7.3	7.45	7.69	7.65	7.59
EC (μS cm^{-1})	130.8	141.3	144	113.5	133	99.7	117.8	155.2	99.4	124.1
Ca (mg kg^{-1})	1608	1496	1478	1537	**1504***	596	585	613	598	599
Cu (mg kg^{-1})	10.44	10.71	8.93	11.74	10.46	5.23	5.16	5.14	5.03	5.11
Fe (mg kg^{-1})	138.7	128.4	134.1	133.9	132.2	72.3	78.3	73.3	79.4	77.6
K (mg kg^{-1})	401.5	354.6	555.5	312.5	407.5	25.3	48.7	89.9 ˙	28.3	55.6
Mg (mg kg^{-1})	1481	**1358****	**1300****	1415	**1358****	94.3	104.5	107.5	103.3	105.1
Mn (mg kg^{-1})	191.6	176.6	178.5	185.1	180.1 ˙	45	46.6	47.1	44.2	44
P (mg kg^{-1})	58.3	51.4	61.1	48.1	53.5	26.9	30.6	35.7	26.9	30.1
Zn (mg kg^{-1})	4.25	4.19	4.86	4.5	4.52	5.64	5.45	5.82	5.59	5.62
Water stable aggregates (%)	21	34.8	37.2	41.2	37.8	28.1	42 ˙	40.4	24.9	35.8
Moisture (%)	15.6	14.9	18.6 ˙	16.9	16.7	16.2	11.4	12.4	10.2	11.4 ˙
PLFA Biomass (nmol g^{-1})	67.2	69.6	67.6	65.6	66.8	29.9	38	37.4	33	36.1 ˙
Cy17/pre PLFA ratio	0.322	0.302	0.286	0.323	0.303	0.497	**0.363***	**0.341***	0.423	**0.375****
Cy19/pre PLFA ratio	0.523	0.475	0.477	0.479	0.477	0.771	**0.462***	**0.459***	0.652	**0.524***
F/B PLFA ratio	0.1	0.093	0.101	0.095	0.097	0.109	0.16	0.135	0.114	0.135
G+/G- PLFA ratio	1.26	1.21	1.25	1.21	1.23	1.4	1.14	1.23	1.33	1.23
S/U PLFA ratio	0.945	0.918	0.987	0.932	0.946	1.57	**1.17***	1.22 ˙	1.41	**1.26***

PMC = potentially mineralizable carbon; POXC = permanganate oxidizable carbon; DOC = dissolved organic carbon; PMN = potentially mineralizable nitrogen; EC = electrical conductivity; PLFA = phospholipid fatty acid; PLFA ratios designated as follows: Cy17/pre = cyclopropyl 17:0 to precursors; Cy19/pre = cyclopropyl 19:0 to precursors; F/B = fungal to bacterial; G+/G- = gram-positive to gram-negative bacteria; S/U = saturated to monounsaturated

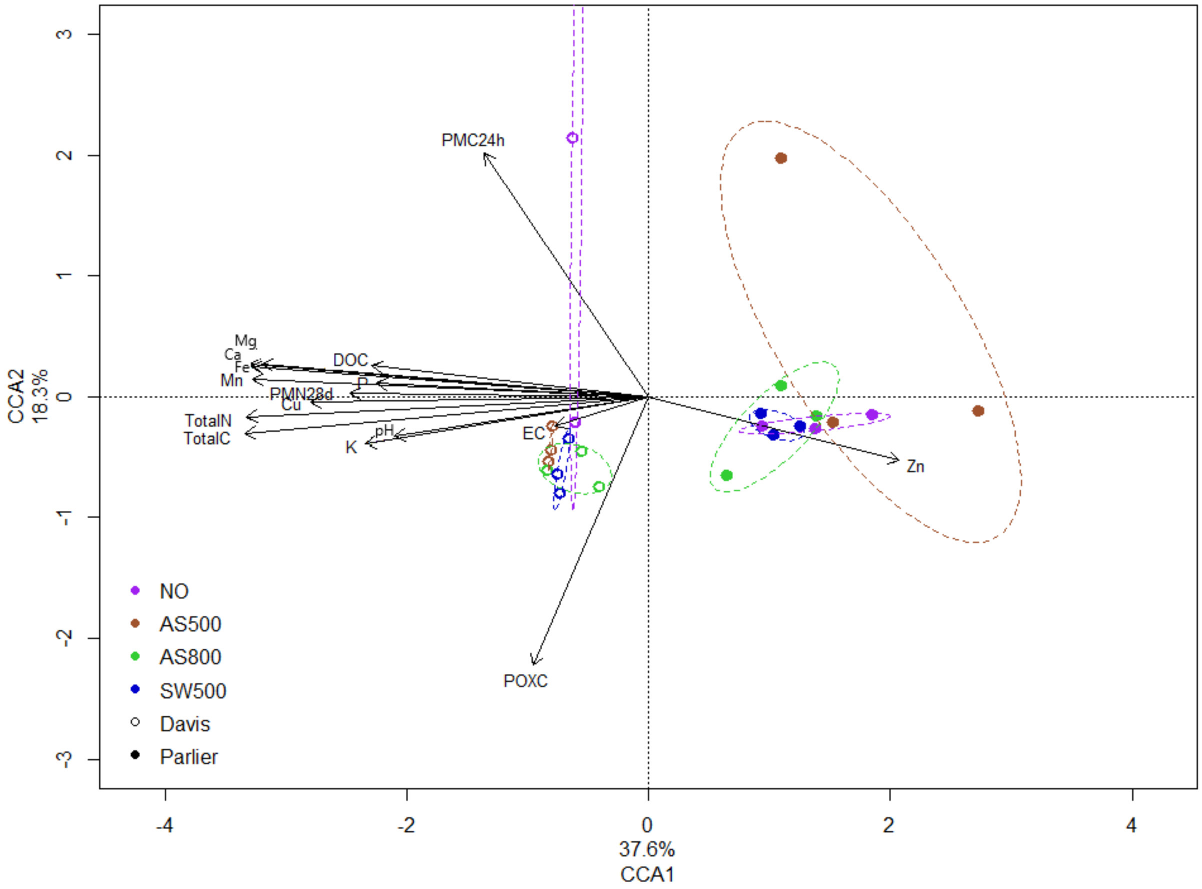

Figure 3.S1. The impact of location, biochar, and environmental variables on soil microbial community composition 2.5 years after biochar was amended to the soil in three-year processing tomato field trials in Davis and Parlier. Arrows represent the vectors for key environmental variables.

REFERENCES

(1) Web of Science. Core Collection Database, “Biochar.” **2020**.

(2) US Patent and Trademark Office. Patent Application Full Text and Image Database http://appft.uspto.gov/netacgi/nph-Parser?Sect1=PTO2&Sect2=HITOFF&p=1&u=%2Fnetahtml%2FPTO%2Fsearch-bool.html&r=0&f=S&l=50&TERM1=biochar&FIELD1=&co1=AND&TERM2=&FIELD2=&d=PG01 (accessed Aug 20, 2020).

(3) International Biochar Initiative (IBI). Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil. *Int. Biochar Initiat.* **2015**, No. November, 23.

(4) Downie, A.; Crosky, A.; Munroe, P. Characteristics of Biochar – Physical and Structural Properties. *Biochar Environ. Manag. - Sci. Technol.* **2009**, 89–108.

(5) Glaser, B.; Lehmann, J.; Zech, W. Ameliorating Physical and Chemical Properties of Highly Weathered Soils in the Tropics with Charcoal - A Review. *Biol. Fertil. Soils* **2002**, *35* (4), 219–230.

(6) Hestrin, R.; Torres-Rojas, D.; Dynes, J. J.; Hook, J. M.; Regier, T. Z.; Gillespie, A. W.; Smernik, R. J.; Lehmann, J. Fire-Derived Organic Matter Retains Ammonia through Covalent Bond Formation. *Nat. Commun.* **2019**, *10* (1), 1–8.

(7) Glaser, B.; Lehr, V. I. Biochar Effects on Phosphorus Availability in Agricultural Soils: A Meta-Analysis. *Sci. Rep.* **2019**, *9* (1), 1–9.

(8) Haider, G.; Joseph, S.; Steffens, D.; Müller, C.; Taherymoosavi, S.; Mitchell, D.; Kammann, C. I. Mineral Nitrogen Captured in Field-Aged Biochar Is Plant-Available. *Sci. Rep.* **2020**, *10* (1), 1–12.

(9) Glaser, B.; Wiedner, K.; Seelig, S.; Schmidt, H. P.; Gerber, H. Biochar Organic Fertilizers from Natural Resources as Substitute for Mineral Fertilizers. *Agron. Sustain. Dev.* **2015**, *35* (2), 667–678.

(10) Blanco-Canqui, H. Biochar and Soil Physical Properties. *Soil Sci. Soc. Am. J.* **2017**, *81* (4), 687–711.

(11) Griffin, D. E.; Wang, D.; Parikh, S. J.; Scow, K. M. Short-Lived Effects of Walnut Shell Biochar on Soils and Crop Yields in a Long-Term Field Experiment. *Agric. Ecosyst. Environ.* **2017**, *236*, 21–29.

(12) Jones, D. L.; Rousk, J.; Edwards-Jones, G.; DeLuca, T. H.; Murphy, D. V. Biochar-Mediated Changes in Soil Quality and Plant Growth in a Three Year Field Trial. *Soil Biol. Biochem.* **2012**, *45*, 113–124.

(13) Martos, S.; Mattana, S.; Ribas, A.; Albanell, E.; Domene, X. Biochar Application as a Win-Win Strategy to Mitigate Soil Nitrate Pollution without Compromising Crop Yields: A Case Study in a

Mediterranean Calcareous Soil. *J. Soils Sediments* **2020**, *20* (1), 220–233.

