

# Acidity, water retention, and mechanical physical quality of a strongly acidic Ultisol amended with biochars derived from different feedstocks

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#### Abstract

*Purpose* Strongly acidic Ultisols in tropical and subtropical regions of China present one of the most important degraded soils. The improvement of soil quality for these soils is a key goal for sustainable agriculture. The purpose of this study is to evaluate the beneficial effects of biochar amendments on the soil acidity, plant available nutrient contents, and physical properties of a strongly acidic Ultisol.

Materials and methods A Typic Plinthudult with low soil fertility and poor physical properties was amended by three biochars made from straw (SB), woodchips (WCB), and wastewater sludge (WSB) at the rate of 0, 2, 4, and 6 % biochar, respectively. After 180 days of incubation, the chemical, nutrient contents, water retention, consistency, tensile strength, and shear strength of biochar-amended soils were determined. Results and discussion Experimental results indicate that biochars significantly (p < 0.05) increase the pH of the soil and decrease the contents of exchangeable H<sup>+</sup> and Al<sup>3+</sup>. The WCB treatment results in higher pH values than the SB and WSB treatments. The biochars significantly increase total C, available P, K, and exchangeable K, Ca, and Mg contents. Biochar applications significantly enhance water-holding capacity of soil, while not increasing the available water content (AWC) of the soil. Biochar application significantly (p < 0.05) increases the liquid limit (LL) and plastic index (PI) of the soil. The effectiveness of biochar on LL and PL is more pronounced in the SB-amended soils. With application of

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biochar, the tensile strength (TS) of Ultisol decreases from original 466 kPa to 233, 164, and 175 kPa for 6 % WCB-, SB-, and WSB-amended soils, respectively. Direct shear tests indicate WCB significantly reduces the cohesion (*c*) of the soils, while biochars do not alter the internal friction angle ( $\varphi$ ) of soil. Analyses of scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) reveal that soil mineral particles are inserted inside the pores of biochar and attached on the surface of biochar, indicating that biochar greatly changes the microstructure and pore system of soil.

*Conclusions* It is suggested that biochar amendment generally improves the quality of degraded Ultisols with strong acidity, low fertility, and poor physical properties. The physical dilution effect and microstructure change caused by the porous and less dense biochar are identified to be the main mechanism for the biochar to improve the physical properties of strongly acidic Ultisols.

**Keywords** Acidity · Biochar · Mechanical strength · Soil consistency · Ultisol · Water retention capacity

# **1** Introduction

Strongly acidic Ultisols widely cover the tropical and subtropical regions of southern China and present one of the most important soils in China. They are considered to be degraded soil because of their very low pH, organic matter, cation exchangeable capacity and water-holding capacity, poor soil structure, high mechanical strength, surface crusting, and soil loss potential (He and Sun 2008; Jien and Wang 2013). The improvement on the acidification, low fertility, poor structure, and severe soil erosion has been a major concern issue for these degraded soils. In recent years, biochar has been used



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as soil amendment to improve these soils (Yuan et al. 2011; Lei and Zhang 2013; Jien and Wang 2013; Hseu et al. 2014). It has been demonstrated that biochar is able to increase exchangeable bases and nutrient availability, decrease soil density, ameliorate soil acidity, and improve water-holding capacity of the highly weathered soils (Glaser et al. 2002; Lehmann et al. 2003; Steiner et al. 2007, 2008; Yuan and Xu 2011; Xu et al. 2012). The application of biochar has received growing interest as a sustainable technology to improve highly weathered or degraded tropical and subtropical soils.

The application of biochar has demonstrated many advantages in improving the soil quality and plant growth of several types of soils (Novak et al. 2009; Atkinson et al. 2010; Laird et al. 2010; Streubel et al. 2011; Briggs et al. 2012; Herath et al. 2013). For highly weathered Ultisols, benefits of biochar amendment mainly derive from the fertilizer value of biochar and its effects on the improvement of soil physical conditions, in particular, the soil water-holding capacity and hydraulic conductivity (Glaser et al. 2002; Lehmann et al. 2003; Herath et al. 2013; Jien and Wang 2013). Because biochar maintains large amounts of nutrients, adding biochar into soil certainly increases the nutrient content of low fertility soils. Biochar has high porosity and large inner surface area, and applying it to soils ameliorates the soil physical properties (i.e., soil structure, pore size distribution, bulk density, soil water retention capacity and hydraulic conductivity) (Novak et al. 2012; Lei and Zhang 2013; Lu et al. 2014) and decreases soil erosion (Jien and Wang 2013). However, the effects of biochars vary with the soil type and feedstock materials as well as the processing conditions of biochar. For example, Laird et al. (2010) did not find significant influence of hardwood biochar on the soil saturated hydraulic conductivity while Asai et al. (2009) and Uzoma et al. (2011) observed that biochar application improved the saturated hydraulic conductivity of the soil.

