

Article



# Using Agricultural Residue Biochar to Improve Soil Quality of Desert Soils

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**Abstract:** A laboratory study was conducted to test the effects of biochars made from different feedstocks on soil quality indicators of arid soils. Biochars were produced from four locally-available agricultural residues: pecan shells, pecan orchard prunings, cotton gin trash, and yard waste, using a lab-scale pyrolyzer operated at 450 °C under a nitrogen environment and slow pyrolysis conditions. Two local arid soils used for crop production, a sandy loam and a clay loam, were amended with these biochars at a rate of 45 Mg· ha<sup>-1</sup> and incubated for three weeks in a growth chamber. The soils were analyzed for multiple soil quality indicators including soil organic matter content, pH, electrical conductivity (EC), and available nutrients. Results showed that amendment with cotton gin trash biochar has the greatest impact on both soils, significantly increasing SOM and plant nutrient (P, K, Ca, Mn) contents, as well as increasing the electrical conductivity, which creates concerns about soil salinity. Other biochar treatments significantly elevated soil salinity in clay loam soil, except for pecan shell biochar amended soil, which was not statistically different in EC from the control treatment. Generally, the effects of the biochar amendments were minimal for many soil measurements and varied with soil texture. Effects of biochars on soil salinity and pH/nutrient availability will be important considerations for research on biochar application to arid soils.

Keywords: biochar; arid soils; cotton gin trash; pecan shells; orchard prunings; soil salinity

## 1. Introduction

Soil quality is "the capacity of a specific kind of soil to function, within natural or managed ecosystem boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and support human health and habitation" [1]. Generally, arid soils have poor quality due to very low levels of soil organic matter [2]. Organic matter is very central to the quality of any soil [3]. The organic matter levels of arid soils, particularly in New Mexico where this study was conducted, are often less than 1% [4]; to improve the soil organic matter, considerable efforts are needed to add organic materials to the soil. Traditional ways for improving soil organic matter, such as cover cropping, leaving crop residues after harvest, and applying manure, are often difficult to achieve in arid soils due to water availability and salinity [5]. For example, cover cropping has been very challenging for farmers in the arid desert southwest of the United States due to the reduced amounts of available water for agriculture [6]. This region has suffered severe drought over several years and using scarce water for raising cover crops is perceived by many growers as uneconomical.

In order to improve soil organic matter of arid soils, innovative methods that will not compete with water for crop production need to be developed. One such innovative method is to convert locally available waste biomass materials into biochar for soil application. Biochar is a predominantly recalcitrant organic carbon (C) material, created when biomass is heated to temperatures between 300 °C and 1000 °C under low oxygen concentrations (*i.e.*, pyrolysis) [7]. Since the organic carbon produced in biochar is very stable, addition of biochar to the soil has the potential to both improve soil quality and sequester carbon, which is important for mitigation of excessive carbon dioxide in the atmosphere [8]. Biochar application to the soil has been shown by different studies to have significant impacts on several soil quality parameters [9–12]. Positive impacts of biochar amendment on soils include:

- (i) increasing soil capacity to sorb plant nutrients, consequently reducing leaching losses of nutrients [13,14];
- (ii) decreasing soil bulk density, leading to less-compacted soil conditions favorable for root growth and water permeability [15];
- (iii) increasing the soil cation exchange capacity [16];
- (iv) increasing soil microbial activity and diversity [17,18];
- (v) increasing plant available water retention [15,19]; and
- (vi) increasing crop yields [20,21].

From a biomass systems engineering perspective, using available biomass resources to meet the community's needs is critical to ecological sustainability. In arid agricultural communities, crop residues are often the primary available biomass feedstock and fresh water is often the primary need. Biomass can be used to help meet water needs in several ways, including providing the energy needed for water treatment. A way in which biomass for water treatment and biomass for soil amendments can be combined is to use slow pyrolysis to produce thermal energy for brackish groundwater desalination and biochars for application to agricultural soils.

New Mexico state usually ranks 3rd for pecan production in the United States with >17,000 pecan orchards covering more than 15,800 ha. Doña Ana County is New Mexico's highest pecan producing county at approximately 19,500 Mg· year<sup>-1</sup> [22]. Pecan production creates two residual biomass streams: pecan shells and pecan orchard prunings (leaves, branches, *etc.*). Estimates of the amount of pecan shells available from the New Mexico/western Texas pecan industries range from 14,000 to 26,000 Mg· year<sup>-1</sup>; some of these shells have been used in horticulture as mulch and alternative potting media [23]. Estimates of orchard pruning residues available from the Mesilla Valley region of New Mexico range from 11,000–37,000 Mg· year<sup>-1</sup> on a dry basis. Air quality restrictions have caused pecan farmers to look for alternatives to conventional open-air pruning residue burning [24].

After harvest and prior to textile production, cotton bolls must be ginned to remove the seeds (used to make cottonseed oil and cottonseed meal) and other non-lint materials. The non-seed, non-lint materials, such as stems, leaves and dirt, are collectively referred to as cotton gin trash. An average of 68 kg of gin trash is generated for each 218 kg bale of cotton. In 2013, approximately 12,000 ha of cotton were grown in New Mexico at an average yield of 0.89 bales/ha, resulting in over 725,000 Mg of cotton gin trash [25].