(14) Zhang, D.; Yan, M.; Niu, Y.; Liu, X.; van Zwieten, L.; Chen, D.; Bian, R.; Cheng, K.; Li, L.; Joseph, S.; et al. Is Current Biochar Research Addressing Global Soil Constraints for Sustainable Agriculture? *Agric. Ecosyst. Environ.* **2016**, *226*, 25–32.

(15) Jeffery, S.; Verheijen, F. G. A.; van der Velde, M.; Bastos, A. C. A Quantitative Review of the Effects of Biochar Application to Soils on Crop Productivity Using Meta-Analysis. *Agric. Ecosyst. Environ.* **2011**, *144* (1), 175–187.

(16) Hassan, M.; Liu, Y.; Naidu, R.; Parikh, S. J.; Du, J.; Qi, F.; Willett, I. R. Influences of Feedstock Sources and Pyrolysis Temperature on the Properties of Biochar and Functionality as Adsorbents: A Meta-Analysis. *Sci. Total Environ.* **2020**, *744*, 140714.

(17) Zhou, L.; Xu, D.; Li, Y.; Pan, Q.; Wang, J.; Xue, L.; Howard, A. Phosphorus and Nitrogen Adsorption Capacities of Biochars Derived from Feedstocks at Different Pyrolysis Temperatures. *WATER* **2019**, *11* (8).

(18) Sanford, J. R.; Larson, R. A.; Runge, T. Nitrate Sorption to Biochar Following Chemical Oxidation. *Sci. Total Environ.* **2019**, *669*, 938–947.

(19) Zeng, Z.; Zhang, S.; Li, T.; Zhao, F.; He, Z.; Zhao, H.; Yang, X.; Wang, H.; Zhao, J.; Rafiq, M. T. Sorption of Ammonium and Phosphate from Aqueous Solution by Biochar Derived from Phytoremediation Plants. *J. ZHEJIANG Univ. B* **2013**, *14* (12), 1152–1161.

(20) Hollister, C. C.; Bisogni, J. J.; Lehmann, J. Ammonium, Nitrate, and Phosphate Sorption to and Solute Leaching from Biochars Prepared from Corn Stover (Zea Mays L.) and Oak Wood (Quercus Spp.). *J. Environ. Qual.* **2013**, *42* (1), 137–144.

(21) Hale, S. E.; Alling, V.; Martinsen, V.; Mulder, J.; Breedveld, G. D.; Cornelissen, G. The Sorption and Desorption of Phosphate-P, Ammonium-N and Nitrate-N in Cacao Shell and Corn Cob Biochars. *Chemosphere* **2013**, *91* (11), 1612–1619.

(22) Gai, X.; Wang, H.; Liu, J.; Zhai, L.; Liu, S.; Ren, T.; Liu, H. Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate. *PLoS One* **2014**, *9* (12).

(23) Wang, B.; Yang, D.-Y.; Li, F.-Y. REMOVAL OF NITRATE AND PHOSPHATE BY IMMOBILIZED BIOCHARS PREPARED FROM REEDS AND HEMATITE. *FRESENIUS Environ. Bull.* **2017**, *26* (7), 4825–4833.

(24) Li, S.; Barreto, V.; Li, R.; Chen, G.; Hsieh, Y. P. Nitrogen Retention of Biochar Derived from Different Feedstocks at Variable Pyrolysis Temperatures. *J. Anal. Appl. Pyrolysis* **2018**, *133*, 136–146.

(25) Chandra, S.; Medha, I.; Bhattacharya, J. Potassium-Iron Rice Straw Biochar Composite for Sorption of Nitrate, Phosphate, and Ammonium Ions in Soil for Timely and Controlled Release.

Sci. Total Environ. **2020**, *712*, 136337.

(26) Ahmadvand, M.; Soltani, J.; Ebrahim, S.; Garmdareh, H.; Varavipour, M. The Relationship between the Characteristics of Biochar Produced at Different Temperatures and Its Impact on the Uptake of NO3--N. *Environ. Heal. Eng. Manag. J.* **2018**, *5* (2), 67–75.

(27) Zhang, M.; Song, G.; Gelardi, D. L.; Huang, L.; Khan, E.; Parikh, S. J.; Ok, Y. S.; Song, G.; Gelardi, D. L.; Huang, L.; et al. Evaluating Biochar and Its Modifications for the Removal of Ammonium, Nitrate, and Phosphate in Water. *Water Res.* **2020**, *Preprint*.

(28) Hale, S. E.; Alling, V.; Martinsen, V.; Mulder, J.; Breedveld, G. D.; Cornelissen, G. The Sorption and Desorption of Phosphate-P, Ammonium-N and Nitrate-N in Cacao Shell and Corn Cob Biochars. *Chemosphere* **2013**, *91* (11), 1612–1619.

(29) Wang, B.; Lehmann, J.; Hanley, K.; Hestrin, R.; Enders, A. Adsorption and Desorption of Ammonium by Maple Wood Biochar as a Function of Oxidation and PH. *Chemosphere* **2015**, *138*, 120–126.

(30) Paramashivam, D.; Clough, T. J.; Dickinson, N. M.; Horswell, J.; Lense, O.; Clucas, L.; Robinson, B. H. Effect of Pine Waste and Pine Biochar on Nitrogen Mobility in Biosolids. *J. Environ. Qual.* **2016**, *45* (1), 360–367.

(31) Tian, J.; Miller, V.; Chiu, P. C.; Maresca, J. A.; Guo, M.; Imhoff, P. T. Nutrient Release and Ammonium Sorption by Poultry Litter and Wood Biochars in Stormwater Treatment. *Sci. Total Environ.* **2016**, *553*, 596–606.

(32) Zhang, H.; Voroney, R. P.; Price, G. W. Effects of Temperature and Activation on Biochar Chemical Properties and Their Impact on Ammonium, Nitrate, and Phosphate Sorption. *J. Environ. Qual.* **2017**, *46* (4), 889–896.

(33) Uttran, A.; Loh, S. K.; Kong, S. H.; Bachmann, R. T. ADSORPTION OF NPK FERTILISER AND HUMIC ACID ON PALM KERNEL SHELL BIOCHAR. *J. OIL PALM Res.* **2018**, *30* (3), 472–484.

(34) Yin, Q.; Liu, M.; Ren, H. Removal of Ammonium and Phosphate from Water by Mg-Modified Biochar: Influence of Mg Pretreatment and Pyrolysis Temperature. *BIORESOURCES* **2019**, *14* (3), 6203–6218.

(35) Song, H.; Wang, J.; Garg, A.; Lin, X.; Zheng, Q.; Sharma, S. Potential of Novel Biochars Produced from Invasive Aquatic Species Outside Food Chain in Removing Ammonium Nitrogen: Comparison with Conventional Biochars and Clinoptilolite. *Sustain.* **2019**, *11* (24), 1–18.

(36) Yin, Q.; Zhang, B.; Wang, R.; Zhao, Z. Phosphate and Ammonium Adsorption of Sesame Straw Biochars Produced at Different Pyrolysis Temperatures. *Environ. Sci. Pollut. Res.* **2018**, *25* (5), 4320–4329.

(37) Gao, F.; Xue, Y.; Deng, P.; Cheng, X.; Yang, K. Removal of Aqueous Ammonium by Biochars Derived from Agricultural Residuals at Different Pyrolysis Temperatures. *Chem. Speciat. Bioavailab.* **2015**, *27* (2), 92–97.

(38) Gai, X.; Wang, H.; Liu, J.; Zhai, L.; Liu, S.; Ren, T.; Liu, H. Effects of Feedstock and Pyrolysis Temperature on Biochar Adsorption of Ammonium and Nitrate. *PLoS One* **2014**, *9* (12), 1–19.

(39) Yang, H. I.; Lou, K.; Rajapaksha, A. U.; Ok, Y. S.; Anyia, A. O.; Chang, S. X. Adsorption of Ammonium in Aqueous Solutions by Pine Sawdust and Wheat Straw Biochars. *Environ. Sci. Pollut. Res.* **2017**, *25* (26), 25638–25647.

(40) Zheng, H.; Wang, Z.; Deng, X.; Zhao, J.; Luo, Y.; Novak, J.; Herbert, S.; Xing, B. Characteristics and Nutrient Values of Biochars Produced from Giant Reed at Different Temperatures. *Bioresour. Technol.* **2013**, *130*, 463–471.

(41) Kameyama, K.; Miyamoto, T.; Shiono, T.; Shinogi, Y. Influence of Sugarcane Bagasse-Derived Biochar Application on Nitrate Leaching in Calcaric Dark Red Soil. *J. Environ. Qual.* **2012**, *41* (4), 1131–1137.

(42) Haider, G.; Steffens, D.; Müller, C.; Kammann, C. I. Standard Extraction Methods May Underestimate Nitrate Stocks Captured by Field-Aged Biochar. *J. Environ. Qual.* **2016**, *45* (4), 1196–1204.

(43) Pratiwi, E. P. A.; Hillary, A. K.; Fukuda, T.; Shinogi, Y. The Effects of Rice Husk Char on Ammonium, Nitrate and Phosphate Retention and Leaching in Loamy Soil. *Geoderma* **2016**, *277*, 61–68.

(44) Yao, Y.; Gao, B.; Zhang, M.; Inyang, M.; Zimmerman, A. R. Effect of Biochar Amendment on Sorption and Leaching of Nitrate, Ammonium, and Phosphate in a Sandy Soil. *Chemosphere* **2012**, *89* (11), 1467–1471.

(45) Bu, X.; Xue, J.; Zhao, C.; Wu, Y.; Han, F. Nutrient Leaching and Retention in Riparian Soils as Influenced by Rice Husk Biochar Addition. *Soil Sci.* **2017**, *182* (7), 1.

(46) Teutscherova, N.; Houska, J.; Navas, M.; Masaguer, A.; Benito, M.; Vazquez, E. Leaching of Ammonium and Nitrate from Acrisol and Calcisol Amended with Holm Oak Biochar: A Column Study. *Geoderma* **2018**, *323*, 136–145.