Although numerous studies have evaluated the effect of biochar on chemical fertility and crop growth in highly weathered or degraded tropical soils, few works were focused on the physical properties (Glaser et al. 2002; Steiner et al. 2008; Atkinson et al. 2010). Some authors proposed that biochar could decrease soil bulk density and improve water-holding capacity of Ultisols (Busscher et al. 2010; Herath et al. 2013; Jien and Wang 2013; Lei and Zhang 2013). The effects of biochar on other physical properties, such as soil aggregation, consistency, mechanical strength, and cracking, have not yet been fully evaluated. Especially, the effect of biochar on soil consistency and mechanical strength has not been reported. Overall, positive effects of biochar on soil chemical properties and plant growth have been well documented (Glaser et al. 2002; Steiner et al. 2008; Atkinson et al. 2010), whereas there is still a lack in information on the effect of biochar on soil physical properties.

In order to evaluate the physical quality of soil, the water retention, consistency, and mechanical strength of the soil have been widely used as the indicator (Lal and Shukla 2004). The degraded soils in tropical and subtropical regions commonly exhibit poor mechanical qualities, such as high mechanical impedance to root growth, hard surface crusting, and difficult tillage. For agronomic aspect, the soil with high hardness might restrict root extensibility and therefore inhibit growth of crops. The improvement of soil mechanical properties is important for soil aeration, water-holding capacity, plant growth, and soil workability. However, few studies have focused on the application of biochar for this purpose. There is a need for understanding the role of biochar in altering soil structure, water retention, and mechanical strength. In this work, we evaluate the effect of biochar amendments on the improvement of the physical quality of strongly acidic Ultisols in terms of various soil physical quality indicators by using a pot incubation experiment. Our objectives are to describe the effect of biochar on selected soil physical characteristics of strongly acidic Ultisols by evaluating the possible benefits of biochar in the improvement of degraded soils.

## 2 Materials and methods

#### 2.1 Soil and biochar samples

Soil sample used for this study was collected from the A horizon (0-20 cm) of a low-hilly red soil located in Hangzhou, Eastern China. The soil was classified as a Typic Plinthudult based on USDA Soil Taxonomy (Soil Survey Staff 2010). The soil was air-dried at room temperature and then ground to pass through a 2-mm sieve. The basic properties of soil are given in Table 1. The soil was found to be very low in fertility with organic matter (2.36 g kg<sup>-1</sup>), available phosphorus (7.18 mg kg<sup>-1</sup>), available potassium (47.67 mg kg<sup>-1</sup>), CEC (6.60 cmol kg<sup>-1</sup>), and strong acidity (pH=5.0). X-ray diffraction analyses have revealed that the clay mineralogy is composed mostly of kaolinite, illite, and iron oxides (Zhejiang Province Soil Survey Office 1994). Because of its coarse texture and poor structure, the soil has poor water retention and is easily erodible, which commonly creates crop moisture stress over the growing season and soil loss.

The biochars used in this study were obtained from commercial biochar producer, which were made from wheat straw, woodchips, and wastewater sludge by slow pyrolysis at 500 °C for 2 h in a factory-scale reactor as the fertilizer. These three biochar represent a range of natural biomass sources, and designated as SB, WCB, and WSB, respectively. The biochar was ground to pass through a 2-mm sieve to obtain similar particle size. The basic properties of biochars are given in Table 1 and Fig. 1.

