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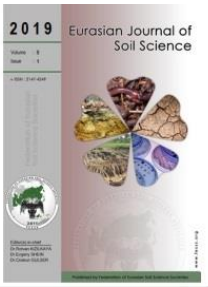

Characterization of soil amendment potential of 18 different biochar types produced by slow pyrolysis

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Abstract

Feedstock type is the most dominant factor influencing the physical characteristics and chemical composition of biochar. The main purpose of this study was to characterize and compare some of the physical and chemical properties of biochars produced by slow pyrolysis of 18 feedstocks, which are locally available agricultural residues. Moreover, elucidating the potential agronomic benefits of these biochars was the other objective of the study. Biochars were produced at 500 ^{o}C in an ingeniously developed reactor. The biochars were characterized for specific surface area (SSA), field capacity (FC), wilting point (WP), plant available water content (AW), pH, electrical conductivity (EC), cation exchange capacity (CEC), total carbon (C) and nitrogen (N), plant available phosphorus (P) and potassium (K) concentrations. Considerable variation of characteristics among biochars indicates the dominant impact of feedstock type on physical properties and chemical composition of biochars. Total C contents were highly variable with values up to 91.9% for pine sawdust. Phosphorus and K in feedstocks were concentrated in the biochars and were two to four times higher in the biochars. The CEC of biochars varied from 79.5 cmol kg^{-1} (pepper residues) to 5.77 cmol kg^{-1} (poplar sawdust). The CEC and SSA had a significant negative correlation (P<0.01, r= -0.70) that probably be attributed to the loss of functional groups during pyrolysis. The results revealed that depending on the feedstock, some biochars have potential to serve as nutrient sources as well as an additive to improve soil quality.

Keywords: Agricultural residues, feedstock type, biochar, physical and chemical properties, soil quality.

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Introduction

Biochar is a carbon-rich solid and stable material produced by pyrolysis of biomass in an oxygen-limited environment (Lehmann and Joseph, 2009). The pyrolytic conversion of the feedstocks mainly composed of agricultural residues to biochar and agricultural applications of the biochar can be considered as their environmentally and economically acceptable management (Hossain et al., 2011). The biochar can be produced from thermochemical processing of a wide variety of feedstocks with different ratios of cellulose, hemicellulose, lignin, extractives, etc. such as organic farm waste, waste treatment plant slurry, and forestry residue with high cellulose/lignin content. After pyrolysis, the solid byproduct is a porous network of carbonates and/or aromatic carbon (Herbert et al., 2012). Biochar types produced from various feedstocks have different physical and chemical characteristics as a function of variability in the composition of feedstocks (Brewer, 2012). Therefore, comparing the impacts of different biochar types on soil properties reported in the literature is difficult to extrapolate to other soils. Biochar improves fertility of soils and has no reported controversial effect on soils. The magnitude of beneficial effect is related to physical and chemical properties of biochars (Lehmann et al., 2006). Biochar improves water holding capacity of soils

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(Günal et al., 2018), promotes development and bioactivity of soil micro-flora, reduces nutrient leaching (Kanthle et al., 2018), recycles soil nutrients (Oldfield et al., 2018), and increases soil organic carbon (Smith, 2016) and thus plant growth (Gaskin et al., 2010). Lim et al. (2016) stated that saturated hydraulic conductivities of the biochar amended soils were significantly influenced by the rate and type of biochar, as well as the original particle size of soil. The researchers reported that biochar addition significantly reduced the saturated hydraulic conductivity of coarse and fine sands. Cation exchange capacity (CEC) of a biochar is affected by both feedstock type and pyrolysis temperature (Brewer, 2012). CEC values decrease with higher pyrolysis temperature due to loss of functional groups. Formation of carboxylic and other oxygenated functional groups at the surface by long term oxidation of biochar increases the negative charges and CEC of a biochar (Cheng and Lehmann, 2009). Surface area is another important physical property of a biochar that has a significant impact on the extent of interactions between biochar and the soil environment (Chu et al., 2018). The nature of feedstock and pyrolysis process have significant impact on surfaces areas of biochars which might vary in the hundreds and even thousands of meters squared per gram, potentially making them suitable as the sustainable amendments of soils (Brewer, 2012).

The increasing demand for food and fiber with increasing population causes a significant amount of agricultural residues. Biochar production is a sustainable way to reduce the agricultural residues produced in food industry or farm activities (Schellekens et al., 2018) and converts them to environmentally friendly additives. Vast amounts of waste biomass are generated by agro-food industries, forestry activities and agricultural crop production in Turkey. Large portion of crops such as 2.5 t ha^{-1} of bread wheat, 13 t ha^{-1} of tomato and 10.5 t ha^{-1} of corn (Di Blasi et al., 1997) is left in the field each year following the harvest. Citak et al. (2006) reported that more than 4 million tons year^{-1} of citrus and fruit pruning residues, 12.7 million tons year^{-1} of tomato and eggplant residues, 350.000 tons ha^{-1} of nut slag and many other crop residues need to be reused to overcome environmental pollution problems created by these residues. Most of crop residues in Turkey are burned onsite, collected and thrown away from the field and dumped to the drainage channels or burned in the houses for energy (Günal et al., 2015). Burning or removing the crop residues for any of the stated purposes have negative impact on soil organic carbon and consequently to functioning ability of soils.

Characterization of biochars produced from several feedstocks is important to predict the stability, potential in contribution to soil quality and risks in the environment (Schellekens et al., 2018). Thus, the objective of this study was to characterize and compare some of the physicochemical properties, critical for agricultural use, of 18 biochars produced at 500 ^{o}C by slow pyrolysis of 18 feedstocks.

Material and Methods

Material

The feedstocks used to produce biochars were vegetable crop residues (tomatoes, bean, pepper, eggplant, cabbage, cauliflower, gooseberry and kidney bean), woody materials (walnut shell, pine sawdust and rosehip seed), field crop residues (rice husk, corn cob and wheat straw) and animal manure (poultry litter, sheep manure and dairy manure) collected from agricultural fields, farms and local carpenters in Tokat province of Turkey.

Methods

Biochar Production

Prior to pyrolysis processing, the biomass of the all sources were ground in a hammer mill to pass a 6 mm screen and oven dried at 60 ^{o}C to <10% moisture (Brewer et al., 2011). The biochars were produced by slow pyrolysis of feedstocks (maximum size 2 mm) at 500 ^{o}C in an ingeniously developed reactor. Slow pyrolysis process was characterized by slow heating rates (a rate of approximately 10 ^{o}C min^{-1}) and long residence times of biomass. The pyrolysis temperature was kept constant at 500 ^{o}C and biochar was held in the unit until pyrolysis gas disappeared. After heating for almost 4 to 6 hours, the biochars were allowed to cool to room temperature.