(47) Clough, T. J.; Condron, L. M. Biochar and the Nitrogen Cycle: Introduction. *J. Environ. Qual.* **2010**, *39* (4), 1218.

(48) Lim, T. J.; Spokas, K. A.; Feyereisen, G.; Novak, J. M. Predicting the Impact of Biochar Additions on Soil Hydraulic Properties. *Chemosphere* **2016**, *142*, 136–144.

(49) Quin, P. R.; Cowie, A. L.; Flavel, R. J.; Keen, B. P.; Macdonald, L. M.; Morris, S. G.; Singh, B. P.; Young, I. M.; Van Zwieten, L. Oil Mallee Biochar Improves Soil Structural Properties-A Study

with x-Ray Micro-CT. *Agric. Ecosyst. Environ.* **2014**, *191*, 142–149.

(50) Kammann, C. I.; Schmidt, H. P.; Messerschmidt, N.; Linsel, S.; Steffens, D.; Müller, C.; Koyro, H. W.; Conte, P.; Stephen, J. Plant Growth Improvement Mediated by Nitrate Capture in Co-Composted Biochar. *Sci. Rep.* **2015**, *5*, 1–13.

(51) Gaskin, J. W.; Steiner, C.; Harris, K.; Das, K. C.; Bibens, B. Effect of Low-Temperature Pyrolysis Conditions on Biochar for Agricultural Use. *Trans. ASABE* **2008**, *51* (6), 2061–2069.

(52) Mulvaney, R. L.; Yaremych, S. A.; Khan, S. A.; Swiader, J. M.; Horgan, B. P. Use of Diffusion to Determine Soil Cation-Exchange Capacity by Ammonium Saturation. *Commun. Soil Sci. Plant Anal.* **2004**, *35* (1–2), 51–67.

(53) Mukome, F. N. D.; Zhang, X.; Silva, L. C. R.; Six, J.; Parikh, S. J. Use of Chemical and Physical Characteristics to Investigate Trends in Biochar Feedstocks. *J. Agric. Food Chem.* **2013**, *61* (9), 2196–2204.

(54) ISO [International Organization for Standardization]. Determination of the Specific Surface Area of Solids by Gas Adsorption - BET Method (ISO 9277:2010(E)). *Ref. number ISO* **2010**.

(55) Parikh, S. J.; Goyne, K. W.; Margenot, A. J.; Mukome, F. N. D.; Calderón, F. J. *Soil Chemical Insights Provided through Vibrational Spectroscopy*; 2014; Vol. 126.

(56) Gürsoy, D.; De Carlo, F.; Xiao, X.; Jacobsen, C. TomoPy: A Framework for the Analysis of Synchrotron Tomographic Data. *J. Synchrotron Radiat.* **2014**, *21* (5), 1188–1193.

(57) Pandolfi, R. J.; Allan, D. B.; Arenholz, E.; Barroso-Luque, L.; Campbell, S. I.; Caswell, T. A.; Blair, A.; De Carlo, F.; Fackler, S.; Fournier, A. P.; et al. Xi-Cam: A Versatile Interface for Data Visualization and Analysis. *J. Synchrotron Radiat.* **2018**, *25* (4), 1261–1270.

(58) Soil Survey Staff. Web Soil Survey, Natural Resources Conservation Service, United States Department of Agriculture http://websoilsurvey.nrcs.usda.gov/ (accessed Jan 1, 2021).

(59) Doane, T. A.; Horwath, W. R. Spectrophotometric Determination of Nitrate with a Single Reagent. *Anal. Lett.* **2003**.

(60) Verdouw, H.; Van Echteld, C. J. A.; Dekkers, E. M. J. Ammonia Determination Based on Indophenol Formation with Sodium Salicylate. *Water Res.* **1978**.

(61) Watanabe, F. S.; Olsen, S. R. Test of an Ascorbic Acid Method for Determining Phosphorus in Water and NaHCO 3 Extracts from Soil . *Soil Sci. Soc. Am. J.* **1965**, *29* (6).

(62) Thomas, C. W. *Soil PH and Soil Activity in Methods of Soil Analysis: Part 3 Chemical Methods*; Sparks, D. L., Page, A. L., Helmke, P. A., Loeppert, R. H., Soltanpour, P. N., Tabatabai, M. A., Johnston, C. T., Summer, M. E., Eds.; American Society of Agronomy Inc.; Soil Science Society of America: Madison, WI, 1996.

(63) Sheldrick, B. H.; Wang, C. *Particle Size Distribution*; Lewis Publications/CRC Press: Boca Raton,

FL, 1993.

(64) Wickham, H.; Averick, M.; Bryan, J.; Chang, W.; McGowan, L.; François, R.; Grolemund, G.; Hayes, A.; Henry, L.; Hester, J.; et al. Welcome to the Tidyverse. *J. Open Source Softw.* **2019**, *4* (43), 1686.

(65) R Core Team. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing: Vienna, Austria 2020.

(66) Lenth, R. Emmeans: Estimated Marginal Means. *Aka Least-Squares Means.* **2019**, https://cran.r-project.org/package=emmeans.

(67) Wickham, H. Ggplot2: Elegant Graphics for Data Analysis. *Springer-Verlag New York* **2016**.

(68) Devereux, R. C.; Sturrock, C. J.; Mooney, S. J. The Effects of Biochar on Soil Physical Properties and Winter Wheat Growth. *Earth Environ. Sci. Trans. R. Soc. Edinburgh* **2013**, *103* (1), 13–18.

(69) Lehmann, J.; Joseph, S. Biochar for Environmental Management: An Introduction. In *Biochar for environmental management: science, technology, and implementation*; Lehmann, J., Joseph, S., Eds.; Routledge: New York, 2015; p 928.

(70) Ibarrola, R.; Shackley, S.; Hammond, J. Pyrolysis Biochar Systems for Recovering Biodegradable Materials: A Life Cycle Carbon Assessment. *Waste Manag.* **2012**, *32* (5), 859–868.

(71) Sparrevik, M.; Field, J. L.; Martinsen, V.; Breedveld, G. D.; Cornelissen, G. Life Cycle Assessment to Evaluate the Environmental Impact of Biochar Implementation in Conservation Agriculture in Zambia. *Environ. Sci. Technol.* **2013**, *47* (3), 1206–1215.

(72) Dutta, B.; Raghavan, V. A Life Cycle Assessment of Environmental and Economic Balance of Biochar Systems in Quebec. *Int. J. Energy Environ. Eng.* **2014**, *5* (2–3), 1–11.

(73) Sadowska, U.; Domagała-Świątkiewicz, I.; Żabiński, A. Biochar and Its Effects on Plant–Soil Macronutrient Cycling during a Three-Year Field Trial on Sandy Soil with Peppermint (Mentha Piperita L.). Part I: Yield and Macro Element Content in Soil and Plant Biomass. *Agronomy* **2020**, *10* (12), 1950.

(74) Nan, Q.; Wang, C.; Wang, H.; Yi, Q.; Liang, B.; Xu, J.; Wu, W. Biochar Drives Microbially-Mediated Rice Production by Increasing Soil Carbon. *J. Hazard. Mater.* **2020**, *387*.

(75) Oladele, S. O. Changes in Physicochemical Properties and Quality Index of an Alfisol after Three Years of Rice Husk Biochar Amendment in Rainfed Rice – Maize Cropping Sequence. *Geoderma* **2019**, *353* (June), 359–371.

(76) Solaiman, Z. M.; Shafi, M. I.; Beamont, E.; Anawar, H. M. Poultry Litter Biochar Increases Mycorrhizal Colonisation, Soil Fertility and Cucumber Yield in a Fertigation System on Sandy Soil. *Agric.* **2020**, *10* (10), 1–14.

(77) MacCarthy, D. S.; Darko, E.; Nartey, E. K.; Adiku, S. G. K.; Tettey, A. Integrating Biochar and

Inorganic Fertilizer Improves Productivity and Profitability of Irrigated Rice in Ghana, West Africa. *Agronomy* **2020**, *10* (6), 1–23.

(78) McDonald, M. R.; Bakker, C.; Motior, M. R. Evaluation of Wood Biochar and Compost Soil Amendment on Cabbage Yield and Quality. *Can. J. Plant Sci.* **2019**, *99* (5), 624–638.

(79) Gajić, A.; Koch, H.-J. Sugar Beet (Beta Vulgaris L.) Growth Reduction Caused by Hydrochar Is Related to Nitrogen Supply . *J. Environ. Qual.* **2012**, *41* (4), 1067–1075.

(80) Jeffery, S.; Abalos, D.; Prodana, M.; Bastos, A. C.; van Groenigen, J. W.; Hungate, B. A.; Verheijen, F. Biochar Boosts Tropical but Not Temperate Crop Yields. *Environ. Res. Lett.* **2017**, *12* (5), 053001.

(81) Atkinson, C. J.; Fitzgerald, J. D.; Hipps, N. A. Potential Mechanisms for Achieving Agricultural Benefits from Biochar Application to Temperate Soils: A Review. *Plant Soil* **2010**, *337* (1), 1–18.

(82) Ye, L.; Camps-Arbestain, M.; Shen, Q.; Lehmann, J.; Singh, B.; Sabir, M. Biochar Effects on Crop Yields with and without Fertilizer: A Meta-Analysis of Field Studies Using Separate Controls. *Soil Use Manag.* **2020**, *36* (1), 2–18.

(83) Sanchez-Monedero, M. A.; Cayuela, M. L.; Roig, A.; Jindo, K.; Mondini, C.; Bolan, N. Role of Biochar as an Additive in Organic Waste Composting. *Bioresour. Technol.* **2018**, *247* (July 2017), 1155–1164.

(84) Hagemann, N.; Kammann, C. I.; Schmidt, H. P.; Kappler, A.; Behrens, S. Nitrate Capture and Slow Release in Biochar Amended Compost and Soil. *PLoS One* **2017**, *12* (2), 1–16.