 Table 1
 Basic physical and chemical characteristics of the soil and biochars

Parameters	Soil	SB	WCB	WSB
pН	5.0	8.6	8.4	8.3
TOC (g $kg^{-1}$ )	2.36	502	642	477
Particle size analysis (g $kg^{-1}$ )				
Clay (<2 µm)	280	ND	ND	ND
Silt (2-20 µm)	440	ND	ND	ND
Sand (20-2000 µm)	280	ND	ND	ND
Available N (mg kg <sup>-1</sup> )	45.20	388.82	36.46	277.06
Available P (mg kg <sup>-1</sup> )	7.18	762.63	102.00	152.94
Available K (mg kg <sup>-1</sup> )	47.67	850.11	350.07	240.45
$CEC (cmol(+) kg^{-1})$	6.60	ND	ND	ND
Alkalinity (cmol kg <sup>-1</sup> )	ND	110.0	198.0	96.8

SB, WCB, and WSB represent biochar produced with straw, woodchip, and wastewater sludge, respectively

ND not detectable, TOC total organic carbon, CEC cation exchangeable capacity

#### 2.2 Incubation experiment

The required amounts of soils and biochars were weighed by a total 2000 g dry weight of sample and mixed in the dry state. Four biochar rates (0, 2, 4, 6 % biochar, w/w) were used. The mixtures of soil and biochar were packed into plastic pots (10 cm diameter, 17 cm height) and controlled a bulk density of about 1.2 g cm<sup>-3</sup> by artificial compaction. Treatments were replicated four times. The soil without any biochar was used as the control. The mixtures were wetted up to field capacity using de-ionized water and left for incubation in a temperature-controlled glasshouse. Soil was kept at constant moisture (70 % of water-holding capacity) during the whole incubation by adjusting the weight. After 180 days of incubation, the untreated soils and biochar-amended soils were taken for physical and chemical analyses.

#### 2.3 Analysis of soil chemical properties

Soil properties were determined using routine methods. Particle size distribution was measured by pipette method (Gee and Bauder 1986), soil organic carbon by oxidation method with potassium dichromate (Nelson and Sommers 1982), alkali-hydrolyzable nitrogen (AN) by the NaOH hydrolyzable method, available phosphorus (AP) by the Olsen method (Zhang and Gong 2012), cation exchange capacity (CEC) and exchangeable bases by the ammonium acetate method (pH=7) (Thomas 1982), and pH by a pH meter in 1:2.5 soil to water suspension. Soil exchangeable acidity was extracted with 1 mol L<sup>-1</sup> KCl and determined by titration with 0.02 mol L<sup>-1</sup> NaOH. Alkalinity of biochars was measured by an acid-base titration method (Yuan et al. 2011).

#### 2.4 Characterization of biochar

The mineralogy, chemical composition, pore, and structure of biochars were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) with X-ray energy-dispersive spectroscopy (EDS), mercury intrusion porosimetry (MIP), and Fourier-transform infrared spectroscopy (FTIR). XRD was performed on non-oriented powder samples using Cu K a radiation (45 kV, 30 mA) on a Rigaku X-ray diffractometer at 2° to 80° at a speed of  $0.2^{\circ}\theta$ / min. The morphology of biochar was observed using a SIRION-100 field emission scanning electron microscopy (FESEM) (FEI, The Netherlands) operated at 25 kV and  $280 \ \mu A$  for the acceleration voltage and beam current, respectively. The IR spectra of biochars were determined by the FTIR-8900 spectrometer (Shimadzu Ltd., Japan) using pressed potassium bromide (KBr) pellets. The spectra were recorded with a 4 cm<sup>-1</sup> resolution between wave numbers of 4000 and 400  $\text{cm}^{-1}$ . The pore structure was determined using mercury intrusion porosimetry (MIP) (Autopore IV 9500; Micromeritics Inc. USA).

## 2.5 Analysis of soil physical properties

#### 2.5.1 Soil consistency

Soil consistency has important implications because it directly measures the soil mechanical behavior and represents an integration of soil properties, which can be used to estimate such properties as compressibility and the optimum and workable water content range for tillage operations without undue effort. Soil consistency was determined using the cone penetrometer technique in accordance with the China National Standard for Soil Test Method (GB/T50123-1999) (SSPRC 1999). Briefly, 200 g of air-dried soil samples (<0.5 mm) was wetted with distilled water and then was prepared into paste and kept for 24 h. A GYS-2 Photoelectric Liquid and Plastic Limit Tester (Nanjing Soil Instrument Factory Co. Ltd.) was used to determine liquid limit (LL) and plastic limit (PL). The tester was equipped with a timer. The soil paste was placed into a sample cup. The depth of cone penetrometer into the soil sample within 5 s was recorded. The water content of soil paste was determined gravimetrically. According to the standard procedure, at least three cone penetration tests for each sample were carried out by adjusting different water content. The linear graph of water contents against the penetration depth values was plotted. The water content corresponding to a cone penetration of 17 and 2 mm was defined as the liquid limit and plastic limit, respectively. The difference between LL and PL was defined as the plasticity index (PI).