Many municipalities collect tree branches, grass clippings, garden residues, and other yard wastes from residential and commercial properties for composting, mulching, and other uses. The City of Las Cruces, New Mexico (population approximately 100,000) receives 1800–2700 Mg· year<sup>-1</sup> of wet green waste for processing into compost (Lisa LaRocque, City of Las Cruces Sustainability Officer, 23 September 2013). This represents a significant source of biomass that could be used for pyrolysis, especially for municipalities that are looking for alternative, higher-value uses for yard waste.

Pyrolysis of locally available waste biomass can help produce energy that can potentially be used for desalination of increasingly salty well waters used for irrigation and, at the same time, improve soil quality through the application of biochars. Exploration of the water desalination potential is the topic of another study. The objectives of the current study were to:

(i) Evaluate the yields and properties of biochars from four different local feedstocks (pecan shells, pecan orchard prunings, urban yard waste, and cotton gin trash).

(ii) Assess the impacts of biochar amendments on multiple soil quality indicators in two different soil textures (sandy loam and clay loam).

#### 2. Experimental Section

#### 2.1. Biomass Feedstocks

Four feedstocks were selected to represent underutilized biomass available locally. All feedstocks were air dried and stored in sealed buckets prior to pyrolysis.

Pecan (*Carya illinoinensis* (Wangenh.) K. Koch) orchard prunings (PP) were collected from the NMSU Leyendecker Plant Science Center in Las Cruces, NM, USA. Prunings consisted primarily of small branches and twigs, with some leaf material. Prunings were allowed to dry in the field, then were collected and chipped in a standard yard waste chipper. Pecan shells (PS) were collected from a local pecan processing facility and were used as received.

Cotton (*Gossypium hirsutum* L.) gin trash (CGT) was collected from Mesa Farmers Coop Cotton Gin in Vado, NM, USA. The gin trash contained mostly cotton leaf and stem pieces, with noticeable amounts of lint and seed residues, and dust particles.

Yard waste (YW) was collected from the NMSU green waste yard on 17 April 2014. The waste consisted primarily of freshly cut and chipped wood waste from tree pruning around campus, with a small amount of mixed leaves, shrubs, and grasses collected from maintenance of xeriscaped areas.

#### 2.2. Biochar Preparation

Biochars were produced from the four biomass feedstocks using a custom-built, lab-scale slow pyrolysis system. The system consists of a GHA 12/450 single zone horizontal tube furnace (Carbolite, Hope Valley, UK) sized to fit a 5.5 inch (14 cm) O.D. 304 stainless steel reaction tube with a 1/4 inch (6 mm) wall thickness. The programmable furnace provided an 18 inch (46 cm) heated zone. Inside the reaction tube, two circular 303 stainless steel plates with large holes were held in place with screws; 304 stainless steel 40-mesh wire cloth was placed between the plates on the biomass side to contain the biomass particles while allowing for gas flow. End caps for the reaction tube, with high temperature glass-mica ceramic O-rings, were held in place by clamps. One end cap contained openings for a thermocouple (Super OMEGACLAD XL, Omega Engineering Inc., Stamford, CT, USA) and a nitrogen gas inlet. A handheld data logger (OM-EL-ENVIROPAD-TC, Omega Engineering Inc., Stamford, CT, USA) was connected to the thermocouple to record the temperature of the biomass every 5 min. Pyrolysis vapors exited through the other end cap into a 0.95 cm O.D. tube maintained at 300 °C by heat tape (XtremeFLEX BWH, BriskHeat Corp, Columbus, OH, USA) with a temperature controller (SDC Digital Benchtop, BriskHeat Corp., Columbus, OH, USA) to prevent early vapor condensation and clogs. Vapors were bubbled through approximately 700 mL of distilled water in a large, glass Erlenmeyer flask set in an ice bath. The entire pyrolysis system was operated within a fume hood.

Biomass (200–250 g) was loaded into the reaction tube between the perforated plates. The furnace was heated at a rate of 5  $^{\circ}$ C·min<sup>-1</sup> to 450  $^{\circ}$ C and maintained at 450  $^{\circ}$ C for 60 min, after which the furnace and heat tape were turned off and the system allowed to cool overnight. An inert atmosphere was maintained by flowing nitrogen gas through the reactor at a rate of 1.0 L·min<sup>-1</sup>. Once the biochar had cooled to room temperature, the reactor was disassembled and the biochar removed, weighed, and stored in sealed containers. Bio-oil yields were estimated from the change in mass in the water condenser; this yield did not include the non-trivial amounts of tar that had condensed inside the pyrolyzer and exit tubing. Non-condensable gas (plus tar) yield was estimated by difference. The reactor was cleaned by placing the reaction tube in the tube furnace without the end caps and heating the tube to 600  $^{\circ}$ C for an hour to burn off tar residues.