(85) Pandit, N. R.; Mulder, J.; Hale, S. E.; Zimmerman, A. R.; Pandit, B. H.; Cornelissen, G. Multi-Year Double Cropping Biochar Field Trials in Nepal: Finding the Optimal Biochar Dose through Agronomic Trials and Cost-Benefit Analysis. *Sci. Total Environ.* **2018**, *637–638*, 1333–1341.

(86) Cornelissen, G.; Martinsen, V.; Shitumbanuma, V.; Alling, V.; Breedveld, G.; Rutherford, D.; Sparrevik, M.; Hale, S.; Obia, A.; Mulder, J. Biochar Effect on Maize Yield and Soil Characteristics in Five Conservation Farming Sites in Zambia. *Agronomy* **2013**, *3* (2), 256–274.

(87) Zhang, M.; Song, G.; Gelardi, D. L.; Huang, L.; Khan, E.; Mašek, O.; Parikh, S. J.; Ok, Y. S. Evaluating Biochar and Its Modifications for the Removal of Ammonium, Nitrate, and Phosphate in Water. *Water Res.* **2020**, *186*, 116303.

(88) Hale, S. E.; Nurida, N. L.; Jubaedah; Mulder, J.; Sørmo, E.; Silvani, L.; Abiven, S.; Joseph, S.; Taherymoosavi, S.; Cornelissen, G. The Effect of Biochar, Lime and Ash on Maize Yield in a Long-Term Field Trial in a Ultisol in the Humid Tropics. *Sci. Total Environ.* **2020**, *719*, 137455.

(89) Liu, X.; Zhou, J.; Chi, Z.; Zheng, J.; Li, L.; Zhang, X.; Zheng, J.; Cheng, K.; Bian, R.; Pan, G. Biochar Provided Limited Benefits for Rice Yield and Greenhouse Gas Mitigation Six Years Following an Amendment in a Fertile Rice Paddy. *Catena* **2019**, *179* (March), 20–28.

(90) Backer, R. G. M.; Schwinghamer, T. D.; Whalen, J. K.; Seguin, P.; Smith, D. L. Crop Yield and SOC Responses to Biochar Application Were Dependent on Soil Texture and Crop Type in Southern Quebec, Canada. *J. Plant Nutr. Soil Sci.* **2016**, *179* (3), 399–408.

(91) Omara, P.; Aula, L.; Oyebiyi, F. B.; Eickhof, E. M.; Carpenter, J.; Raun, W. R. Biochar Application in Combination with Inorganic Nitrogen Improves Maize Grain Yield, Nitrogen Uptake, and Use Efficiency in Temperate Soils. *Agronomy* **2020**, *10* (9).

(92) Marks, E. A. N.; Mattana, S.; Alcañiz, J. M.; Pérez-Herrero, E.; Domene, X. Gasifier Biochar Effects on Nutrient Availability, Organic Matter Mineralization, and Soil Fauna Activity in a Multi-Year Mediterranean Trial. *Agric. Ecosyst. Environ.* **2016**, *215*, 30–39.

(93) Nelissen, V.; Ruysschaert, G.; Manka'Abusi, D.; D'Hose, T.; De Beuf, K.; Al-Barri, B.; Cornelis, W.; Boeckx, P. Impact of a Woody Biochar on Properties of a Sandy Loam Soil and Spring Barley during a Two-Year Field Experiment. *Eur. J. Agron.* **2015**, *62*, 65–78.

(94) Ramlow, M.; Foster, E. J.; Del Grosso, S. J.; Cotrufo, M. F. Broadcast Woody Biochar Provides Limited Benefits to Deficit Irrigation Maize in Colorado. *Agric. Ecosyst. Environ.* **2019**, *269* (August 2018), 71–81.

(95) Razzaghi, F.; Obour, P. B.; Arthur, E. Does Biochar Improve Soil Water Retention? A Systematic Review and Meta-Analysis. *Geoderma* **2020**, *361* (October).

(96) Kerré, B.; Willaert, B.; Cornelis, Y.; Smolders, E. Long-Term Presence of Charcoal Increases Maize Yield in Belgium Due to Increased Soil Water Availability. *Eur. J. Agron.* **2017**, *91* (September), 10–15.

(97) Madari, B. E.; Silva, M. A. S.; Carvalho, M. T. M.; Maia, A. H. N.; Petter, F. A.; Santos, J. L. S.; Tsai, S. M.; Leal, W. G. O.; Zeviani, W. M. Properties of a Sandy Clay Loam Haplic Ferralsol and Soybean Grain Yield in a Five-Year Field Trial as Affected by Biochar Amendment. *Geoderma* **2017**, *305* (June 2016), 100–112.

(98) Nawaz, H.; Hussain, N.; … M. A.-I.; 2019, U. Biochar Application Improves the Wheat Productivity under Different Irrigation Water-Regimes. *Intl. J. Agric. Biol* **2019**, *21* (April), 936–942.

(99) Jin, Z.; Chen, C.; Chen, X.; Jiang, F.; Hopkins, I.; Zhang, X.; Han, Z.; Billy, G.; Benavides, J. Soil Acidity, Available Phosphorus Content, and Optimal Biochar and Nitrogen Fertilizer Application Rates: A Five-Year Field Trial in Upland Red Soil, China. *F. Crop. Res.* **2019**, *232* (September 2018), 77–87.

(100) Raboin, L. M.; Razafimahafaly, A. H. D.; Rabenjarisoa, M. B.; Rabary, B.; Dusserre, J.; Becquer, T. Improving the Fertility of Tropical Acid Soils: Liming versus Biochar Application? A Long Term Comparison in the Highlands of Madagascar. *F. Crop. Res.* **2016**, *199* (April 2013), 99–108.

(101) Sun, Y. peng; Yang, J. song; Yao, R. jiang; Chen, X. bing; Wang, X. ping. Biochar and Fulvic Acid Amendments Mitigate Negative Effects of Coastal Saline Soil and Improve Crop Yields in a Three Year Field Trial. *Sci. Rep.* **2020**, *10* (1), 1–12.

(102) Akhtar, S. S.; Andersen, M. N.; Liu, F. Biochar Mitigates Salinity Stress in Potato. *J. Agron. Crop Sci.* **2015**, *201* (5), 368–378.

(103) Mahmoud, E.; El-Beshbeshy, T.; El-Kader, N. A.; El Shal, R.; Khalafallah, N. Impacts of Biochar Application on Soil Fertility, Plant Nutrients Uptake and Maize (Zea Mays L.) Yield in Saline Sodic Soil. *Arab. J. Geosci.* **2019**, *12* (23).

(104) Beesley, L.; Moreno-Jiménez, E.; Gomez-Eyles, J. L. Effects of Biochar and Greenwaste Compost Amendments on Mobility, Bioavailability and Toxicity of Inorganic and Organic Contaminants in a Multi-Element Polluted Soil. *Environ. Pollut.* **2010**, *158* (6), 2282–2287.

(105) Almaroai, Y. A.; Eissa, M. A. Effect of Biochar on Yield and Quality of Tomato Grown on a Metal-Contaminated Soil. *Sci. Hortic. (Amsterdam).* **2020**, *265* (August 2019), 109210.

(106) Sánchez-Monedero, M. A.; Cayuela, M. L.; Sánchez-García, M.; Vandecasteele, B.; D’Hose, T.; López, G.; Martínez-Gaitán, C.; Kuikman, P. J.; Sinicco, T.; Mondini, C. Agronomic Evaluation of Biochar, Compost and Biochar-Blended Compost across Different Cropping Systems: Perspective from the European Project FERTIPLUS. *Agronomy* **2019**, *9* (5).

(107) Kätterer, T.; Roobroeck, D.; Andrén, O.; Kimutai, G.; Karltun, E.; Kirchmann, H.; Nyberg, G.; Vanlauwe, B.; Röing de Nowina, K. Biochar Addition Persistently Increased Soil Fertility and Yields in Maize-Soybean Rotations over 10 Years in Sub-Humid Regions of Kenya. *F. Crop. Res.* **2019**, *235* (March), 18–26.

(108) O’Geen, A. T.; Southard, S. B.; Southard, R. J. Revised Storie Index for Use with Digital Soils Information. *Revis. Storie Index Use with Digit. Soils Inf.* **2008**, No. September.

(109) USDA National Resource Conservation Service. Yolo Series https://soilseries.sc.egov.usda.gov/OSD_Docs/Y/YOLO.html (accessed Apr 20, 2021).

(110) USDA National Resource Conservation Service. Hanford Series https://soilseries.sc.egov.usda.gov/OSD_Docs/H/HANFORD.html (accessed Apr 20, 2021).

(111) Santos-Medellin, C.; Zinke, L. A.; ter Horst, A. M.; Gelardi, D. L.; Parikh, S. J.; Emerson, J. B. Viromes Outperform Total Metagenomes in Revealing the Spatiotemporal Patterns of Agricultural Soil Viral Communities. *ISME J.* **2021**.

(112) Hartz, T.; Miyao, G.; Mickler, J.; Lestrange, M.; Stoddard, S.; Nuñez, J.; Aegerter, B. Processing Tomato Production in California. *Process. Tomato Prod. Calif.* **2008**.

(113) Bates, D.; Mächler, M.; Bolker, B. M.; Walker, S. C. Fitting Linear Mixed-Effects Models Using Lme4. *J. Stat. Softw.* **2015**, *67* (1).

(114) United States Department of Agriculture National Agriculture Statistics Service. USDA NASS Quick Stats https://quickstats.nass.usda.gov/results/A6B3F010-B1FC-3153-AB4B-D387B869DDC5 (accessed Apr 28, 2021).

(115) De Coninck, H.; Revi, A.; Babiker, M.; Bertoldi, P.; Buckeridge, M.; Cartwright, A.; Dong, W.; Ford, J.; Fuss, S.; Hourcade, J.-C.; et al. Strengthening and Implementing the Global Response. In *Global warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global response to the threat of climate change*; Masson-Delmotte, V., Zhai, P., Pörtner, H. O., Roberts, D., Skea, J., Shukla, P. R., Pirani, A., Moufouma-Okia, W., Péan, C., Pidcock, R., et al., Eds.; 2018.