◄ Fig. 1 Characterization of biochars. a Cumulative pore volume (CPV) determined by mercury intrusion porosimetry (MIP); b FTIR spectrum of biochars; c x-ray diffraction (XRD) pattern of biochars. Q quartz, Ca calcite, Mu mulinite. d Scanning electron microscopy (SEM) images and energy-dispersive spectroscopy (EDS) of biochars. SB straw biochar, WCB woodchip biochar, WSB wastewater sludge biochar

#### 2.5.2 Soil water retention measurements

The soil water characteristics curve (SWCC) was determined using a pressure plate system (Soil Moisture Equipment Corp., Santa Barbara, CA, USA). The soil was packed manually to a bulk density of  $1.2 \text{ g cm}^{-3}$ . The soil cores were fully saturated and allowed to drain freely for 24 h before pressure was applied. In order to construct a water release characteristics curve, the pressure was increased step by step and the core weight was recorded before each increase in pressure. Moisture contents of the samples at the matric potential of -100, -50, -33, -20, -10, -8, -5, and -1 kPa were determined in 1 bar ceramic plate cells. Moisture contents of the samples at the matric potentials of -1500, -1000, -200, and -150 kPa were measured in a 15 bar pressure plate extractor. Finally, the samples were oven-dried at 105 °C for 24 h and weighed. Volumetric water content ( $\theta v$ ) at each matric potential was calculated based on the gravimetric water content and bulk density. Field capacity (FC) was defined as the soil water content measured at a matric potential of -33 kPa and permanent wilting point (PWP) was defined as the water content at -1500 kPa. The available water capacity (AWC) was calculated as the difference in volumetric soil water content between field capacity and -1500 kPa matric potential. The amount of macropores, which was defined the pores with diameters  $>75 \ \mu m$  (corresponding to suction  $>-40 \ cm$ ), was derived from the soil water retention curve (Hseu et al. 2014).

#### 2.5.3 Soil mechanical strength test

Mechanical strength is a sensitive indicator of the soil physical condition and has been commonly used to evaluate soil water erosion, structural stability, tillage performance, and root penetration. Higher strength found in the Ultisols often impedes seedling emergence and root penetration. Soil mechanical strength test includes the unconfined compression test and direct shear test. Standard unconfined compression test was applied as described in SSPRC (1999). The test samples with dimensions of 2.54 cm in diameter and 6.35 cm in length were prepared according to SSPRC standard specifications. The cylindrical specimen was broken in a digital unconfined compression apparatus (YYM-2; Nanjing Soil Instrument Factory Co. Ltd.). The maximum load before specimen breaking was recorded as the tensile strength (TS) of soil.

The direct shear test (DST) was carried out as described in standard procedures (SSPRC 1999). Samples are prepared

according to SSPRC standard specifications. A quadruplex strain controlled direct shear apparatus (Nanjing Soil Instrument Factory Co. Ltd.) was used to determine the shear strength. The shear box had a diameter of 6.18 mm and a height of 2 cm. Four normal stresses of 50, 100, 200, and 400 kPa were used. The shear displacement rate was 0.8 mm min<sup>-1</sup>. The relative displacement versus shear force was plotted and the soil shear strength properties, soil cohesion (*c*) and angle of internal friction ( $\varphi$ ), were calculated based on the Mohr-Coulomb equation.

#### 2.6 Scanning electron microscope (SEM) observation

The morphology of biochar-amended soils after incubation was examined by FESEM (SIRION-100; FEI, The Netherlands) operated at 25 kV and 280  $\mu$ A for the acceleration voltage and beam current, respectively. The samples were Au coated prior to FESEM analysis. The chemical composition of the sample was analyzed using FESEM and GENESIS 4000 X-ray energy-dispersive spectroscopy (EDAX Corp. USA) to identify its micro-scale structure and element distribution.