Characterization of Biochars

The biochar samples underwent the following analyzes: pH, electrical conductivity (EC), specific surface area (SSA), cation exchange capacity (CEC), total carbon (C), total nitrogen (N), plant available potassium (K) and phosphorus (P), field capacity (FC) and wilting point (WP) water contents. The biochar production rate or mass yield (MY) is defined as the ratio of carbonized product mass to the mass of feedstock (Weber and Quicker, 2018). The mass yield was calculated using the following equation:

$$MY\ (\%) = (\text{Biochar weight after pyrolysis}/\text{Feedstock weight}) \times 100.$$

The total C and N contents of the biochars were determined using a Leco CN-2000 analyzer (Leco Corp., St. Joseph, MI, USA) at 1200 ^{o}C. The pH and EC were measured in deionized water at the ratio of 1:5 wt wt^{-1} ratio. The samples were thoroughly mixed and allowed to equilibrate for 1 h; the pH and EC were then measured using an Orion 720 pH-EC meter with a combination electrode. The K and P concentrations of the biochars and raw materials were determined in duplicate following digestion at in H_2O_2 - HNO_3 acid mixture and burned in a microwave (Mars 6). The K and P concentrations in the H_2O_2 - HNO_3 solution were determined by Atomic Absorption Spectrophotometer (AAS-Agilent 240 FS). Ethylene glycol mono-ethyl ether (EGME) method was to measure specific surface area that is typically used for soils (Cerato and Lutenegger, 2002). Cation exchange capacity was determined by ammonium acetate method (Chapman, 1965). The method was modified to apply for biochars due to the low bulk density of biochars creating a problem for liquid-solid separation (Brewer et al., 2009).

Biochars were analyzed for field capacity and permanent wilting point, from which plant-available water capacity (AW) was calculated by difference between water retained at permanent wilting point and at field capacity (Laird et al., 2010). Biochars were filled in rings with a height of 10 mm and an interior diameter of 35 mm. The biochars were carefully wetted from below and drained in a pressurized chamber to either 1.1 or 15 bar on ceramic plates specific to each pressure (Chamber 1600 and 1500, Soil Moisture Equipment, Santa Barbara CA, USA), allowed to equilibrate, and weighed after reaching constant water contents. Water content was determined by drying at 105°C for overnight and field capacity and permanent wilting point were calculated.

Statistical Analyses

All data were checked for normality using by the Kolmogorov–Smirnov (Lilliefors) test. Non-normal data were transformed to meet the analysis of variances (ANOVA) assumptions. Differences between means of feedstock groups were tested with the standard least-squares mode of one-way ANOVA, followed by a Duncan comparison using SPSS 23.0 software (SPSS Inc., Chicago, IL, USA). Differences with probability larger than 95% were taken as significant. Correlation analyses were conducted among the characteristics of biochars produced.

Results and Discussion

The benefits of biochar such as a fertilizer replacement and additive to improve the nutrient availability in soil depend on characteristics of biochar types. Characterization of the biochar encompasses physical characteristics, compositional analysis and soil additive potential. Several physical and chemical characteristics of biochars produced are presented in Table 1-4. The mass yields and some physical and chemical characteristics of biochars obtained from the different sources are given in Figure 1-6. The type of feedstock had significant effect on mass yield of biochars. All feedstocks were pyrolyzed at 500 ^{o}C for almost 4 to 6 hours; however, mass yield varied from 19.68% (poplar sawdust) to 62.99% (dairy manure) with a mean of 33.48%.

Table 1. Physical and chemical properties of biochars produced from vegetable residues

	Yield, (wg),%	SSA, m^{2}g^{-1}	FC, %	WP, %	AW, %	pH	EC, dSm^{-1}	CEC, cmol kg^{-1}
Tomatoes	33.08	208.9	108.5	120.8	4.1	11.61	6.64	49.5
Bean	30.40	117.9	111.2	98.3	7.9c	12.18	8.75j	74.7
Pepper	34.09	133.6	128.2	128.1	5.6	11.40	4.29	79.5
Eggplant	33.02	174.2	119.9	126.8	5.7	11.60	10.30	42.9
Cabbage	34.19	78.07	86.8	76.4	10.4	11.84	18.24	43.4
Cauliflower	37.68	46.53	80.4	58.6	21.9	11.88	15.76	50.9
Gooseberry	32.09	179.7	131.6	111.7	19.9	12.42	14.79	78.2
Kidney Bean	30.62	286.6	110.1	108.8	1.3	10.52	5.72	28.9

	C, %	N, %	C:N	P in Row, g kg^{-1}	P in Bioc. , g kg^{-1}	K in Row, g kg^{-1}	K in Bioc., g kg^{-1}
Tomatoes	65.3	0.42	156.4	1.43	3.69	10.82	34.31
Bean	79.0	0.71	111.2	2.33	5.61	24.52	36.54
Pepper	67.4	0.49	136.3	2.05	6.56	20.68	44.40
Eggplant	67.7	1.17	57.8	1.65	3.88	23.58	39.51
Cabbage	39.4	0.92	42.6	1.65	4.00	16.58	44.54
Cauliflower	42.3	0.84	50.3	0.26	5.65	2.10	41.08
Gooseberry	52.2	0.65	80.8	1.64	3.92	36.52	52.03
Kidney Bean	75.8	0.75	100.6	0.96	3.08	6.27	9.29

EC: Electrical Conductivity, CEC: Cation Exchange Capacity, SA: Specific Surface Area, FC: Field Capacity, WP: Wilting Point, AW: Available Water Content; C: Total Carbon, N: Total Nitrogen, P: Phosphorus, K: Potassium

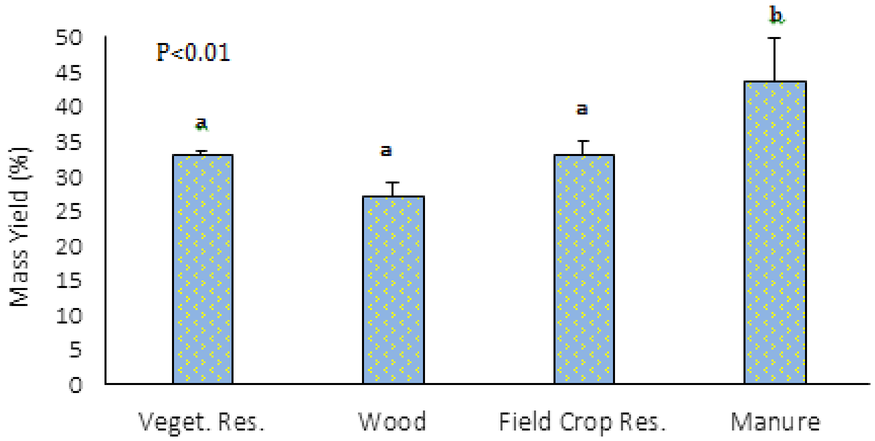

Figure 1. Mass yield (%) ± SE of means of different biochar types (n=18). Any two means sharing different letters are statistically significant (P≤0.05)