### 2.3. Biomass and Biochar Characterization

Moisture content of the biomass feedstocks and biochars was measured by heating ground samples in an oven at 105 °C for 2 h. Ash content was measured by heating 0.5 g of sample in a muffle furnace to 575 °C and 750 °C for 6 h for biomass and biochar, respectively. Ash measurements were done in duplicate. Methods were based on ASTM E1755-01(2007) [26] and ASTM D1762-84(2007) [27]; 0.5 g samples were used instead of 1.0 g due to limited amounts of sample. Higher heating values (HHV) of the biomass feedstocks and biochars were determined in duplicate using a Model 6725 semi-micro bomb calorimeter (Parr Instrument Co., Moline, IL, USA). Mineral oil of known energy content was used as a spike for samples which did not easily ignite in order to ensure complete combustion. Elemental content of the biochars was measured in triplicate using a 2400 Series II CHNS

#### 2.4. Biochar-Amended Soil Incubation

Elemental Analyzer (Perkin Elmer, Waltham, MA, USA).

Two local arid soils used for agriculture, a sandy loam and a clay loam, were amended with the biochars at a rate of 45 Mg· ha<sup>-1</sup> and incubated for three weeks in a growth chamber. The sandy loam soil (a Thermic Typic Torrifluvents [28]) was collected from the NMSU Fabian Garcia Agriculture Experiment Station in Las Cruces, NM, USA (32°27′998″ N; 106°77′163″ W). The clay loam soil (a Thermic Vertic Torrifluvents [28]) was collected from the NMSU Leyendecker Plant Science Center in Las Cruces, NM, USA (32°20′238″ N, 106°74′277″ W). Las Cruces, NM has an arid climate with mean annual rainfall of about 160 mm. The average high temperature is 25 °C and the average low temperature is 8.5 °C. Soil properties of the soils are shown in Table 1.

**Table 1.** Soil quality measurements of original soils including pH, electrical conductivity (EC), permanganate-degradable (Walkley-Black) soil organic matter (SOM), cations (Na, Ca, Mg), calculated sodium adsorption ratio (SAR), and extractable macronutrients (NO<sub>3</sub>-N, P, K) and micronutrients (Cu, Mn, Fe, Zn).

Soil	рН	EC (dS·m <sup>-1</sup> )	SOM (g· kg <sup>-1</sup> )	Na (mg∙ kg <sup>-1</sup> )	Ca (mg· kg <sup>-1</sup> )	Mg (mg⋅ kg <sup>-1</sup> )	SAR
Sandy Loam	7.3	1.49	0.76	1.77	4.54	1.36	1.03
Clay Loam	7.1	5.94	1.13	16.75	39.48	8.18	3.43
	$NO_3-N$ (mg· kg <sup>-1</sup> )	Olsen P (mg· kg <sup>−1</sup> )	K (mg· kg <sup>-1</sup> )	Cu (mg⋅ kg <sup>-1</sup> )	Mn (mg· kg <sup>-1</sup> )	Fe (mg∙ kg <sup>-1</sup> )	Zn (mg· kg <sup>-1</sup> )
Sandy Loam Clay Loam	14.2 132.1	10.1 13.1	31.4 56.7	0.87 1.27	4.56 8.37	3.51 5.78	0.91 0.75

Biochars were ground to pass a 2 mm sieve prior to addition to the soil. Soil samples were thoroughly mixed then packed into pots. Soils were first slowly saturated with water then allowed to drain for 24 h, after which they were placed into a growth chamber for 3 weeks. About 100 cm<sup>3</sup> of water was added twice a week to prevent the soil from drying out. The temperature of the growth chamber was set at a day temperature of 28 °C and a night temperature of 20 °C.

#### 2.5. Soil Quality Assessments

Soil chemical analyses were conducted on the biochars and the biochar-amended soils after incubation using standard procedures. The pH, electrical conductivity, calcium, magnesium, sodium, and sodium adsorption ratio of the soils were measured using the filtered solution from a saturated paste preparation [29]. Soil organic matter (SOM) was measured using the Walkley-Black method [30]. Sodium bicarbonate-extractable phosphorus (Olsen P) [31] and potassium were measured by inductively coupled plasma (ICP) spectroscopy [32]. Nitrate-N concentration was measured by water extract using a cadmium reduction column [33]. Copper, iron, manganese and zinc

micronutrients were measured by DTPA extract and analyzed by ICP [33]. These soil measurements are all important to crop growth and production of the study region.

#### 2.6. Statistical Data Analysis

The experimental design for the biochar soil amendment trial was a randomized complete block design, with treatment combinations replicated four times. Experimental treatments consisted of biochars from the four feedstocks (pecan shells (PS), pecan prunings (PP), yard waste (YW) and cotton gin trash (CGT)) and a control treatment with no biochar addition, tested in two soil types (sandy loam and clay loam), for a total of 10 treatment combinations. Analysis of variance was performed on soil measurements and the means of the treatment values were separated using the Student Newman Keuls test after a significant *F*-ratio.