# 2.7 Data analysis

SPSS 13.0 (SPSS, Inc., Chicago, IL, USA) was used for the statistical analysis of data. A one-way analysis of variance (ANOVA) was carried out to determine significant differences between treatments using Tukey's test with a significant level of p < 0.05 and p < 0.01.

# **3 Results**

# 3.1 Characterization of biochars

Characterization of biochars is shown in Table 1 and Fig. 1. XRD pattern of biochar indicates the presence of quartz and calcite in the biochar. The SB sample has relatively higher calcite content and WSB contains mulinite. The cumulative pore volume (CPV) curves of biochars indicate that the SB has the largest pore volume (2.910 cm<sup>3</sup> g<sup>-1</sup>), while the WSB has the least (0.413 cm<sup>3</sup> g<sup>-1</sup>). The CPV curves of SB and WCB become essentially flat at diameters less than 1 µm, suggesting almost all pores in SB and WCB have a diameter larger than 1 µm. The IR spectra of biochars contain several adsorption bands associated with aromatic C-H, C=C, C=O stretching, aliphatic C-H stretching, and O-H stretching. Field emission scanning electron microscopy (FESEM) images of the biochars are presented in Fig. 1d, showing that the biochar is highly heterogeneous with large macropores from several to tens of microns in size. These macropores are important with regard to the role of biochars in improving the water-holding capacity and mechanical strength of soil. The EDS analysis indicates that the biochar particles consist of high carbon content with small amount of Si, Al, and Ca.

# 3.2 Changes in soil chemical properties and nutrient contents

The effect of biochar on soil pH and exchangeable acidity is shown in Table 2. After incubating for 180 days, the biocharamended soils have a significantly (p < 0.01) higher soil pH and lower exchangeable acidity than the control treatment. The effect of biochar on soil pH increases with the increased addition level of biochar, especially for WCB-amended soils. At the addition level of 6 %, soil pH increases by 0.14 for SB, 2.33 for WCB, and 0.28 for WSB, respectively (Table 2). Among these three biochars, the WCB increases the soil pH most due to its higher alkalinity (Table 1). This result is consistent with previous studies that incorporation of biochar significantly increased the pH of strongly acidic soils (Yuan and Xu 2011; Yuan et al. 2011). Application of three biochars significantly decreases soil exchangeable H<sup>+</sup> and Al<sup>3+</sup> contents (Table 2). Similarly, the largest effect was made by the WCB-amended soils.

Table 3 shows the changes of soil nutrient content and exchangeable cations of biochar-amended soils. The application of biochars significantly increases the total C and available P and K contents, indicating an increase in the nutrient status of strongly acidic soils after biochar application. The WSB treatments do not significantly affect the available N content. The available P and K increases with the level of biochar, which is most likely due to the presence of these nutrients in the biochar itself. SB contains much higher K content than WCB and WSB; therefore, its addition leads to the highest increase in the K content. Compared with the control, the exchangeable K, Ca, and Mg contents also are significantly increased in the biochar-amended soils. Although there is no significant increase in the CEC of biochar-amended soils, the trend of increasing CEC is still observable (Table 3). These results highlight the potential effectiveness of the biochar as a soil conditioner for improving the low fertility of strongly acidic Ultisols.

# 3.3 Changes in soil water retention capacity

The soil water characteristic curve (SWCC) is a very important measurement for characterizing soil physical properties since it indicates the ability of the soil water retention (Lal and Shukla 2004). The SWRCs of biochar-amended soils are shown in Fig. 2. The SWCC shows a sharp decrease in the low suction and is typical for sandy soils containing large pores, where the majority of water is released at low suction. At the same potential, biochar amendments significantly (p < 0.05) increase the  $\theta v$  of soils compared with the control (Fig. 2). The  $\theta v$  at -33 kPa in the 6 % biochar-amended soil is increased by 34 % for SB, 28 % for WCB, and 24 % for WSB, respectively. The  $\theta v$  of biochar-amended soils at permanent wilting point (-1500 kPa) is significantly (p < 0.01) greater than that of the control. At the same matric potential, the SB-amended soils possess higher values of  $\theta v$  than the WCB- and WSB-amended soils, which are attributed to the greater pore volume of the former (Fig. 1). These results are in line with the previous findings that the biochar amendments enhance the water retention capacity of Ultisols (Glaser et al. 2002; Novak et al. 2012). In general, biochar amendments