Specific surface area and cation exchange capacity of biochar types

Chemical interactions between biochar and soil environment are mostly governed by its surface chemistry. (Weber and Quicker, 2018). The type of feedstock had significant effect (P<0.01) on specific surface area (SSA) of biochars which ranged from mean value of 153.2 $m^2 g^{-1}$ (vegetable residues) to 313.9 $m^2 g^{-1}$ (wood) (Fig. 2). The lowest SSA was obtained for cauliflower (46.53 $m^2 g^{-1}$) and the highest SSA for corncob (397.5 $m^2 g^{-1}$) (Table 1 and 3). The higher the SSA of a biochar, the biochar can be more active in chemical interactions in per gram (Brewer, 2012), and hold more nutrients in addition to the direct supply of nutrients. Mean SSA of all biochar was 222.48 $m^2 g^{-1}$ which is quite high as compared to many clay minerals in soils. Lee et al. (2013) also reported surface area values for wood stem, sugarcane bagasse and palm kernel shell as over 190 $m^2 g^{-1}$ which was similar to the SSA reported in this study.

Table 2. Physical and chemical properties of biochar types produced from woody materials

	Yield, (wg),%	SSA, m^2g^{-1}	FC, %	WP, %	AW, %	pH	EC, dSm^{-1}	CEC, cmol kg^{-1}
Poplar Sawdust	19.68	391.6	30.0	28.0	2.0	8.77	1.44	5.8
Walnut Shell	31.23	318.8	45.3	41.3	4.0	9.63	3.55	20.6
Pine Sawdust	25.27	267.2	58.2	18.4	39.8	7.89	5.06	13.9
Rosehip Seed	32.65	278.0	17.4	16.3	1.1	8.46	1.73	6.8
	C, %	N, %	C:N	P in Row, g kg^{-1}	P in Bioc. , g kg^{-1}		K in Row, g kg^{-1}	K in Bioc., g kg^{-1}
Poplar Sawdust	83.6i	0.38	221.9	0.26	0.57		2.10	3.20
Walnut Shell	85.4	0.32	267.9	1.65	0.92		4.43	5.30
Pine Sawdust	91.9	0.26	348.9	0.31	0.31		0.61	0.63
Rosehip Seed	87.2	1.01	86.2	1.38	3.61		1.56	1.56

EC: Electrical Conductivity, CEC: Cation Exchange Capacity, SA: Specific Surface Area, FC: Field Capacity, WP: Wilting Point, AW: Available Water Content; C: Total Carbon, N: Total Nitrogen, P: Phosphorus, K: Potassium

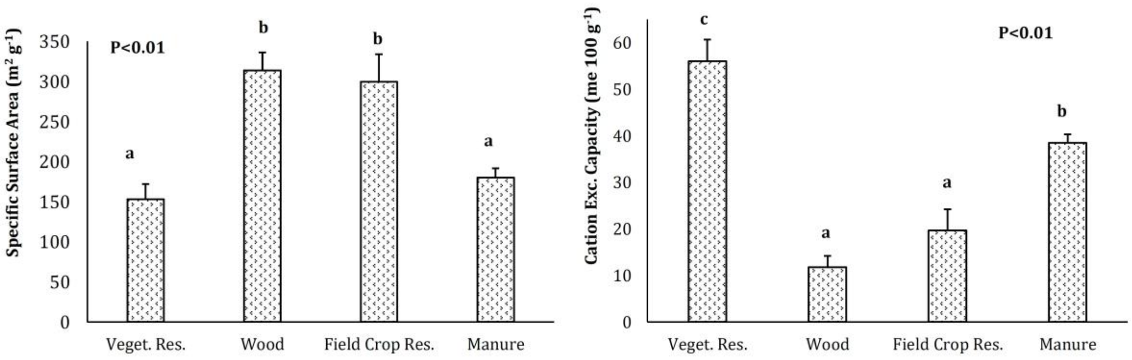

Figure 2. Specific surface area ($m^2 g^{-1}$) ± SE od means and cation exchange capacity (me 100 g^{-1}) ± SE of means of biochar types (n=18). Any two means sharing different letters are statistically significant (P≤0.05)

Cation exchange capacity (CEC) is the ability to adhere and exchange positively charged cations such as important nutrients like potassium (K), calcium (Ca), magnesium (Mg) and etc. The CEC of biochars was significantly affected by type of feedstock. Although CEC of a biochar is directly related to its surface structure and surface area (Brewer, 2012), the mean CEC of woody materials (11.8 me 100 g^{-1}) which had the highest SSA was significantly lower than the CEC of the rest of biochar groups (Figure 2). The CEC values of biochar types were considerably lower than those reported for 2:1-type clay minerals (70–250 cmol kg^{-1}) or humic substances (400–900 cmol kg^{-1}) (Sposito, 1989). The biochar produced from pepper residues had the largest CEC (79.5 cmol kg^{-1}); the CEC of biochars rated between 79.5 cmol kg^{-1} (pepper) and 5.8 cmol kg^{-1} (poplar sawdust) (Table 1 and 2). Biochars with high CEC and surface area values can be efficiently used as a soil amendment to improve soil quality. However, the CEC values obtained in this study are much lower than that reported by Yuan et al. (2011) for canola and corn straw biochars (which from 179 to 304 cmol kg^{-1}). The CEC of biochars may increase by aging. Cheng and Lehmann (2009) showed that functional groups, acidity and negative charge at the surface of oak biochar particles significantly increased in a controlled aerobic incubation experiment which resulted in increased CEC of biochar by aging.