#### 3. Results and Discussion

#### 3.1. Biochar Yields and Characteristics

Pyrolysis product yields, and biomass and biochar characteristics are shown in Table 2. There was a lag of approximately 25–50  $^{\circ}$ C during pyrolysis between the biomass temperature and the furnace set temperature due to heat transfer limitations; the actual highest heating temperatures were 433, 423, 425, and 419 °C for PS, PP, CGT, and YW, respectively. Biochars retained the particle size distribution and shape of the biomass feedstocks. Biochars were uniformly black in color, had little or no perceivable odor, and left no oily residue when smeared; these observations are consistent with complete biomass conversion. One exception was the cotton gin trash biochar, which had some interspersed dark brown particles, especially in the shape of the cotton lint residues, suggesting a slightly less severe pyrolysis intensity [34]. The cotton gin trash feedstock also had a significantly higher ash content (13% on a feedstock weight basis, compared to 1%-5%), which resulted in a higher biochar yield (42%, compared to 28%–35%), higher biochar ash content (32%, compared to 4%–19%) and lower biochar HHV (24 MJ  $kg^{-1}$ , compared to 31–32 MJ  $kg^{-1}$ ); these results indicate that the feedstock's mineral matter was concentrated in the biochar ash fraction and that the biomass contained a notable amount of soil. The biomass feedstock pyrolysis properties, yields, and higher heating values were consistent with other biomass slow pyrolysis processes. The collected bio-oil yields (11%–18%) were lower, and the non-condensable gas (NCG) yields higher, than would generally be expected for this slow pyrolysis temperature since the tars coating the reactor and exit plumbing were not measured and thus were included in the NCG estimation.

Sample	Biochar Yield (%)	Bio-Oil Yield (%)	NCG + Tar Yield (%)	Moisture (%)	Ash (%)	HHV (MJ $\cdot$ kg <sup>-1</sup> )
Pecan shell	_	_	_	5.8	$1.5\pm0.3$	$18\pm0.5$
Pecan prunings	-	_	-	5.7	$2.9\pm0.2$	$23\pm3$
Cotton gin trash	-	-	-	6.1	$13 \pm 1$	$17 \pm 1$
Yard waste	-	-	-	4.2	$4.9 \pm 0.3$	$22 \pm 2$
Pecan shell biochar	28	18	54	3.9	$4.4\pm0.1$	$31 \pm 1$
Pecan prunings biochar	35	13	52	4.3	$11.3\pm0.1$	$31 \pm 2$
Cotton gin trash biochar	42	11	57	3.3	$32 \pm 4$	$24\pm3$
Yard waste biochar	32	17	51	2.4	$19\pm2$	$32 \pm 4$

**Table 2.** Yields of biochar, collected bio-oil, non-condensable gases (NCG) and uncollected tars from biochar production, reported on a wet feedstock basis.

Moisture content and higher heating values (HHV) of biomass feedstocks and biochars, and yields, reported on a wet weight basis; ash content reported a dry weight basis;  $\pm$  is standard deviation where n = 2.

Tables 3 and 4 show the chemical characteristics and the extractable soil nutrients of the biochars. Again, the cotton gin trash biochars had noticeably different properties than the other biochars including higher EC (44 dS·m<sup>-1</sup> compared to 2–3 dS·m<sup>-1</sup>), higher degradable organic carbon content

(24% compared to 1%–8%), lower total carbon content (55% compared to 72%–83%), higher total nitrogen content (2.3% compared to 0.8%–1.1%), and higher sodium, calcium, magnesium, nitrate, extractable phosphorus, and potassium contents (Tables 3 and 4). The high EC is consistent with the high levels of salts in the cotton gin trash biochar; the higher levels of plant nutrients, especially nitrate, may be the result of the amount of leaf material and the presence of the soil/dust particles in the feedstock. The low amounts of organic carbon for all of the biochars, compared to the total carbon (Table 4), relates to the recalcitrant nature of the condensed aromatic carbon structures in the biochars since these structures are unlikely to degrade completely under the Walkley-Black digestion conditions.

**Table 3.** Chemical characteristics of biochars including pH, electrical conductivity (EC), permanganatedegradable (Walkley-Black) organic carbon, and CHNS elemental content.

Biochar	pН	EC (dS· $m^{-1}$ )	Walkley-Black Org C (%)	C (%)	H (%)	N (%)	S (%)
PS	8.2	2.98	$1.5\pm0.2$	$76.0\pm1.1$	$3.07\pm0.01$	$0.77\pm0.04$	$1.72\pm0.24$
PP	9.5	2.66	$7.5\pm2$	$71.9\pm0.8$	$3.50\pm0.10$	$1.09\pm0.71$	$1.96\pm0.12$
CGT	8.4	44.6	$24\pm 0$	$55.4\pm3.0$	$2.75\pm0.17$	$2.29\pm0.09$	$1.84\pm0.02$
YW	9.7	2.01	$4.4\pm0.5$	$83.2\pm1.2$	$3.55\pm0.04$	$1.02\pm0.22$	$1.61\pm0.13$

Pecan shell (PS), pecan prunings (PP), cotton gin trash (CGT) and yard waste (YW);  $\pm$  is standard deviation where n = 2 for organic C and n = 3 for elemental contents.