(116) Yang, Q.; Mašek, O.; Zhao, L.; Nan, H.; Yu, S.; Yin, J.; Li, Z.; Cao, X. Country-Level Potential of Carbon Sequestration and Environmental Benefits by Utilizing Crop Residues for Biochar Implementation. *Appl. Energy* **2021**, *282* (May 2020).

(117) Wang, D.; Fonte, S. J.; Parikh, S. J.; Six, J.; Scow, K. M. Biochar Additions Can Enhance Soil Structure and the Physical Stabilization of C in Aggregates. *Geoderma* **2017**, *303* (March), 110–117.

(118) Liu, S.; Zhang, Y.; Zong, Y.; Hu, Z.; Wu, S.; Zhou, J.; Jin, Y.; Zou, J. Response of Soil Carbon Dioxide Fluxes, Soil Organic Carbon and Microbial Biomass Carbon to Biochar Amendment: A Meta-Analysis. *GCB Bioenergy* **2016**, *8* (2), 392–406.

(119) Gelardi, D. L.; Li, C.; Parikh, S. J. An Emerging Environmental Concern: Biochar-Induced Dust Emissions and Their Potentially Toxic Properties. *Sci. Total Environ.* **2019**, *678*.

(120) Godlewska, P.; Ok, Y. S.; Oleszczuk, P. THE DARK SIDE OF BLACK GOLD: Ecotoxicological Aspects of Biochar and Biochar-Amended Soils. *J. Hazard. Mater.* **2021**, *403* (August 2020), 123833.

(121) Ding, Y.; Liu, Y.; Liu, S.; Li, Z.; Tan, X.; Huang, X.; Zeng, G.; Zhou, L.; Zheng, B. Biochar to Improve Soil Fertility. A Review. *Agron. Sustain. Dev.* **2016**, *36* (2).

(122) Yu, H.; Zou, W.; Chen, J.; Chen, H.; Yu, Z.; Huang, J.; Tang, H.; Wei, X.; Gao, B. Biochar Amendment Improves Crop Production in Problem Soils: A Review. *J. Environ. Manage.* **2019**, *232* (May 2018), 8–21.

(123) Saha, A.; Basak, B. B.; Gajbhiye, N. A.; Kalariya, K. A.; Manivel, P. Sustainable Fertilization through Co-Application of Biochar and Chemical Fertilizers Improves Yield, Quality of Andrographis Paniculata and Soil Health. *Ind. Crops Prod.* **2019**, *140* (July), 111607.

(124) Dangi, S.; Gao, S.; Duan, Y.; Wang, D. Soil Microbial Community Structure Affected by Biochar and Fertilizer Sources. *Appl. Soil Ecol.* **2020**, *150* (August 2019), 103452.

(125) Janzen, H. H.; Janzen, D. W.; Gregorich, E. G. The ‘Soil Health’ Metaphor: Illuminating or Illusory? *Soil Biol. Biochem.* **2021**, 108167.

(126) Baveye, P. C. Soil Health at a Crossroad. *Soil Use Manag.* **2021**, No. November 2020, 1–5.

(127) Lehmann, J.; Bossio, D. A.; Kögel-Knabner, I.; Rillig, M. C. The Concept and Future Prospects of Soil Health. *Nat. Rev. Earth Environ.* **2020**, *1* (10), 544–553.

(128) Stewart, R. D.; Jian, J.; Gyawali, A. J. What We Talk About When We Talk about Soil Health. *Colon. Jews* **2018**, 327–340.

(129) Askari, M. S.; Holden, N. M. Quantitative Soil Quality Indexing of Temperate Arable Management Systems. *Soil Tillage Res.* **2015**, *150*, 57–67.

(130) de Moraes Sá, J. C.; Potma Gonçalves, D. R.; Ferreira, L. A.; Mishra, U.; Inagaki, T. M.; Ferreira Furlan, F. J.; Moro, R. S.; Floriani, N.; Briedis, C.; de Oliveira Ferreira, A. Soil Carbon Fractions and Biological Activity Based Indices Can Be Used to Study the Impact of Land Management and Ecological Successions. *Ecol. Indic.* **2018**, *84* (August 2017), 96–105.

(131) de Paul Obade, V.; Lal, R. A Standardized Soil Quality Index for Diverse Field Conditions. *Sci. Total Environ.* **2016**, *541* (2016), 424–434.

(132) Morrow, J. G.; Huggins, D. R.; Carpenter-Boggs, L. A.; Reganold, J. P. Evaluating Measures to Assess Soil Health in Long-Term Agroecosystem Trials. *Soil Sci. Soc. Am. J.* **2016**, *80* (2), 450–462.

(133) Norris, C. E.; Bean, G. Mac; Cappellazzi, S. B.; Cope, M.; Greub, K. L. H.; Liptzin, D.; Rieke, E. L.; Tracy, P. W.; Morgan, C. L. S.; Honeycutt, C. W. Introducing the North American Project to Evaluate Soil Health Measurements. *Agron. J.* **2020**, *112* (4), 3195–3215.

(134) Rinot, O.; Levy, G. J.; Steinberger, Y.; Svoray, T.; Eshel, G. Soil Health Assessment: A Critical Review of Current Methodologies and a Proposed New Approach. *Sci. Total Environ.* **2019**, *648*, 1484–1491.

(135) Powlson, D. S. Is “Soil Health” Meaningful as a Scientific Concept or as Terminology? *Soil Use Manag.* **2021**, *n/a* (n/a).

(136) Stott, D. E. Recommended Soil Health Indicators and Associated Laboratory Procedures. *USDA NRCS Soil Heal. Tech. Note No. 450-03* **2019**, No. 450, 76.

(137) Jastrow, D. Soil Aggregate Formation and the Accrual of Particulate and Mineral-Associated Organic Matter. *Soil Biol. Biochem.* **1996**, *28* (415), 665–676.

(138) Farres, P. J. The Dynamics of Rainsplash Erosion and the Role of Soil Aggregate Stability. *Catena* **1987**, *14* (1–3), 119–130.

(139) Abu-Hamdeh, N. H.; Abo-Qudais, S. A.; Othman, A. M. Effect of Soil Aggregate Size on Infiltration and Erosion Characteristics. *Eur. J. Soil Sci.* **2006**, *57* (5), 609–616.

(140) Miner, G. L.; Delgado, J. A.; Ippolito, J. A.; Stewart, C. E. Soil Health Management Practices and Crop Productivity. *Agric. Environ. Lett.* **2020**, *5* (1), 1–8.

(141) Jordan-Meille, L.; Holland, J. E.; McGrath, S. P.; Glendining, M. J.; Thomas, C. L.; Haefele, S. M. The Grain Mineral Composition of Barley, Oat and Wheat on Soils with PH and Soil Phosphorus Gradients. *Eur. J. Agron.* **2021**, *126* (April), 126281.

(142) Lazicki, P.; Geisseler, D. Relating Indicators to Soil Health Functions in Conventional and Organic Mediterranean Cropping Systems. *Soil Sci. Soc. Am. J.* **2021**, *Accepted A*.

(143) Baveye, P. C. Bypass and Hyperbole in Soil Research: Worrisome Practices Critically Reviewed through Examples. *European Journal of Soil Science*. 2021.

(144) El-Naggar, A.; Awad, Y. M.; Tang, X. Y.; Liu, C.; Niazi, N. K.; Jien, S. H.; Tsang, D. C. W.; Song, H.; Ok, Y. S.; Lee, S. S. Biochar Influences Soil Carbon Pools and Facilitates Interactions with Soil: A Field Investigation. *L. Degrad. Dev.* **2018**, *29* (7), 2162–2171.

(145) Spokas, K. A. Review of the Stability of Biochar in Soils: Predictability of O:C Molar Ratios. *Carbon Manag.* **2010**, *1* (2), 289–303.

(146) Wang, J.; Xiong, Z.; Kuzyakov, Y. Biochar Stability in Soil: Meta-Analysis of Decomposition and Priming Effects. *GCB Bioenergy* **2016**, *8* (3), 512–523.

(147) Cross, A.; Sohi, S. P. The Priming Potential of Biochar Products in Relation to Labile Carbon Contents and Soil Organic Matter Status. *Soil Biol. Biochem.* **2011**, *43* (10), 2127–2134.

(148) Farrell, M.; Kuhn, T. K.; Macdonald, L. M.; Maddern, T. M.; Murphy, D. V.; Hall, P. A.; Singh, B. P.; Baumann, K.; Krull, E. S.; Baldock, J. A. Microbial Utilisation of Biochar-Derived Carbon. *Sci. Total Environ.* **2013**, *465*, 288–297.

(149) Steinbeiss, S.; Gleixner, G.; Antonietti, M. Effect of Biochar Amendment on Soil Carbon Balance and Soil Microbial Activity. *Soil Biol. Biochem.* **2009**, *41* (6), 1301–1310.

(150) Liu, X. H.; Han, F. P.; Zhang, X. C. Effect of Biochar on Soil Aggregates in the Loess Plateau: Results from Incubation Experiments. *Int. J. Agric. Biol.* **2012**, *14* (6), 975–979.

(151) Soinne, H.; Hovi, J.; Tammeorg, P.; Turtola, E. Effect of Biochar on Phosphorus Sorption and Clay Soil Aggregate Stability. *Geoderma* **2014**, *219–220*, 162–167.

(152) Bååth, E.; Anderson, T. H. Comparison of Soil Fungal/Bacterial Ratios in a PH Gradient Using Physiological and PLFA-Based Techniques. *Soil Biol. Biochem.* **2003**, *35* (7), 955–963.

(153) Ullah, M. R.; Carrillo, Y.; Dijkstra, F. A. Drought-Induced and Seasonal Variation in Carbon Use Efficiency Is Associated with Fungi:Bacteria Ratio and Enzyme Production in a Grassland Ecosystem. *Soil Biol. Biochem.* **2021**, *155* (April 2020), 108159.