Table 2. Physical and chemical properties of biochar types produced from woody materials

	Yield, (wg),%	SSA, m^2g^{-1}	FC, %	WP, %	AW, %	pH	EC, dSm^{-1}	CEC, cmol kg^{-1}
Rice Husk	37.83	211.8	63.3	61.9	1.4	10.20	3.29	15.2
Corncob	27.12	397.5	119.9	107.9	12.1	9.20	9.30	10.0
Wheat Straw	31.18	214.8	167.5	161.9	5.6	10.90	2.60	39.4

	C, %	N, %	C:N	P in Row, g kg^{-1}	P in Bioc. , g kg^{-1}	K in Row, g kg^{-1}	K in Bioc., g kg^{-1}
Rice Husk	61.7	0.45	136.7	0.32	0.05	4.29	3.89
Corncob	88.3	0.29	306.9	0.40	0.39	6.78	9.53
Wheat Straw	71.7	0.91	78.7	0.57	1.30	14.14	27.59

EC: Electrical Conductivity, CEC: Cation Exchange Capacity, SA: Specific Surface Area, FC: Field Capacity, WP: Wilting Point, AW: Available Water Content; C: Total Carbon, N: Total Nitrogen, P: Phosphorus, K: Potassium

Hydrological properties of biochar types

Hydrologic properties: field capacity (FC), permanent wilting point (PWP) and available water content (AW) of biochars exhibited a wide range depending on feedstock type. Similarly, Gray et al. (2014) indicated that water uptake by biochars depends on feedstock type, which controls the residual macroporosity. The FC is a measure for the water held in a material that has been saturated and allowed to freely drain. Mean biochar FC, accepted as an indication of water availability to plants ranged from 37.7% (woody materials) to 109.6% (vegetable residue) (Figure 3). The FC of biochar produced from rosehip seed was only 17.4% and wheat straw biochar had ten-fold higher water content (161.9%) at the FC (Table 2 and 3). The biochar with the most desirable hydrological property (the highest FC) was produced with the wheat straw (FC=167.5%), however, most of the water in straw biochar was also held in PWP which made only 5.6% of the water available to plant consumption. Majority of the biochars with high FC had also high WP (Table 1). The mean PWP content of biochars was between 26% (woody materials) and 103.7% (vegetable residues) (Figure 3). In contrast to FC and PWP, AW content of biochars did not significantly change (P=0.466) with the type of biochar. Biochars produced from vegetable residues, field crop residues and animal manures hold significantly higher water at FC and PWP, however, majority of water hold by these biochars is tightly held and not available for plant use.

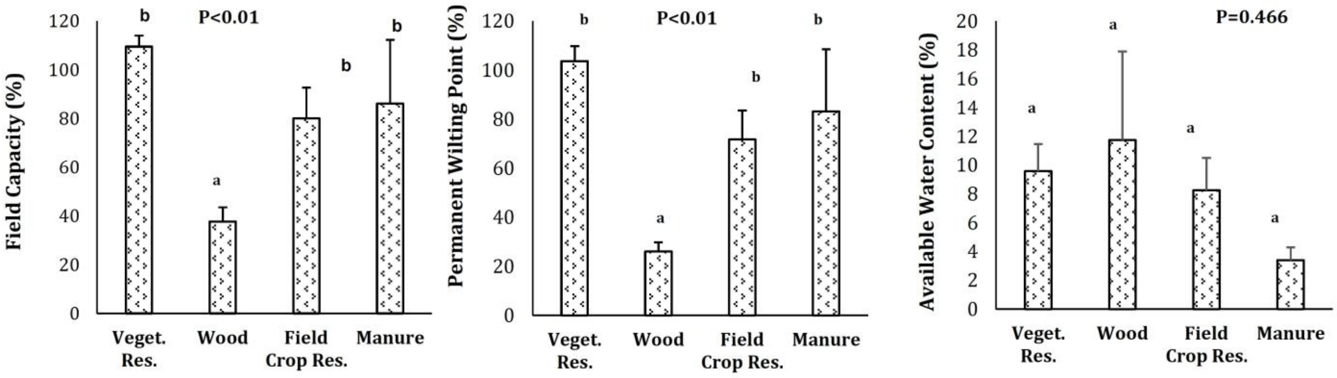

Figure 3. Field capacity (%) ± SE of means, permanent wilting point (%) ± SE of means and available water content (%) ± SE of means of biochar types (n=18). Any two means sharing different letters are statistically significant (P≤0.05)

Biochar types generated from animal manure had the lowest mean AW content (3.4%), while biochars of woody materials had the highest AW content (11.7%) (Figure 3). Pine sawdust biochars had significantly higher AW (39.8%) as compared to the rest of the biochars (mean AW was 9.25%). The AW contents of biochars produced from rosehip seed (1.1%), kidney bean (1.3%), rice husk (1.4%), ship manure (1.5%) and poplar sawdust (2.0%) were significantly lower than the other biochars (Table 1-4). In contrast to the high-water holding capacity of biochars produced in this study, Jeffery et al. (2015) reported that the biochars used in their study were highly hydrophobic and the strong hydrophobicity prevented water from infiltrating into the biochar particles, prohibiting an effect on soil water retention. Weber and Quicker (2018) indicated that hydrophobicity and water holding capacity have counteracting or overlapping effects, and the surface functional groups and the porosity of the biochar's bulk volume are responsible from the first and second factors, respectively. In another study conducted on a mesic Typic Hapludolls by Laird et al. (2010), the biochar amendment increased the water content held at gravity drained equilibrium (up to 15%), at – 1 and –5 bars soil water matric potential, (13 and 10% greater, respectively).

Table 4. Some of physical and chemical properties of biochar types produced from animal manure

	Yield, (wg),%	SSA, m^2g^{-1}	FC, %	WP, %	AW, %	pH	EC, dSm^{-1}	CEC, cmol kg^{-1}
Sheep Manure	36.80	161.3	58.1	57.7	1.5	11.82	15.37	36.0
Poultry Litter	31.83	192.9	78.7	56.1	22.6	11.60	5.00	58.0
Dairy Manure	*62.99*	163.7	32.8	29.7	3.1	10.57	4.01	40.0
	C, %	N, %	C:N	P in Row, g kg^{-1}	P in Bioc. , g kg^{-1}	K in Row, g kg^{-1}	K in Bioc., g kg^{-1}	
Sheep Manure	58.9	0.74	79.4	1.76	3.98	7.44	9.94	
Poultry Litter	58.8	0.88	66.6	*8.44*	*25.6*	25.90	44.46	
Dairy Manure	*35.9*	0.79	45.2	4.38	13.48	10.35	9.98	

EC: Electrical Conductivity, CEC: Cation Exchange Capacity, SA: Specific Surface Area, FC: Field Capacity, WP: Wilting Point, AW: Available Water Content; C: Total Carbon, N: Total Nitrogen, P: Phosphorus, K: Potassium

Carbon (C) and nitrogen (N) contents and C:N Ratio of biochar types

Total C contents of biochar types were significantly different (P<0.01) among feedstock groups. The C content of woody materials (87.03%) and field crop residues (73.90%) were significantly higher than biochars produced from vegetable residues (61.14%) and manures (51.20%) (Figure 4). Carbonization increased the total C content of pine sawdust to 91.9% and rosehip seed to 87.2%. The biochar became highly carbonaceous, with a C content ranging from 35.9% (dairy manure) to 91.9% (pine sawdust) (Table 4 and 2). The property of a biochar is a function of the feedstock origin, particle size, temperature and rate of temperature increase during pyrolysis, residence time, pressures, and conditions of the starting material (Guerro et al., 2005). Along with the C enrichment of biochars, Vaccari et al. (2011) stated that the carbon structures present in the biochar become highly resilient to the degradation by microorganisms. Therefore, the biochars with high C concentrations have capacity to store carbon for a long period of time contributing to mitigation of climate change. Lehmann et al. (2006) also indicated that biochar production from agricultural and forestry wastes or urban wastes have an estimated C sequestration capacity of 0.16 Pg C yr^{-1}.