**Table 4.** Extractable macronutrients (NO<sub>3</sub>-N, P, K) and micronutrients (Cu, Mn, Fe, Zn), cations (Na, Ca, Mg), and calculated sodium adsorption ratio (SAR) in biochars.

Biochar	NO <sub>3</sub> -N	Olsen P	К	Cu	Mn	Fe	Zn	Na	Ca	Mg	SAR
$(mg \cdot kg^{-1})$											
PS	0.32	12.0	330.3	0.65	33.2	3.28	13.21	0.42	0.74	1.01	0.45
PP	0.43	72.3	562.3	0.61	4.48	0.08	10.69	6.45	2.81	1.93	4.19
CGT	6.2	866.4	26,360	0.53	2.45	0.49	8.20	18.91	35.09	40.43	3.08
YW	0.57	65.8	640.4	1.00	3.99	0.37	13.37	1.20	1.08	0.37	3.99

Pecan shell (PS), pecan prunings (PP), yard waste (YW) and cotton gin trash (CGT).

#### 3.2. Biochar-Amended Soil Quality

Mean values of soil quality indicator measurements are presented in Tables 5 and 6. The results were analyzed separately according to soil textures.

**Table 5.** Soil quality measurements of biochar-amended soils including pH, electrical conductivity (EC), permanganate-degradable (Walkley-Black) soil organic matter (SOM), cations (Na, Ca, Mg), and calculated sodium adsorption ratio (SAR).

Soil	Biochar Treatment	pН	EC (dS·m <sup>-1</sup> )	$\frac{SOM}{(g \cdot kg^{-1})}$	Na (mg∙ kg <sup>-1</sup> )	Ca (mg· kg <sup>-1</sup> )	Mg (mg· kg <sup>-1</sup> )	SAR
	Control	7.45	1.45 a	0.55 a	8.3 a	5.0 a	1.4 a	4.5 b
	PS	7.48	1.28 a	0.49 a	6.6 a	4.9 a	1.2 a	3.7 ab
Sandy loam	PP	7.40	2.00 a	0.51 a	9.5 a	8.8 a	2.6 a	3.9 ab
	CGT	7.41	7.12 b	1.16 b	17.0 b	49.6 b	16.3 b	2.9 a
	YW	7.43	1.25 a	0.65 a	6.7 a	4.8 a	1.4 a	3.8 ab
		ns						
	Control	6.90 a	6.86 a	1.19 a	23.5 a	47.2 a	13.8 a	4.3 a
Class	PS	7.03 ab	7.47 a	1.20 a	28.4 a	52.0 a	15.4 a	4.9 ab
loam	PP	6.88 a	15.5 c	1.24 a	62.9 c	133 c	35.3 b	6.9 c
	CGT	7.08 b	9.12 ab	1.89 b	35.2 ab	64.5 ab	23.0 a	5.3 b
	YW	6.90 a	12.0 b	1.33 a	44.5 b	94.9 b	24.7 a	5.7 b

Pecan shell (PS), pecan prunings (PP), yard waste (YW) and cotton gin trash (CGT). Data are separated by soil type and data entries in the same column labeled with different letters exhibited statistically significant differences (p < 0.05, n = 4); ns: not significant at p < 0.05.

Soil	Biochar Treatment	NO <sub>3</sub> -N	Olsen P	К	Cu	Mn	Fe	Zn		
		$(\mathrm{mg}\cdot\mathrm{kg}^{-1})$								
	Control	3.7	6.0 a	26 a	1.2	3.4 a	2.7 b	0.86 a		
	PS	2.5	6.1 a	34 a	1.1	6.1 b	2.8 b	0.88 a		
Sandy loam	PP	2.7	7.1 a	43 a	1.0	8.4 c	2.6 ab	1.12 b		
	CGT	0.8	25 b	361 b	0.9	11.6 d	2.4 a	1.08 b		
	YW	1.9	6.4 a	35 a	1.2	8.7 c	2.5 ab	0.90 a		
		ns			ns					
	Control	136 a	12 a	60 a	2.3	4.5 a	3.4 b	0.88		
	PS	138 a	13 a	70 a	1.6	7.0 b	3.6 b	0.95		
Clay loam	PP	759 с	12 a	113 c	2.1	7.5 bc	2.5 a	1.19		
	CGT	1 a	28 b	252 d	1.7	8.2 cd	2.8 a	1.07		
	YW	466 b	13 a	92 b	1.5	8.8 d	2.7 a	1.94		
					ns			ns		

**Table 6.** Extractable macronutrients (NO<sub>3</sub>-N, P, K) and micronutrients (Cu, Mn, Fe, Zn) of original and biochar-amended soils.

Pecan shell (PS), pecan prunings (PP), yard waste (YW) and cotton gin trash (CGT). Data are separated by soil type and data entries in the same column labeled with different letters exhibited statistically significant differences (p < 0.05, n = 4); ns: not significant at p < 0.05.