(154) Schimel, J.; Balser, T. C.; Wallenstein, M. Microbial Stress-Response Physiology and Its Implications for Ecosystem Function. *Ecology* **2007**, *88* (6), 1386–1394.

(155) Zhang, L.; Jing, Y.; Xiang, Y.; Zhang, R.; Lu, H. Responses of Soil Microbial Community Structure Changes and Activities to Biochar Addition: A Meta-Analysis. *Sci. Total Environ.* **2018**, *643*, 926–935.

(156) Guckert, J. B.; Hood, M. A.; White, D. C. Phospholipid Ester-Linked Fatty Acid Profile Changes during Nutrient Deprivation of Vibrio Cholerae: Increases in the Trans/Cis Ratio and Proportions of Cyclopropyl Fatty Acids. *Appl. Environ. Microbiol.* **1986**, *52* (4), 794–801.

(157) Yu, L.; Yu, M.; Lu, X.; Tang, C.; Liu, X.; Brookes, P. C.; Xu, J. Combined Application of Biochar and Nitrogen Fertilizer Benefits Nitrogen Retention in the Rhizosphere of Soybean by Increasing Microbial Biomass but Not Altering Microbial Community Structure. *Sci. Total Environ.* **2018**, *640–641*, 1221–1230.

(158) Wang, D.; Felice, M. L.; Scow, K. M. Impacts and Interactions of Biochar and Biosolids on Agricultural Soil Microbial Communities during Dry and Wet-Dry Cycles. *Appl. Soil Ecol.* **2020**, *152* (May 2019), 103570.

(159) Palansooriya, K. N.; Wong, J. T. F.; Hashimoto, Y.; Huang, L.; Rinklebe, J.; Chang, S. X.; Bolan, N.; Wang, H.; Ok, Y. S. Response of Microbial Communities to Biochar-Amended Soils: A Critical Review. *Biochar* **2019**, *1* (1), 3–22.

(160) Ameloot, N.; Sleutel, S.; Case, S. D. C.; Alberti, G.; McNamara, N. P.; Zavalloni, C.; Vervisch, B.; delle Vedove, G.; De Neve, S. C Mineralization and Microbial Activity in Four Biochar Field Experiments Several Years after Incorporation. *Soil Biol. Biochem.* **2014**, *78*, 195–203.

(161) Hardy, B.; Sleutel, S.; Dufey, J. E.; Cornelis, J.-T. The Long-Term Effect of Biochar on Soil Microbial Abundance, Activity and Community Structure Is Overwritten by Land Management. *Front. Environ. Sci.* **2019**, *7* (July), 1–14.

(162) CIMIS. California Irrigation Management Information System http://www.cimis.water.ca.gov/WSNReportCriteria.aspx (accessed Mar 23, 2020).

(163) Buyer, J. S.; M, S.; Sasser, M. High Throughput Phospholipid Fatty Acid Analysis of Soils - Buyer_Sasser_ApplSoilEcol2012.Pdf. *Appl. Soil Ecol.* **2012**, *61*, 127–130.

(164) Oregon State University. Methods Used in the Soil Health Laboratory. **2021**, 1–63.

(165) Bossio, D. A.; Scow, K. M. Impacts of Carbon and Flooding on Soil Microbial Communities: Phospholipid Fatty Acid Profiles and Substrate Utilization Patterns. *Microb. Ecol.* **1998**, *35* (3), 265–278.

(166) Oksanen, J.; Blanchet, F. G.; Friendly, M.; Kindt, R.; Legendre, P.; McGlinn, D.; Minchin, P. R.; O’Hara, R. B.; Simpson, G. L.; Solymos, P.; et al. Vegan: Community Ecology Packate. *R Packag. version 2.5-7* **2020**.

(167) Safaei Khorram, M.; Zhang, G.; Fatemi, A.; Kiefer, R.; Mahmood, A.; Jafarnia, S.; Zakaria, M. P.;

Li, G. Effect of Walnut Shell Biochars on Soil Quality, Crop Yields, and Weed Dynamics in a 4-Year Field Experiment. *Environ. Sci. Pollut. Res.* **2020**, *27* (15), 18510–18520.

(168) Aktas, T.; Thy, P.; Williams, R. B.; McCaffrey, Z.; Khatami, R.; Jenkins, B. M. Characterization of Almond Processing Residues from the Central Valley of California for Thermal Conversion. *Fuel Process. Technol.* **2015**, *140*, 132–147.

(169) Oades, J. M. Soil Organic Matter and Structural Stability: Mechanisms and Implications for Management. *Plant Soil* **1984**, *76* (1–3), 319–337.

(170) Jensen, J. L.; Schjønning, P.; Watts, C. W.; Christensen, B. T.; Peltre, C.; Munkholm, L. J. Relating Soil C and Organic Matter Fractions to Soil Structural Stability. *Geoderma* **2019**, *337* (November 2018), 834–843.

(171) Culman, S. W.; Snapp, S. S.; Freeman, M. A.; Schipanski, M. E.; Beniston, J.; Lal, R.; Drinkwater, L. E.; Franzluebbers, A. J.; Glover, J. D.; Grandy, A. S.; et al. Permanganate Oxidizable Carbon Reflects a Processed Soil Fraction That Is Sensitive to Management. *Soil Sci. Soc. Am. J.* **2012**, *76* (2), 494–504.

(172) Hurisso, T. T.; Culman, S. W.; Horwath, W. R.; Wade, J.; Cass, D.; Beniston, J. W.; Bowles, T. M.; Grandy, A. S.; Franzluebbers, A. J.; Schipanski, M. E.; et al. Comparison of Permanganate-Oxidizable Carbon and Mineralizable Carbon for Assessment of Organic Matter Stabilization and Mineralization. *Soil Sci. Soc. Am. J.* **2016**, *80* (5), 1352–1364.

(173) Web of Science. Core Collection Database, “Colorado River.” **2020**.

(174) Novak, J. M.; Busscher, W. J.; Watts, D. W.; Amonette, J. E.; Ippolito, J. A.; Lima, I. M.; Gaskin, J.; Das, K. C.; Steiner, C.; Ahmedna, M.; et al. Biochars Impact on Soil-Moisture Storage in an Ultisol and Two Aridisols. *Soil Sci.* **2012**, *177* (5), 310–320.

(175) Basso, A. S.; Miguez, F. E.; Laird, D. A.; Horton, R.; Westgate, M. Assessing Potential of Biochar for Increasing Water-Holding Capacity of Sandy Soils. *GCB Bioenergy* **2013**, *5* (2), 132–143.

(176) Laird, D.; Fleming, P.; Wang, B.; Horton, R.; Karlen, D. Biochar Impact on Nutrient Leaching from a Midwestern Agricultural Soil. *Geoderma* **2010**, *158* (3–4), 436–442.

(177) Knowles, O. A.; Robinson, B. H.; Contangelo, A.; Clucas, L. Biochar for the Mitigation of Nitrate Leaching from Soil Amended with Biosolids. *Sci. Total Environ.* **2011**, *409* (17), 3206–3210.

(178) Zhang, Q. Z.; Wang, X. H.; Du, Z. L.; Liu, X. R.; Wang, Y. D. Impact of Biochar on Nitrate Accumulation in an Alkaline Soil. *Soil Res.* **2013**, *51* (6), 521–528.

(179) Kolb, S. E.; Fermanich, K. J.; Dornbush, M. E. Effect of Charcoal Quantity on Microbial Biomass and Activity in Temperate Soils. *Soil Sci. Soc. Am. J.* **2009**, *73* (4), 1173.

(180) Woolf, D.; Amonette, J. E.; Street-Perrott, F. A.; Lehmann, J.; Joseph, S. Biochar as Carbon Negative in Carbon Credit under Changing Climate. *Curr. Sci.* **2014**, *107* (7), 1090–1091.

(181) Zhang, X.; Wang, H.; He, L.; Lu, K.; Sarmah, A.; Li, J.; Bolan, N. S.; Pei, J.; Huang, H. Using Biochar for Remediation of Soils Contaminated with Heavy Metals and Organic Pollutants. *Environ. Sci. Pollut. Res.* **2013**, *20* (12), 8472–8483.

(182) Kavitha, B.; Reddy, P. V. L.; Kim, B.; Lee, S. S.; Pandey, S. K.; Kim, K. H. Benefits and Limitations of Biochar Amendment in Agricultural Soils: A Review. *J. Environ. Manage.* **2018**, *227* (August), 146–154.

(183) Roberts, K. G.; Gloy, B. A.; Joseph, S.; Scott, N. R.; Lehmann, J. Life Cycle Assessment of Biochar Systems: Estimating the Energetic, Economic, and Climate Change Potential. *Environ. Sci. Technol.* **2010**, *44* (2), 827–833.

(184) Gaunt, J. L.; Lehmann, J. Energy Balance and Emissions Associated with Biochar Sequestration and Pyrolysis Bioenergy Production. *Environ. Sci. Technol.* **2008**, *42* (11), 4152–4158.

(185) Genesio, L.; Vaccari, F. P.; Miglietta, F. Black Carbon Aerosol from Biochar Threats Its Negative Emission Potential. *Glob. Chang. Biol.* **2016**, *22* (7), 2313–2314.

(186) Chow, J. C.; Watson, J. G.; Lowenthal, D. H.; Solomon, P. A.; Magliano, K. L.; Ziman, S. D.; Willard Richards, L. PM10 Source Apportionment in California's San Joaquin Valley. *Atmos. Environ. Part A, Gen. Top.* **1992**, *26* (18), 3335–3354.

(187) Madden, N. M.; Southard, R. J.; Mitchell, J. P. Soil Water Content and Soil Disaggregation by Disking Affects PM Emissions. *J. Environ. Qual.* **2009**, *38* (1), 36.

(188) Madden, N. M.; Southard, R. J.; Mitchell, J. P. Soil Water and Particle Size Distribution Influence Laboratory-Generated PM10. *Atmos. Environ.* **2010**, *44* (6), 745–752.