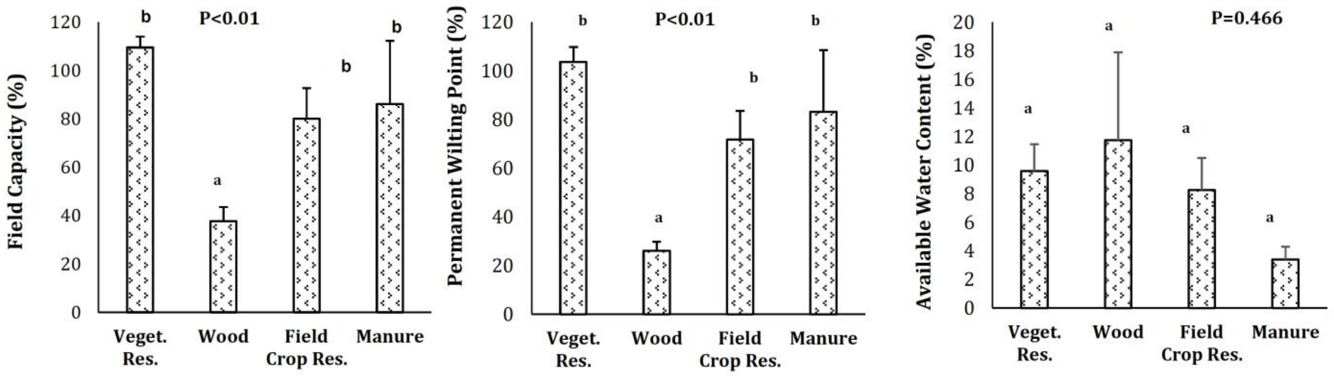

Figure 4. Total carbon (%) ± SE of means, total nitrogen (%) ± SE of means and carbon/nitrogen ratio of biochar types (n=18). Any two means sharing different letters are statistically significant (P≤0.05)

Nutrient-rich vegetable residues contained relatively more minerals than the other feedstocks, which decreased the C content. The feedstock type had no significant impact (P=0.054) on total N content of biochars. Mean total N content of biochars produced from manures (0.80%) were significantly higher than total N content of woody materials (0.50%) (Figure 4). The amount of total N conserved in biochars ranged from 0.26% (pine sawdust) and to 1.17% (eggplant) which was inversely proportional to the total C concentrations (Table 2 and 1). Although total C contents varied widely and immobilization of N depends on relative amounts of C sources and N availability, total N contents proved equally useful to estimate N availability.

The C:N ratio is an indication of the ability for an organic substrate to release inorganic N when mixed with a soil. The effect of feedstock type on C:N ratio was statistically significant ($P<0.01$). The mean C:N ratio for biochars of woody materials (232.3) was almost four times higher than biochars of manures and three times higher than biochars of vegetables residues (92.2) (Figure 4). In general, the C:N ratio of biochars varied between 42.6 and (cabbage) to 348.9 (pine sawdust) (Table 1 and 2). Mukome et al. (2013) also stated that biochars produced from feedstocks high in C content (woody) had high C:N ratio. Therefore, the type of feedstock has been considered the main predictor of C:N ratio of biochar. High C:N ratios may lead to N immobilization after application of biochars to soil. Pretreating the biochar prior to soil application with a nutrient rich source such as compost or dairy effluents (Ghezzehei et al., 2014; Wang et al., 2015; Cui et al., 2016) to adsorb N and excess nutrients lowers the C:N ratio of biochars. The C:N ratio of biochars had significant negative correlations with pH, EC and CEC and positive correlation with SSA of the biochar types (Table 5).

Available phosphorus and potassium contents of biochar types

The most important characteristics of biochar types affecting the short-term crop performance were reported as the nutrient contents such as phosphorus (P) and potassium (K) (Rajkovich et al., 2012). Mean P content of biochar groups was ranked as field crop residues (0.45 g kg^{-1}), woody materials (1.35 g kg^{-1}), vegetable residue (4.55 g kg^{-1}) and animal manures (6.25 g kg^{-1}) (Figure 5). Large variations of P and K concentrations in the feedstocks and biochars indicate that feedstock type plays a significant role ($P<0.01$) in regulating the nutrient contents of biochars (Table 5). Biochar types contained two to four times higher P than that of the raw materials. Higher contents of K and P in the biochar types compared with their feedstocks accord with the common observation that chemical components concentrate in the solid biochar phase during the pyrolysis of feedstock (Gaskin et al., 2008; Chan and Xu, 2009; Yuan et al., 2011). Gaskin et al. (2008) reported that about 60% of P in the poultry litter and pine sawdust and 100% of the P in peanut hulls feedstock were retained in the biochars produced at 500 °C. The P and K contents of the biochar types were significantly different ($P<0.05$) from each other. The P content varied from 0.05 g kg^{-1} (rice husk) to 25.6 g kg^{-1} (poultry litter) (Table 2 and 4). The concentration content was between 0.63 g kg^{-1} (pine sawdust) and 52.03 g kg^{-1} (gooseberry) (Table 2 and 1). Cantrell et al. (2012) also indicated that pyrolysis of manures rich in nutrients yield nutrient rich biochars.