#### 3.2.1. Coarse Textured Soil (Sandy Loam)

While pH did not show a significant difference with biochar treatment (Table 5), the trends of the biochar treatment impact on soil EC, SOM, Na, Ca, and Mg were similar across the coarse textured soil samples. CGT led to significantly higher EC, SOM, Na, Ca, and Mg compared to the control and the other biochar treatments (Table 6). The EC increase in the sandy soil amended with CGT (7.12 dS·m<sup>-1</sup>) is of a great concern and implies that biochar produced from CGT may lead to high salinity. Since salinity management is very critical to the success of the cropping systems in the desert southwest region, it is important to avoid addition of materials that exacerbate salinity problems. Although the SOM was significantly increased by the CGT in sandy soil, the corresponding increase in salinity will likely limit the use of CGT biochar. SAR gave significant differences in the sandy soil, but these values were well below the SAR level at which sodicity becomes a problem (SAR > 13).

While NO<sub>3</sub>-N was not significantly affected by different biochars, both P and K were significantly increased by the biochar from CGT (Table 6). Amending sandy soil with CGT biochar led to a P increase of about 4.2 times and a K increase of about 13.9 times compared with the control treatment. These increases are considerable in terms of nutrient additions to the soil. For micronutrients, Cu was not significantly affected by the biochar treatments, but Mn was significantly increased by the biochar treatments relative to the control (Table 6). There were statistical significant differences in Fe for the coarse textured soil, however, these differences do not have crop management significance since all the Fe values measured were in the medium range based on soil nutrient sufficiency levels for arid soils [35]. Addition of CGT and PP biochars led to significantly higher Zn level moved to the high range with the addition of CGT and PP biochars, while it stayed in the medium range for the control, PS and YW biochar treatments [35].

#### 3.2.2. Fine Textured Soil (Clay Loam Soil)

In the fine textured soil, the CGT led to slightly higher pH (7.08) compared to the control treatment (pH = 6.90, see Table 5). This slight rise in pH was statistically significant yet would not have much management significance since nutrient availability, which is governed by soil pH, would be similar within the range of pH differences measured in this experiment. EC in the fine textured soil was highest with PP biochar amendment (15.5 dS·m<sup>-1</sup>) followed by YW biochar (12.0 dS·m<sup>-1</sup>) and CGT biochar

(9.12 dS·m<sup>-1</sup>); these high EC levels show the need for caution in using these biochars in clay soils since high EC can limit crop productivity and act as a yield constraint. Similar to the sandy soil results, CGT led to a significant increase in SOM. Na, Ca, and Mg concentrations were also affected by biochar treatments, with PP biochar-amended soils having the highest concentrations of these elements.

NO<sub>3</sub>-N levels were generally very high in the fine textured soil relative to the coarse textured soil, except for the CGT treatment, which was very low (Table 6). NO<sub>3</sub>-N was significantly highest under the PP biochar treatment followed by YW. The reason for the very low level of NO<sub>3</sub>-N for CGT treatment in fine textured soil is not clear, however, similar observation was made in the coarse textured soil in which the NO<sub>3</sub>-N was quantitatively the lowest, though not significantly different. One possible explanation is that the CGT contained sufficient quantity of labile carbon such that soil microbial decomposition of the labile carbon led to immobilization of plant-available nitrogen [36]; this possibility is supported by the observation of some dark brown rather than black components of the CGT biochar, the higher level of Walkley-Black organic carbon in the CGT biochar compared to the other biochars, and the decrease in nitrate-N from the content in the biochar before incubations to the content in the soil after incubation.

Similar to the coarse textured soil, the CGT treatment had the highest P and K levels (Table 6) suggesting the possibility of nutrient additions to the soil through biochar produced from CGT. For micronutrients in the fine textured soil, Cu and Zn did not give any significant treatment effects, while Mn was highest in YW biochar treatment and Fe was highest in PS treatment. Such increases in Fe and Mn may not have significant crop management effects, however, since the measurements for all treatments belong to the same crop management ranges (medium for Fe and high for Mn [35]).

#### 3.3. Implications of This Study

This study has demonstrated the potential of biochar from different feedstocks for soil amendment. While different biochars have shown the potential to add nutrients such as nitrate, phosphate and potassium to the soil, care has to be taken with respect to the potential of each biochar to cause soil salinity. Also, the reaction of the soil to biochar produced from different feedstocks varies with soil texture. The CGT biochar, with its higher mineral content, exhibits a great potential to add organic matter to the soil and high quantities of nutrients such as P and K in both fine and coarse textured soil [37]; however, for arid soils, the high level of salinity encountered in the CGT biochar-amended soil will likely limit the use of this biomass feedstock. In the coarse textured soil, other biochars apart from CGT did not appear to deliver much nutrient benefits to the soil, however, they did not raise the salinity of the soil compared to the control treatment, indicating that they might be used for long term building of the soil organic matter and soil quality. In the fine textured soil, the control soil had initially high salinity and all of the biochars except for the PS biochar further increased the salinity. Therefore, pecan shell biochar may be the best choice among the locally available feedstocks for the clay soil when salinity is considered. In order to better understand the effects of these biochar on soil quality, especially the effects on soil salinity, biochar amendments need to be tested at different application rates, under real field conditions and under different cropping systems.