3+	Treatment	рН	Exchangeable acid (cmol kg $^{-1}$ )	Exchangeable $H^+$ (cmol kg <sup>-1</sup> )	Exchangeable Al <sup>3+</sup> (cmol kg <sup>-1</sup> )
	Control	5.01±0.02b	3.34±0.09a	0.34±0.05a	3.00±0.11a
	2 % SB	4.95±0.01c	$2.00{\pm}0.29b$	0.18±0.04b	1.82±0.30b
	4 % SB	$5.01{\pm}0.01b$	1.06±1.06c	$0.16 \pm 0.08b$	0.90±0.10c
	6 % SB	5.15±0.02a	0.57±0.09d	$0.11 {\pm} 0.07 b$	0.45±0.11d
	Control	5.01±0.02d	3.34±0.09a	0.34±0.05a	3.00±0.11a
	2 % WCB	5.67±0.08c	0.17±0.06b	$0.15 {\pm} 0.05 b$	$0\pm 0b$
	4 % WCB	$6.51 {\pm} 0.05b$	$0\pm0c$	$0.03 \pm 0.02c$	$0{\pm}0b$
	6 % WCB	7.34±0.06a	$0\pm 0c$	$0\pm 0c$	$0{\pm}0b$
	Control	$5.01{\pm}0.02c$	3.34±0.09a	0.34±0.05a	3.00±0.11a
	2 % WSB	$5.24{\pm}0.03b$	2.47±0.12b	$0.21 {\pm} 0.02b$	2.26±0.14b
	4 % WSB	5.31±0.03a	1.78±0.02c	0.15±0.06b	1.62±0.05c
	6 % WSB	5.29±0.03ab	0.85±0.27d	0.13±0.09b	0.72±0.20d

The values are presented in mean value±standard deviation (n=4). The columns with the same letter are not significantly different at p < 0.05

SB straw biochar, WCB woodchip biochar, WSB wastewater sludge biochar

**Table 2** Changes in pH,exchangeable acid,  $H^+$ , and  $Al^{3+}$ of biochar-amended soilsmeasured after the 180-dayincubation

Table 3 Changes in nutrient contents and chemical properties of biochar-amended soils measured after the 180-day incubation

Treatment	Total C (g kg <sup>-1</sup> )	Available N $(mg kg^{-1})$	Available P (mg kg <sup>-1</sup> )	Available K (mg kg <sup>-1</sup> )	CEC (cmol kg <sup>-1</sup> )	Exchangeable cations (cmol kg <sup>-1</sup> )			
						K	Na	Са	Mg
Control	2.36±0.26d	45.21±1.25b	7.18±1.66c	47.67±1.24d	6.60±0.77a	0.15±0.01d	0.19±0.04b	4.06±0.17c	1.54±0.08d
2 % SB	10.09±2.76c	44.26±0.67b	20.37±1.30c	176.07±8.34c	$7.23{\pm}0.86a$	0.51±0.03c	$0.39{\pm}0.10b$	4.88±0.17b	1.90±0.07c
4 % SB	$13.92{\pm}1.40b$	51.36±1.14a	43.50±1.39b	259.01±6.63b	7.55±0.81a	$0.73{\pm}0.05b$	0.84±0.28a	5.17±0.14ab	2.12±0.04b
6 % SB	18.75±1.11a	55.02±4.08a	63.24±12.90a	304.98±11.51a	7.82±0.29a	0.84±0.03a	1.11±0.22a	5.44±0.30a	2.31±0.03a
Control	$2.36{\pm}0.26d$	45.20±1.25a	7.18±1.66c	47.67±1.24d	$6.60{\pm}0.77a$	0.15±0.01d	0.19±0.04a	4.06±0.17d	1.54±0.08c
2 % WCB	15.74±0.71c	$36.48 {\pm} 2.99 b$	$14.26 {\pm} 1.90b$	102.09±2.12c	5.82±0.91a	$0.31{\pm}0.003c$	0.16±0.02a	8.68±0.18c	2.19±0.06a
4 % WCB	$27.25 {\pm} 1.04b$	37.83±4.79b	18.05±1.37a	135.84±2.41b	5.37±0.46a	$0.39{\pm}0.002b$	0.12±0.02a	11.53±0.36b	1.72±0.04b
6 % WCB	37.68±1.06a	$34.81 \pm 1.44b$	21.12±1.91a	164.78±6.33a	5.38±0.35a	0.49±0.02a	$0.05{\pm}0.01b$	14.80±0.37a	1.29±0.08d
Control	2.36±0.26c	45.21±1.25ab	7.18±1.66d	47.67±1.24d	6.60±0.77a	0.15±0.01d	0.19±0.04a	4.06±0.17b	1.54±0.08d
2 % WSB	8.26±1.96b	47.88±2.87ab	23.50±3.49c	54.13±1.66c	6.82±0.35a	0.19±0.01c	$0.11{\pm}0.04ab$	4.49±0.11b	2.00±0.08c
4 % WSB	$10.03 \pm 1.11b$	41.94±4.80b	55.11±3.99b	72.19±2.31b	7.19±1.74a	$0.23{\pm}0.02b$	$0.08 {\pm} 0.05 b$	5.24±0.20a	2.66±0.06b
6 % WSB	18.74±1.44a	48.74±0.80a	122.50±4.32a	93.44±2.21a	7.00±0.44a	0.28±0.01a	$0.16{\pm}0.05ab$	5.65±0.51a	3.40±0.13d