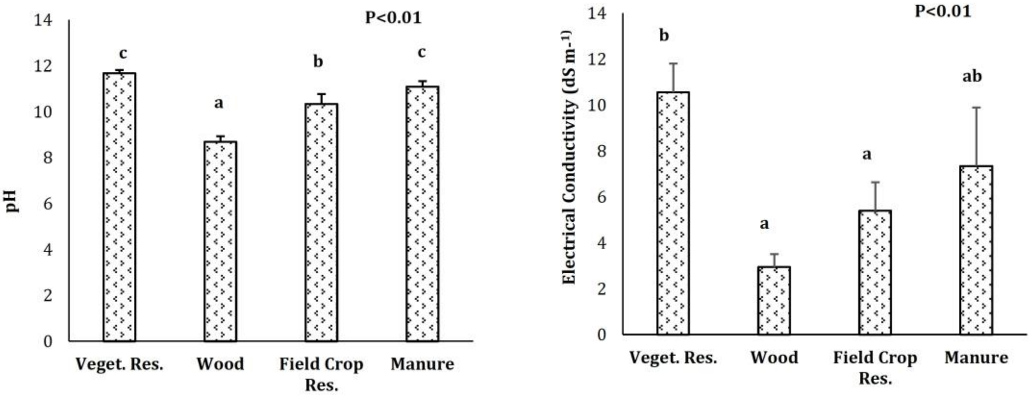

Figure 5. Available phosphorus (g kg^{-1}) ± SE of means and potassium (g kg^{-1}) ± SE of means contents of biochar types (n=18). Any two means sharing different letters are statistically significant ($P\leq0.05$)

Desorption of plant nutrients from biochar has direct benefits for plant growth. Initial desorption rate of minerals from biochar is quite rapid and followed by a zero-order reaction that continues as long as the system is far from chemical equilibrium (Silber et al., 2010). Poultry litter was rich in P (8.44 mg kg^{-1}) and K (25.90 mg kg^{-1}), however addition to soil in fresh form may create problems due to the diseases and pathogens in fresh manure (Chan et al., 2009). Application of poultry manure in biochar form eliminates the problems, and provides higher amount of P and K as well as N. The amounts of P (25.6 mg kg^{-1}) and K (44.46 mg kg^{-1}) in poultry biochar were very high and may replace conventional P and K fertilizers for many crops (Table 4). Considering the application rates of 5 and 10 ton biochar ha^{-1}, application of poultry biochar to soil will provide 128 kg P ha^{-1} to 256 kg P ha^{-1} and 222.3 kg K ha^{-1} to 444.6 kg K ha^{-1}. Mineral release rate of a biochar is important for the availability of nutrients in biochar. Silber et al. (2010) showed that P release of corn straw biochar produced at 500 °C significantly increased within 24 h as pH decreased from 8.9 to 4.5. The authors stated that a reasonable biochar application rate may successfully meet almost whole P need of a crop throughout the growing season. pH-dependent mineral release study of Silber et al. (2010) revealed that 1/3 of total K amount (48.7 g kg^{-1}) in the corn straw biochar was released during the first hour. The mean K content vegetable residue biochars (37.71 g kg^{-1}) is similar to that reported by Silber et al. (2010) and the significant amount of K release from the biochar may replace conventional K fertilizers for many of crops grown. However, as indicated by Silber et al. (2010), K release from the biochar will not adequately supply long-term plant K demand. In contrast to vegetable residues, biochars produced from woody biomass have lower K concentration (2.67 g kg^{-1}) and far from supplying the K demand of crops (Figure 5).

pH and electrical conductivity of biochar types

The pH and EC values of biochar types were significantly influenced by type of feedstock (P<0.01) (Figure 6). The pH value is the most important factor of a biochar in effectiveness of the agricultural applications (Weber and Quicker, 2018). The mean pH values of manures (11.1) and vegetable residues (11.7) were significantly higher than pH values of field crop residues (10.3) and woody materials (8.7) (Figure 6). All biochar types had a pH of 7.89 or greater, and the pH values ranged from slightly alkaline (pine sawdust, 7.89) to very strongly alkaline (gooseberry, 12.42) (Table 2 and 1). The addition of pine sawdust biochar to high pH biochar types may lower the pH value. Although only K concentrations of biochars have been analyzed among the alkali-earth elements, pine sawdust biochar had also the lowest concentrations of K. This could be the main reason for the lowest pH of the pine sawdust biochar. Significant positive linear correlation (r=0.86, P<0.01) between pH and K concentration of biochars supports the above discussion (Table 5). Fidel et al. (2012) also stated that the alkalinity of a biochar is influenced by organic functional groups, carbonates, and inorganic alkali composition. Low pH value of palm kernel shell (6.9) was attributed to the lowest concentrations of alkali and alkali-earth elements (Lee et al., 2013).

In many cases, biochars have been used to ameliorate acidic soils where alkalinity of biochar is favorable for improving the soil quality, and increasing the productivity of crops grown in acidic soils. Alkaline and strongly alkaline biochars may increase soil pH depending on the rate of application. However, Al-Wabel et al. (2017) indicated that biochar application in alkaline soils may not affect soil pH due to the buffering capacity of alkaline soils. Moreover, the concentration of basic sites was reported decreasing through oxidative interactions with microbes as biochar ages, thus a decrease in soil pH was obtained due to the oxidation of alkaline biochar (Liu et al., 2012). Therefore, biochars produced in this study can be used as soil additive without considering the alkalinity effect on soils.

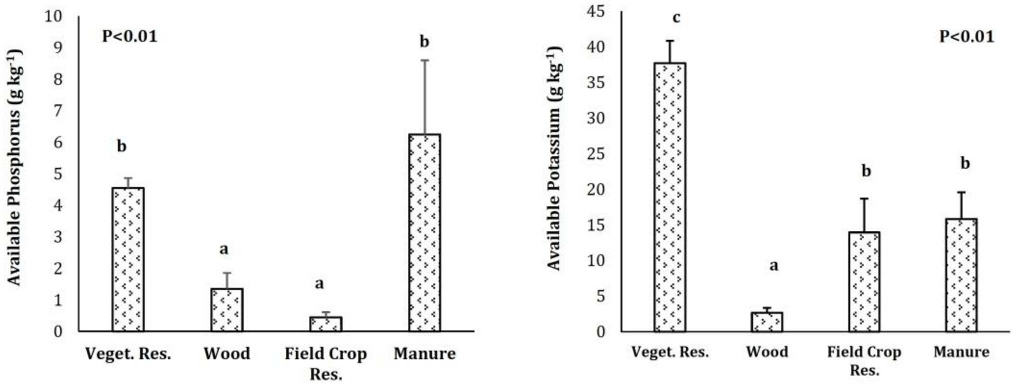

Figure 6. The pH and electrical conductivity (dS m^{-1}) ± SE of means of biochar types (n = 18). Any two means sharing different letters are statistically significant (P≤0.05)

Electrical conductivity (EC) values of biochar types should be determined to avoid salinity problems in soils, especially at high biochar application rates. The type of feedstock had significant (P<0.01) effect on EC of biochar types (Figure 6). The EC values of biochars produced from woody materials (2.95 dS m^{-1}) and field crop residues (5.39 dS m^{-1}) were significantly lower from the EC values of vegetable residue biochars (10.56 dS m^{-1}). The salinity of all biochars was high, with EC varying from 18.24 dS m^{-1} (cabbage) to 1.44 dS m^{-1} (poplar sawdust) (Table 1 and 2). The EC values of biochar types had significant positive correlations with pH, CEC, FC, WP, P and K, while it had significant negative correlations with SSA, total C and C:N ratio of biochars. The best predictor for biochar EC values was K producing r value of 0.60 (Table 5)