#### 4. Conclusions

Biochar yields for 450  $^{\circ}$ C slow pyrolysis of pecan shells, pecan orchard prunings, yard waste and cotton gin trash ranged from 28% to 42% by weight, which was within the range expected for these conditions. The cotton gin trash had the highest ash content of all the feedstocks, which will likely impact its suitability for pH-, EC-, and ash-sensitive applications.

Amending clay loam and sandy loam agricultural soils with biochars from pecan shells, pecan orchard prunings, and yard waste had few significant impacts, positive or negative, on the soil quality indicators measured in this study after a short soil incubation. Biochar effects were different for the two different soil textures. Cotton gin trash biochar showed the greatest potential to increase soil organic matter and plant nutrients, however, the increases in salinity for both soils is a serious concern.

The biochar application rate in this trial was very high ( $45 \text{ Mg} \cdot \text{ha}^{-1}$ ) and the biochar materials were ground to pass through 2-mm sieve before application to the soil in order to accelerate the biochar's interactions within the soil system. It is possible that the effects seen in this trial, such as biochar's impact on soil salinity, may not be as severe if biochars are applied as larger fragments and at lower rates.

More research is needed on the effects of different biochar amendments on soil quality and plant available water retention in arid agricultural soils. Trials involving impacts of different sizes and rates of biochar are needed in arid regions, to help balance the utility of this potential soil organic matter source without delivering any negative side effect such as increased soil salinity.

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#### References

- 1. Karlen, D.L.; Mausbach, M.J.; Doran, J.W.; Cline, R.G.; Harris, R.F.; Schuman, G.E. Soil quality: A concept, definition, and framework for evaluation (a guest editorial). *Soil Sci. Soc. Am. J.* **1997**, *61*, 4–10. [CrossRef]
- 2. Idowu, O.J.; Flynn, R. *Understanding Soil Health for Production Agriculture in New Mexico, Guide A-148;* New Mexico State University: Las Cruces, NM, USA, 2013.
- 3. Reeves, D.W. The role of soil organic matter in maintaining soil quality in continuous cropping systems. *Soil Tillage Res.* **1997**, *43*, 131–167. [CrossRef]
- 4. Ulery, A.L.; Tugel, A.J. Farming in New Mexico: Soil quality and productivity maintenance. *New Mexico J. Sci.* **1999**, *39*, 86–108.
- 5. Magdoff, F. Concepts, components, and strategies of soil health in agroecosystems. *J. Nematol.* **2001**, 33, 169. [PubMed]
- 6. Idowu, O.J.; Marsalis, M.; Flynn, R. *Agronomic Principles to Help with Farming During Drought Periods, Guide A-147*; New Mexico State University: Las Cruces, NM, USA, 2012.
- 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, 175–187. [CrossRef]
- 8. McHenry, M.P. Agricultural bio-char production, renewable energy generation and farm carbon sequestration in Western Australia: Certainty, uncertainty and risk. *Agric. Ecosyst. Environ.* **2009**, *129*, 1–7. [CrossRef]
- 9. Lehmann, J.; Pereira da Silva, J.; Steiner, C.; Nehls, T.; Zech, W.; Glaser, B. Nutrient availability and leaching in an archaeological Anthrosol and a Ferralsol of the Central Amazon basin: Fertilizer, manure and charcoal amendments. *Plant. Soil* 2003, 249, 343–357. [CrossRef]
- 10. Laird, D.A. The charcoal vision: A win-win-win scenario for simultaneously producing bioenergy, permanently sequestering carbon, while improving soil and water quality. *Agron. J.* **2008**, *100*, 178–181. [CrossRef]
- Lal, R. Black and buried carbons' impact on soil quality and ecosystem services. Soil Tillage. Res. 2008, 99, 1–3. [CrossRef]
- Barrow, C.J. Biochar: Potential for countering land degradation and for improving agriculture. *Appl. Geogr.* 2012, 34, 21–28. [CrossRef]