(189) Li, C.; Bair, D. A.; Parikh, S. J. Estimating Potential Dust Emissions from Biochar Amended Soils under Simulated Tillage. *Sci. Total Environ.* **2018**, *625*, 1093–1101.

(190) Ravi, S.; Sharratt, B. S.; Li, J.; Olshevski, S.; Meng, Z.; Zhang, J. Particulate Matter Emissions from Biochar-Amended Soils as a Potential Tradeoff to the Negative Emission Potential. *Sci. Rep.* **2016**, *6* (September), 1–7.

(191) United States Environmental Protection Agency. Our Nations Air: Status and Trends through 2016 https://gispub.epa.gov/air/trendsreport/2017/#effects (accessed Feb 19, 2019).

(192) Schenker, M. Exposures and Health Effects from Inorganic Agricultural Dusts. *Environ. Health Perspect.* **2000**, *108* (SUPPL. 4), 661–664.

(193) Schenker, M. B.; Farrar, J. A.; Mitchell, D. C.; Green, R. S.; Samuels, S. J.; Lawson, R. J.; McCurdy, S. A. Agricultural Dust Exposure and Respiratory Symptoms among California Farm Operators. *J. Occup. Environ. Med.* **2005**, *47* (11), 1157–1166.

(194) Schenker, M. B.; Pinkerton, K. E.; Mitchell, D.; Vallyathan, V.; Elvine-Kreis, B.; Green, F. H. Y. Pneumoconiosis from Agricultural Dust Exposure among Young California Farmworkers.

Environ. Health Perspect. **2009**, *117* (6), 988–994.

(195) Hendryx, M. Mortality from Heart, Respiratory, and Kidney Disease in Coal Mining Areas of Appalachia. *Int. Arch. Occup. Environ. Health* **2009**, *82* (2), 243–249.

(196) Hendryx, M.; Zullig, K. J. Higher Coronary Heart Disease and Heart Attack Morbidity in Appalachian Coal Mining Regions. *Prev. Med. (Baltim).* **2009**, *49* (5), 355–359.

(197) Castranova, V.; Vallyathan, V. Silicosis and Coal Workers' Pneumoconiosis. *Environ. Health Perspect.* **2000**, *108* (SUPPL. 4), 675–684.

(198) Santo Tomas, L. H. Emphysema and Chronic Obstructive Pulmonary Disease in Coal Miners. *Curr. Opin. Pulm. Med.* **2011**, *17* (2), 123–125.

(199) Graber, J. M.; Stayner, L. T.; Cohen, R. A.; Conroy, L. M.; Attfield, M. D. Respiratory Disease Mortality among US Coal Miners; Results after 37 Years of Follow-Up. *Occup. Environ. Med.* **2014**, *71* (1), 30–39.

(200) Kumari, K. G. I. D.; Moldrup, P.; Paradelo, M.; Elsgaard, L.; de Jonge, L. W. Effects of Biochar on Dispersibility of Colloids in Agricultural Soils. *J. Environ. Qual.* **2017**, *46* (1), 143.

(201) Dunnigan, L.; Morton, B. J.; Hall, P. A.; Kwong, C. W. Production of Biochar and Bioenergy from Rice Husk: Influence of Feedstock Drying on Particulate Matter and the Associated Polycyclic Aromatic Hydrocarbon Emissions. *Atmos. Environ.* **2018**, *190* (March), 218–225.

(202) Ko, J. H.; Wang, J.; Xu, Q. Impact of Pyrolysis Conditions on Polycyclic Aromatic Hydrocarbons (PAHs) Formation in Particulate Matter (PM) during Sewage Sludge Pyrolysis. *Chemosphere* **2018**, *208*, 108–116.

(203) Liu, X.; Ji, R.; Shi, Y.; Wang, F.; Chen, W. Release of Polycyclic Aromatic Hydrocarbons from Biochar Fine Particles in Simulated Lung Fluids: Implications for Bioavailability and Risks of Airborne Aromatics. *Sci. Total Environ.* **2019**, *655*, 1159–1168.

(204) Kong, H.; Zhang, Y.; Li, Y.; Cui, Z.; Xia, K.; Sun, Y.; Zhao, Q.; Zhu, Y. Size-Dependent Cytotoxicity of Nanocarbon Blacks. *Int. J. Mol. Sci.* **2013**, *14* (11), 22529–22543.

(205) Sahu, D.; Kannan, G. M.; Vijayaraghavan, R. Carbon Black Particle Exhibits Size Dependent Toxicity in Human Monocytes. *Int. J. Inflam.* **2014**, *2014*.

(206) Hale, S. E.; Lehmann, J.; Rutherford, D.; Zimmerman, A. R.; Bachmann, R. T.; Shitumbanuma, V.; O'Toole, A.; Sundqvist, K. L.; Arp, H. P. H.; Cornelissen, G. Quantifying the Total and Bioavailable Polycyclic Aromatic Hydrocarbons and Dioxins in Biochars. *Environ. Sci. Technol.* **2012**, *46* (5), 2830–2838.

(207) Liu, G.; Niu, Z.; Van Niekerk, D.; Xue, J.; Zheng, L. Polycyclic Aromatic Hydrocarbons (PAHs) from Coal Combustion: Emissions, Analysis, and Toxicology. *Rev. Environ. Contam. Toxicol.* **2008**, *192*, 1–28.

(208) Buss, W.; Graham, M. C.; MacKinnon, G.; Mašek, O. Strategies for Producing Biochars with Minimum PAH Contamination. *J. Anal. Appl. Pyrolysis* **2016**, *119*, 24–30.

(209) Freddo, A.; Cai, C.; Reid, B. J. Environmental Contextualisation of Potential Toxic Elements and Polycyclic Aromatic Hydrocarbons in Biochar. *Environ. Pollut.* **2012**, *171*, 18–24.

(210) Shackley, S.; Carter, S.; Knowles, T.; Middelink, E.; Haefele, S.; Sohi, S.; Cross, A.; Haszeldine, S. Sustainable Gasification-Biochar Systems? A Case-Study of Rice-Husk Gasification in Cambodia, Part I: Context, Chemical Properties, Environmental and Health and Safety Issues. *Energy Policy* **2012**, *42*, 49–58.

(211) Schimmelpfennig, S.; Glaser, B. One Step Forward toward Characterization: Some Important Material Properties to Distinguish Biochars. *J. Environ. Qual.* **2012**, *41* (4), 1001.

(212) Oleszczuk, P.; Jo, I.; Ku, M. Biochar Properties Regarding to Contaminants Content and Ecotoxicological Assessment. **2013**, *260*, 375–382.

(213) Hilber, I.; Blum, F.; Leifeld, J.; Schmidt, H. P.; Bucheli, T. D. Quantitative Determination of PAHs in Biochar: A Prerequisite to Ensure Its Quality and Safe Application. *J. Agric. Food Chem.* **2012**, *60* (12), 3042–3050.

(214) Keiluweit, M.; Kleber, M.; Sparrow, M. A.; Simoneit, B. R. T.; Prahl, F. G. Solvent-Extractable Polycyclic Aromatic Hydrocarbons in Biochar: In Fl Uence of Pyrolysis Temperature and Feedstock. **2012**.

(215) Liu, Y.; Dai, Q.; Jin, X.; Dong, X.; Peng, J.; Wu, M.; Liang, N.; Pan, B. Negative Impacts of Biochars on Urease Activity : High PH , Heavy Metals , Polycyclic Aromatic Hydrocarbons , or Free Radicals ? *Environ. Sci. Technol.* **2018**, *52*, 12740–12747.

(216) Anjum, R.; Krakat, N.; Toufiq Reza, M.; Klocke, M. Assessment of Mutagenic Potential of Pyrolysis Biochars by Ames Salmonella/Mammalian-Microsomal Mutagenicity Test. *Ecotoxicol. Environ. Saf.* **2014**, *107*, 306–312.

(217) Gondek, K.; Mierzwa-Hersztek, M.; Baran, A.; Szostek, M.; Pieniążek, R.; Pieniążek, M.; Stanek-Tarkowska, J.; Noga, T. The Effect of Low-Temperature Conversion of Plant Materials on the Chemical Composition and Ecotoxicity of Biochars. *Waste and Biomass Valorization* **2017**, *8* (3), 599–609.

(218) Garcia-Perez, M. The Formation of Polyaromatic Hydrocarbons and Dioxins During Pyrolysis. **2008**, No. June, 63.

(219) Ledesma, E. B.; Marsh, N. D.; Sandrowitz, A. K.; Wornat, M. J. Global Kinetic Rate Parameters for the Formation of Polycyclic Aromatic Hydrocarbons from the Pyrolyis of Catechol , A Model Compound Representative of Solid Fuel Moieties. **2002**, *16* (6), 1–6.

(220) Madej, J.; Hilber, I.; Bucheli, T. D.; Oleszczuk, P. Biochars with Low Polycyclic Aromatic

Hydrocarbon Concentrations Achievable by Pyrolysis under High Carrier Gas Flows Irrespective of Oxygen Content or Feedstock. *J. Anal. Appl. Pyrolysis* **2016**, *122*, 365–369.

(221) Björkman, E.; Strömberg, B. Release of Chlorine from Biomass at Pyrolysis and Gasification Conditions [1]. *Energy & Fuels* **1997**, *11* (5), 1026–1032.

(222) Oleszczuk, P. Changes of Total and Freely Dissolved Polycyclic Aromatic Hydrocarbons and Toxicity of Biochars Treated with Various Aging. **2018**, *237*, 65–73.

(223) Sigmund, G.; Bucheli, T. D.; Hilber, I.; Micić, V.; Kah, M.; Hofmann, T. Effect of Ageing on the Properties and Polycyclic Aromatic Hydrocarbon Composition of Biochar. *Environ. Sci. Process. Impacts* **2017**, *19* (5), 768–774.