Relationships between physical and chemical properties of biochar types

Significantly linear relationships ($P<0.01$) were found between biochar pH values and all properties (except available water content) of 18 biochar types. Negative correlations indicated that surface area, total carbon content and C:N ratio of biochars were significantly decreased with increasing pH of biochars. Whereas, EC, CEC, FC and WP water contents available P and K concentrations significantly ($P<0.01$) increased with increased pH values of biochar types. The correlation analysis between the CEC and water contents of biochars at field capacity and wilting point showed a Pearson's correlation coefficients of 0.63 and 0.61 ($P<0.01$), indicating a significant positive correlation (Table 5). Surprisingly, SSA of biochars and water at FC and WP had significant negative correlations ($P<0.05$) which might be related to the loss of functional groups during pyrolysis process. High correlation of CEC with FC and WP also supports the negative correlations of SSA with FC and WP water contents of biochars.

Table 5. Correlations among some physical and biochemical characteristics of different biochar types

	pH	**EC**	**CEC**	**SSA**	**FC**	**WP**	**AW**	**Biochar%**
pH	1.00							
EC	0.69**	1.00						
CEC	0.83**	0.49**	1.00					
SSA	-0.65**	-0.52**	-0.70**	1.00				
FC	0.50**	0.48**	0.63**	-0.33*	1.00			
WP	0.53**	0.46**	0.61**	-0.32*	0.93**	1.00		
AW	0.25	0.29	0.32*	-0.19	0.27	0.01	1.00	
Biochar%	0.36*	0.16	0.29	-0.63**	-0.09	0.03	-0.12	1.000

	pH	**EC**	**CEC**	**SSA**	**C**	**N**	**C:N**	**P**	**K**
C	-0.62**	-0.41**	-0.59**	0.74**	1.00				
N	0.33*	0.30	0.32*	-0.37*	-0.39**	1.00			
C:N	-0.51**	-0.45**	-0.50**	0.59**	0.69**	-0.90**	1.00		
P	0.63**	0.36*	0.78**	-0.71**	-0.62**	0.52**	-0.68**	1.00	
K	0.86**	0.60**	0.87**	-0.56**	-0.56**	0.44**	-0.58**	0.67**	1.00

EC: Electrical Conductivity, CEC: Cation Exchange Capacity, SSA: Specific Surface Area, FC: Field Capacity, WP: Wilting Point, AW: Available Water Content, C: Total Carbon, N: Total Nitrogen, P: Phosphorus, K: Potassium

Positive correlation ($P<0.05$, $r= 0.74$) between SSA of biochars and total C content indicates that the higher the carbon content of the biochar the higher the surface area of the material. Biochar yields of feedstocks and SSA of biochar types had significant negative correlations ($P<0.01$). Lee et al. (2013) also reported very low SSA for cocopeat biochar (13.7 m^2 g^{-1}) despite its' the largest mass yield (45.9% dry ash free basis) among the biochars studied. The CEC and SSA of biochars had significant negative correlation ($P<0.01$, $r= -0.70$) (Table 5). The decrease of CEC with the increased SSA is probably related to the loss of functional groups during pyrolysis of feedstocks. Gaskin et al. (2008) found a considerable reduction of the CEC with an increase in SSA of biochars.

Conclusion

Physical and chemical properties of biochars, produced from several agricultural residues revealed that some of biochars might have many advantages in agriculture in terms of crop productivity and sustainability of soil fertility. Significant differences among biochars produced at the same pyrolysis temperature showed that the feedstock characteristics had the greatest influence on key agricultural characteristics of biochars. Application of biochar with high CEC, SSA and nutrient content can be considered an important additive to improve quality of soils with low CEC (particularly high sand content) and inadequate organic matter. Most of biochars (particularly woody materials and field crop residues) have higher SSA than sandy and comparable to or higher than clayey soils, therefore, water storage and nutrient holding capacities of sandy soils can be improved by the addition of biochars with high SSA.

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References

Al-Wabel, M.I., Hussain, Q., Usman, A.R., Ahmad, M., Abduljabbar, A., Sallam, A.S. Ok, Y.S., 2018. Impact of biochar properties on soil conditions and agricultural sustainability: A review. *Land Degradation & Development* 29(7), 2124-2161.

Barton, C.F., 1948. Photometric analysis of phosphate rock. *Analytical Chemistry* 20(11): 1068-1073.

Brewer, C.E., Schmidt-Rohr, K., Satrio, J.A., Brown, R.C. 2009. Characterization of biochar from fast pyrolysis and gasification systems. *Environmental Progress & Sustainable Energy* 28(3): 386-396.

Brewer, C.E. Unger, R., Rohr, K.S., Brown, R.C., 2011. Criteria to select biochars for field studies based on biochar chemical properties. *Bioenergy Research* 4(4): 312-323.

Brewer, C.E. (2012). Biochar characterization and engineering. PhD. Dissertation, University of Iowa. USA.

Cantrell, K.B., Hunt, P.G., Uchimiya, M., Novak, J.M., Ro, K.S., 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. *Bioresource Technology* 107: 419-428.

Chan, K.Y., Xu, Z., 2009. Biochar: Nutrient properties and their enhancement. In: Biochar for Environmental Management: Science and Technology. Lehmann, J., Joseph, S., (Eds). Earthscan, London, UK. pp.67-84.

Chapman, H.D., 1965. Cation exchange capacity. In: Methods of soil analysis Part 2 Chemical and Microbiological Properties. Black, C.A. (Ed.). Agronomy No. 9. ASA-SSSA, Madison, Wisconsin, USA. pp. 891–901.

Cheng, C., Lehmann, J., 2009. Ageing of black carbon along a temperature gradient, *Chemosphere* 75(8): 1021–1027.

Chu, G., Zhao, J., Huang, Y., Zhou, D., Liu, Y., Wu, M., Peng, H., Zhao, Q., Pan, B., Steinberg, C.E., 2018. Phosphoric acid pretreatment enhances the specific surface areas of biochars by generation of micropores. *Environmental Pollution* 240: 1-9.

Citak, S., Sonmez, S., Okturen, F., 2006. The possibility of using plant originated residues in agriculture. *Derim* 23(1): 40-53. [in Turkish]

Cerato, A.B., Lutenegger, A.J., 2002. Determination of surface area of fine-grained soils by the ethylene glycol monoethyl ether (EGME) method. *Geotechnical Testing Journal* 25(3): 315-321.