- Liang, B.; Lehmann, J.; Solomon, D.; Kinyangi, J.; Grossman, J.; O'Neill, B.; Skjemstad, J.O.; Thies, J.; Luizao, F.J.; Petersen, J.; *et al.* Black carbon increases cation exchange capacity in soils. *Soil Sci. Soc. Am. J.* 2006, 70, 1719–1730. [CrossRef]
- 14. Cheng, C.-H.; Lehmann, J.; Engelhard, M.H. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochim. Cosmochim. Acta* **2008**, *72*, 1598–1610. [CrossRef]
- 15. Laird, D.A.; Fleming, P.; Davis, D.D.; Horton, R.; Wang, B.; Karlen, D.L. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* **2010**, *158*, 443–449. [CrossRef]
- 16. Steiner, C.; Glaser, B.; Teixeira, W.G.; Lehmann, J.; Blum, W.; Zech, W. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *J. Plant. Nutr. Soil Sci.* **2008**, *171*, 893–899. [CrossRef]
- 17. Lehmann, J.; Rillig, M.C.; Thies, J.; Masiello, C.A.; Hockaday, W.C.; Crowley, D. Biochar effects on soil biota—A review. *Soil Biol. Biochem.* **2011**, *43*, 1812–1836. [CrossRef]
- Steinbeiss, S.; Gleixner, G.; Antonietti, M. Effect of biochar amendment on soil carbon balance and soil microbial activity. *Soil Biol. Biochem.* 2009, 41, 1301–1310. [CrossRef]
- Karhu, K.; Mattila, T.; Bergström, I.; Regina, K. Biochar addition to agricultural soil increased CH<sub>4</sub> uptake and water holding capacity—Results from a short-term pilot field study. *Agric. Ecosyst. Environ.* 2011, 140, 309–313. [CrossRef]
- Steiner, C.; Teixeira, W.; Lehmann, J.; Nehls, T.; de Macêdo, J.; Blum, W.; Zech, W. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered Central Amazonian upland soil. *Plant. Soil* 2007, 291, 275–290. [CrossRef]
- 21. Kimetu, J.; Lehmann, J.; Ngoze, S.; Mugendi, D.; Kinyangi, J.; Riha, S.; Verchot, L.; Recha, J.; Pell, A. Reversibility of soil productivity decline with organic matter of differing quality along a degradation gradient. *Ecosystems* **2008**, *11*, 726–739. [CrossRef]
- 22. Lillywhite, J.M.; Heerema, R.; Simonsen, J.E.; Herrera, E. *Pecan Marketing Channels in New Mexico*, 2010, *Guide Z-307*; New Mexico State University Cooperative Extension Service: Las Cruces, NM, USA, 2010; p. 8.
- 23. Mexal, J.G.; Herrera, E.; Sammis, T.W.; Zachritz, W.H. *Noncommensurable Values of the Pecan Industry, Guide H-654*; New Mexico State University Cooperative Extension Service: Las Cruces, NM, USA, 2003; p. 4.
- 24. Kallestad, J.C.; Mexal, J.G.; Sammis, T.W. *Mesilla Valley Pecan Orchard Pruning Residues: Biomass Estimates and Value-Added Opportunities, Research Report 764;* New Mexico State University Agricultural Research Station: Las Cruces, NM, USA, 2008; p. 16.
- 25. Idowu, O.J. New Mexico State University, Las Cruces, NM, USA. Unpublished work. 2013.
- 26. ASTM E1755–01(2007): Standard Test Method for Ash in Biomass. Available online: http://www.astm.org/ DATABASE.CART/HISTORICAL/E1755-01R07.htm (accessed on 7 March 2016).
- 27. ASTM D1762–84(2007): Standard Test Method for Chemical Analysis of Wood Charcoal. Available online: http://www.astm.org/DATABASE.CART/HISTORICAL/D1762-84R07.htm (accessed on 7 March 2016).
- Soil Survey Staff. Soil Taxonomy: A Basic System of Soil Classification for Making and Interpreting Soil Surveys, 2nd ed.; Natural Resources Conservation Service: Washington, DC, USA, 1999.
- 29. United States Salinity Laboratory Staff. Diagnosis and improvement of saline and alkali soils. In *USDA Agricultural Handbook 60*; U.S. Government Print Office: Washington, DC, USA, 1954.
- 30. Nelson, D.W.; Sommers, L.E. Total carbon, organic carbon and organic matter. In *Methods of Soil Analysis Part 3. Chemical Methods*; Sparks, D.L., Ed.; SSSA and ASA: Madison, WI, USA, 1996; Volume 5.
- 31. Olsen, S.R.; Cole, C.V.; Watanabe, F.S.; Dean, L.A. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. *U. S. Dept. Agric. Circ.* **1954**, *939*, 1–18.
- 32. Cihacek, L.J. *Interpreting Soil Analysis*; New Mexico State University Publication Office: Las Cruces, NM, USA, 1983.
- 33. Ludwick, A.E.; Reuess, J.O. *Guide to Fertilizer Recommendations in Colorado*; Colorado State University Cooperative Extension: Fort Collins, CO, USA, 1974.
- 34. Brewer, C.E.; Hu, Y.-Y.; Schmidt-Rohr, K.; Loynachan, T.E.; Laird, D.A.; Brown, R.C. Extent of pyrolysis impacts on fast pyrolysis biochar properties. *J. Environ. Qual.* **2012**, *41*, 1115–1122. [CrossRef] [PubMed]
- 35. Flynn, R. *Appropriate Analyses for New Mexico Soils, Guide A-146;* New Mexico State University Cooperative Extension Service: Las Cruces, NM, USA, 2012; p. 8.

- 36. Deenik, J.L.; McClellan, T.; Goro, U.; Antal, M.J.; Campbell, S. Charcoal volatile matter content influences plant growth and soil nitrogen transformations. *Soil Sci. Soc. Am. J.* **2010**, *74*, 1259–1270. [CrossRef]
- 37. Brewer, C.; Unger, R.; Schmidt-Rohr, K.; Brown, R. Criteria to select biochars for field studies based on biochar chemical properties. *Bioenergy Res.* **2011**, *4*, 312–323. [CrossRef]



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