(224) Devi, P.; Saroha, A. K. Risk Analysis of Pyrolyzed Biochar Made from Paper Mill Effluent Treatment Plant Sludge for Bioavailability and Eco-Toxicity of Heavy Metals. *Bioresour. Technol.* **2014**, *162*, 308–315.

(225) Visioli, G.; Conti, F. D.; Menta, C.; Bandiera, M.; Malcevschi, A.; Jones, D. L.; Vamerali, T. Assessing Biochar Ecotoxicology for Soil Amendment by Root Phytotoxicity Bioassays. *Environ. Monit. Assess.* **2016**, *188* (3), 1–11.

(226) Buss, W.; Mašek, O. Mobile Organic Compounds in Biochar - A Potential Source of Contamination - Phytotoxic Effects on Cress Seed (Lepidiumsativum) Germination. *J. Environ. Manage.* **2014**, *137*, 111–119.

(227) Conesa, J. A.; Font, R.; Fullana, A.; Martín-Gullón, I.; Aracil, I.; Gálvez, A.; Moltó, J.; Gómez-Rico, M. F. Comparison between Emissions from the Pyrolysis and Combustion of Different Wastes. *J. Anal. Appl. Pyrolysis* **2009**, *84* (1), 95–102.

(228) Oleszczuk, P.; Jośko, I.; Kuśmierz, M.; Futa, B.; Wielgosz, E.; Ligeza, S.; Pranagal, J. Microbiological, Biochemical and Ecotoxicological Evaluation of Soils in the Area of Biochar Production in Relation to Polycyclic Aromatic Hydrocarbon Content. *Geoderma* **2014**, *213*, 502–511.

(229) Li, Y.; Shen, F.; Guo, H.; Wang, Z.; Yang, G.; Wang, L.; Zhang, Y.; Zeng, Y.; Deng, S. Phytotoxicity Assessment on Corn Stover Biochar, Derived from Fast Pyrolysis, Based on Seed Germination, Early Growth, and Potential Plant Cell Damage. *Environ. Sci. Pollut. Res.* **2015**, *22* (12), 9534–9543.

(230) Rombolà, A. G.; Marisi, G.; Torri, C.; Fabbri, D.; Buscaroli, A.; Ghidotti, M.; Hornung, A. Relationships between Chemical Characteristics and Phytotoxicity of Biochar from Poultry Litter Pyrolysis. *J. Agric. Food Chem.* **2015**, *63* (30), 6660–6667.

(231) Amaro, A.; Bastos, A. C.; Santos, M. J. G.; Verheijen, F. G. A.; Soares, A. M. V. M.; Loureiro, S. Ecotoxicological Assessment of a Biochar-Based Organic N-Fertilizer in Small-Scale Terrestrial

Ecosystem Models (STEMs). *Appl. Soil Ecol.* **2016**, *108*, 361–370.

(232) Mierzwa-Hersztek, M.; Gondek, K.; Klimkowicz-Pawlas, A.; Baran, A. Effect of Wheat and Miscanthus Straw Biochars on Soil Enzymatic Activity, Ecotoxicity, and Plant Yield. *Int. Agrophysics* **2017**, *31* (3), 367–375.

(233) Sigmund, G.; Huber, D.; Bucheli, T. D.; Baumann, M.; Borth, N.; Guebitz, G. M.; Hofmann, T. Cytotoxicity of Biochar: A Workplace Safety Concern? *Environ. Sci. Technol. Lett.* **2017**, *4* (9), 362–366.

(234) Wang, Y.-Y.; Jing, X.-R.; Li, L.-L.; Liu, W.-J.; Tong, Z.-H.; Jiang, H. Biotoxicity Evaluations of Three Typical Biochars Using a Simulated System of Fast Pyrolytic Biochar Extracts on Organisms of Three Kingdoms. *ACS Sustain. Chem. Eng.* **2017**, *5* (1), 481–488.

(235) Yang, X.; Ng, W.; Shu, B.; Wong, E.; Hun, G.; Wang, C. Characterization and Ecotoxicological Investigation of Biochar Produced via Slow Pyrolysis : Effect of Feedstock Composition and Pyrolysis Conditions. *J. Hazard. Mater.* **2019**, *365* (February 2018), 178–185.

(236) Beesley, L.; Marmiroli, M. The Immobilisation and Retention of Soluble Arsenic, Cadmium and Zinc by Biochar. *Environ. Pollut.* **2011**, *159* (2), 474–480.

(237) Cao, X.; Ma, L.; Liang, Y.; Gao, B.; Harris, W. Simultaneous Immobilization of Lead and Atrazine in Contaminated Soils Using Dairy-Manure Biochar. *Environ. Sci. Technol.* **2011**, *45* (11), 4884–4889.

(238) Fellet, G.; Marchiol, L.; Delle Vedove, G.; Peressotti, A. Application of Biochar on Mine Tailings: Effects and Perspectives for Land Reclamation. *Chemosphere* **2011**, *83* (9), 1262–1267.

(239) Choppala, G. K.; Bolan, N. S.; Megharaj, M.; Chen, Z.; Naidu, R. The Influence of Biochar and Black Carbon on Reduction and Bioavailability of Chromate in Soils. *J. Environ. Qual.* **2012**, *41* (4), 1175.

(240) Inyang, M.; Gao, B.; Yao, Y.; Xue, Y.; Zimmerman, A. R.; Pullammanappallil, P.; Cao, X. Removal of Heavy Metals from Aqueous Solution by Biochars Derived from Anaerobically Digested Biomass. *Bioresour. Technol.* **2012**, *110*, 50–56.

(241) Bair, D. A.; Mukome, F. N. D.; Popova, I. E.; Ogunyoku, T. A.; Jefferson, A.; Wang, D.; Hafner, S. C.; Young, T. M.; Parikh, S. J. Sorption of Pharmaceuticals, Heavy Metals, and Herbicides to Biochar in the Presence of Biosolids. *J. Environ. Qual.* **2016**, *45* (6), 1998.

(242) Wang, D.; Mukome, F. N. D.; Yan, D.; Wang, H.; Scow, K. M.; Parikh, S. J. Phenylurea Herbicide Sorption to Biochars and Agricultural Soil. *J. Environ. Sci. Health. B.* **2015**, *50* (8), 544–551.

(243) Yao, Y.; Gao, B.; Chen, H.; Jiang, L.; Inyang, M.; Zimmerman, A. R.; Cao, X.; Yang, L.; Xue, Y.; Li, H. Adsorption of Sulfamethoxazole on Biochar and Its Impact on Reclaimed Water Irrigation.

J. Hazard. Mater. **2012**, *209–210*, 408–413.

(244) Chai, Y.; Currie, R. J.; Davis, J. W.; Wilken, M.; Martin, G. D.; Fishman, V. N.; Ghosh, U. Effectiveness of Activated Carbon and Biochar in Reducing the Availability of Polychlorinated Dibenzo-p-Dioxins/Dibenzofurans in Soils. *Environ. Sci. Technol.* **2012**, *46* (2), 1035–1043.

(245) Wang, Y.; Wang, L.; Fang, G.; Herath, H. M. S. K.; Wang, Y.; Cang, L.; Xie, Z.; Zhou, D. Enhanced PCBs Sorption on Biochars as Affected by Environmental Factors: Humic Acid and Metal Cations. *Environ. Pollut.* **2013**, *172*, 86–93.

(246) Denyes, M. J.; Langlois, V. S.; Rutter, A.; Zeeb, B. A. The Use of Biochar to Reduce Soil PCB Bioavailability to Cucurbita Pepo and Eisenia Fetida. *Sci. Total Environ.* **2012**, *437*, 76–82.

(247) Chen, B.; Yuan, M. Enhanced Sorption of Polycyclic Aromatic Hydrocarbons by Soil Amended with Biochar. *J. Soils Sediments* **2011**, *11* (1), 62–71.

(248) Khan, S.; Waqas, M.; Ding, F.; Shamshad, I.; Arp, H. P. H.; Li, G. The Influence of Various Biochars on the Bioaccessibility and Bioaccumulation of PAHs and Potentially Toxic Elements to Turnips (Brassica Rapa L.). *J. Hazard. Mater.* **2015**, *300*, 243–253.

(249) European Biochar Foundation (EBC). Guidelines for a Sustainable Production of Biochar. *Eur. Biochar Found.* **2016**, No. June, 1–22.

(250) Major, J. Guidelines on Practical Aspects of Biochar Application to Field Soil in Various Soil Management Systems. *Int. Biochar Initiat.* **2010**, 23.

(251) Silva, F. C.; Borrego, C.; Keizer, J. J.; Amorim, J. H.; Verheijen, F. G. A. Effects of Moisture Content on Wind Erosion Thresholds of Biochar. *Atmos. Environ.* **2015**, *123* (October), 121–128.

(252) Blackwell, P.; Krull, E.; Butler, G.; Herbert, A.; Solaiman, Z. Effect of Banded Biochar on Dryland Wheat Production and Fertiliser Use in South-Western Australia: An Agronomic and Economic Perspective. *Aust. J. Soil Res.* **2010**, *48* (6–7), 531–545.

(253) Schwab, C. V; Hanna, H. M. Master Gardeners' Safety Precautions for Handling, Applying, and Storing Biochar. *Agric. Biosyst. Eng. Ext. Outreach Publ.* **2012**, *5*.

(254) Kołtowski, M.; Oleszczuk, P. Toxicity of Biochars after Polycyclic Aromatic Hydrocarbons Removal by Thermal Treatment. *Ecol. Eng.* **2015**, *75*, 79–85.

(255) Reza, M. T.; Lynam, J. G.; Vasquez, V. R.; Coronella, C. J. Pelletization of Biochar from Hydrothermally Carbonized Wood. *Environ. Prog. Sustain. Energy* **2012**, *31* (2), 225–234.

(256) Hu, Q.; Shao, J.; Yang, H.; Yao, D.; Wang, X.; Chen, H. Effects of Binders on the Properties of Bio-Char Pellets. *Appl. Energy* **2015**, *157* (January), 508–516.