Cui, X., Hao, H., Zhang, C., He, Z., Yang, X., 2016. Capacity and mechanisms of ammonium and cadmium sorption on different wetland-plant derived biochars. *Science of the Total Environment* 539: 566-575.

Di Blasi, C., Tanzı, V., Lanzetta, M., 1997. A study on the production of agricultural residues in Italy. *Biomass and Bioenergy* 12(5): 321–331.

Di Donato, P., Fiorentino, G., Anzelmo, G., Tommonaro, G., Nicolaus, B., Poli, A., 2011. Re-use of vegetable wastes as cheap substrates for extremophile biomass production. *Waste and Biomass Valorization* 2(2): 103-111.

Downie, A., Crosky, A., Munroe, P., 2009. Physical properties of biochar. In: Biochar for Environmental Management: Science and Technology. Lehmann, J., Joseph, S., (Eds). Earthscan, London, UK. pp.13-32.

Fidel, R.B., 2012. Evaluation and ımplementation of methods for quantifying organic and ınorganic components of biochar alkalinity. MSc Thesis, Paper 12752, Iowa State University. USA.

Gaskin, J.W., Steiner, C., Harris, K., Das, K.C., Bibens, B. 2008. Effect of low-temperature pyrolysis conditions on biochar for agricultural use. *Transactions of the ASABE* 51(6): 2061-2069.

Gaskin, J.W., Speir, R.A., Harris, K., Das, K.C., Lee, R.D., Morris, L.A., Fisher, D.S., 2010. Effect of peanut hull and pine chip biochar on soil nutrients, corn nutrient status, and yield. *Agronomy Journal* 102(2): 623–633.

Ghezzehei, T.A., Sarkhot, D.V., Berhe, A.A., 2014. Biochar can be used to capture essential nutrients from dairy wastewater and improve soil physico-chemical properties. *Solid Earth* 5(2): 953-962.

Gray, M., Johnson, M.G., Dragila, M.I., Kleber, M. 2014. Water uptake in biochars: The roles of porosity and hydrophobicity. *Biomass and Bioenergy* 61: 196-205.

Guerro, M., Ruzi, M.P., Alzuet, M.U., Bilbao, R., Miller, A., 2005. Pyrolysis of eucalyptus at different heating rates: studies of char characterization and oxidative reactivity. *Journal of Analytical and Applied Pyrolysis* 74(1-2): 307-314.

Günal, H., Korucu, T., Birkas, M., Özgöz, E. Halbac-Cotoara-Zamfir, R. 2015. Threats to sustainability of soil functions in Central and Southeast Europe. *Sustainability* 7(2): 2161-2188.

Günal, E., Erdem, H. Çelik, İ., 2018. Effects of three different biochars amendment on water retention of silty loam and loamy soils. *Agricultural Water Management* 208: 232-244.

Herbert, L., Hosek, I., Kripalani, R., 2012. The characterization and comparison of biochar produced from a decentralized reactor using forced air and natural draft pyrolysis. California Polytechnic State University, San Luis Obispo Materials Engineering Department.

Hossain, M.K., Strezov, V., Chan, K.Y., Ziolkowski, A., Nelson, P.F., 2011. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *Journal of Environmental Management* 92(1): 223-228.

Jeffery, S., Meinders, M.B., Stoof, C.R., Bezemer, T.M., van de Voorde, T.F., Mommer, L., van Groenigen, J.W., 2015. Biochar application does not improve the soil hydrological function of a sandy soil. *Geoderma* 251-252: 47-54.

Kanthle, A.K., Lenka, N.K., Tedia, K., 2018. Land use and biochar effect on nitrate leaching in a Typic Haplustert of central India. *Catena* 167: 422-428.

Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B., Karlen, D.L., 2010. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* 158(3-4): 443-449.

Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y.K., Jung, J., Hyun, S., 2013. Comparison of biochar properties from biomass residues produced by slow pyrolysis at 500 °C. *Bioresource Technology* 148: 196-201.

Lehmann, J., Gaunt, J., Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems – a review. *Mitigation and Adaptation Strategies for Global Change* 11(2): 403–427.

Lehmann, J., Joseph, S., 2009. Biochar for Environmental Management. Science and Technology, Earthscan, London, UK.

Lim, T.J., Spokas, K.A., Feyereisen, G., Novak, J.M., 2016. Predicting the impact of biochar additions on soil hydraulic properties. *Chemosphere* 142: 136-144.

Liu, X.H., Han, F.P., Zhang, X.C., 2012. Effect of biochar on soil aggregates in the Loess Plateau: Results from incubation experiments. *International Journal of Agriculture and Biology* 14(6): 975-979.

Mukome, F.N.D., Zhang, X., Silva, L.C.R., Six, J., Parikh, S.J., 2013. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *Journal of Agricultural and Food Chemistry* 61(9): 2196-2204.

Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A.R., Lehmann, J., 2012. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils* 48(3): 271-284.

Oldfield, T.L., Sikirica, N., Mondini, C., López, G., Kuikman, P.J., Holden, N.M., 2018. Biochar, compost and biochar-compost blend as options to recover nutrients and sequester carbon. *Journal of Environmental Management* 218: 465-476.

Schellekens, J., Silva, C.A., Buurman, P., Rittl, T.F., Domingues, R.R., Justi, M., Vidal-Torrado, P., Trugilho, P.F., 2018. Molecular characterization of biochar from five Brazilian agricultural residues obtained at different charring temperatures. *Journal of Analytical and Applied Pyrolysis* 130: 106-117.

Silber, A., Levkovitch, I., Graber, E.R., 2010. pH-dependent mineral release and surface properties of corn straw biochar: agronomic implications. *Environmental Science & Technology* 44(24): 9318-9323.

Smith, P., 2016. Soil carbon sequestration and biochar as negative emission technologies. *Global Change Biology* 22(3): 1315-1324.

Sposito, G. 1989. The chemistry of soils. Oxford Univ. Press, New York, USA.

Vaccari, F.P., Baronti, S., Lugato, E., Genesio, L., Castaldi, S., Fornasier, F., Miglietta, F., 2011. Biochar as a strategy to sequester carbon and increase yield in durum wheat. *European Journal of Agronomy* 34(4): 231-238.

Wang, B., Lehmann, J., Hanley, K., Hestrin, R., Enders, A. 2015. Adsorption and desorption of ammonium by maple wood biochar as a function of oxidation and pH. *Chemosphere* 138: 120-126.

Weber, K. Quicker, P., 2018. Properties of biochar. *Fuel* 217: 240-261.

Yuan, J.H., Xu, R.K., Zhang, H., 2011. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresources Technology* 102(3): 3488-3497.