The values are presented in mean value $\pm$ standard deviation (n=4). The columns with the same letter are not significantly different at p <0.05 *SB* straw biochar, *WCB* woodchip biochar, *WSB* wastewater sludge biochar

enhance the water storage capacity of Ultisols and Aridisols, but the effect varies with the feedstock selection and pyrolysis temperature (Novak et al. 2012).

The effects of biochar application on the saturated water content (SWC), field capacity (FC), and AWC of the soil are shown in Table 4. The biochar-amended soils have higher SWC than the control, but only SB-amended soils show a significant effect. The SWCs for the 6 % SB-, WCB-, and WSB-amended soils are respectively 19, 11, and 6 % greater

than the control treatment. The biochar application significantly increases the FC of the soil. The biochar application has no significant effect (p < 0.05) on the AWC of soil, but an increasing trend still can be observed, compared with the control (Table 4). The increase of the water retention capacity and AWC of sandy soils by the addition of biochar has been reported by some authors (Novak et al. 2009; Busscher et al. 2010; Abel et al. 2013). It should be noted that our results were obtained from a short-term incubation experiment.

Fig. 2 Soil water characteristic curves (SWCC) of biocharamended soils. *Vertical error bars* indicate ±1 standard deviation of the mean. *SB* straw biochar, *WCB* woodchip biochar, *WSB* wastewater sludge biochar



Table 4 Saturated water content (SWC), field capacity (FC), permanent wilting point (PWP), and available water content (AWC) of biochar-amended soils (mean±SD)

Treatment	SWC ( $cm^3 cm^{-3}$ )	$FC (cm^3 cm^{-3})$	$PWP (cm^3 cm^{-3})$	AWC ( $cm^3 cm^{-3}$ )
Control	46.5±1.1b	18.8±0.2b	13.5±1.0c	5.3±0.8a
2 % SB	50.2±0.1ab	23.1±1.3a	16.4±0.1b	6.7±1.3a
4 % SB	52.8±1.9a	22.5±0.8a	16.4±0.1b	6.1±0.9a
6 % SB	55.7±2.1a	25.5±0.1a	20.5±0.0a	4.8±0.1a
Control	46.5±1.1a	18.8±0.2b	13.5±1.0b	5.3±0.8a
2 % WCB	49.2±2.3a	23.5±0.7a	17.9±0.1a	5.7±0.5a
4 % WCB	48.5±0.8a	23.8±0.0a	18.1±0.4a	5.7±0.1a
6 % WCB	51.7±0.7a	24.2±0.7a	18.0±0.4a	6.2±1.0a
Control	46.5±1.1a	18.8±0.2b	13.5±1.0b	5.3±0.8a
2 % WSB	48.0±0.4a	21.5±0.9a	15.7±1.0ab	5.9±0.1a
4 % WSB	48.2±1.0a	22.8±0.2a	17.3±0.5ab	5.6±0.7a
6 % WSB	49.5±0.9a	23.4±0.9a	18.5±1.1a	4.9±0.3a

The columns with the same letter are not significantly different at p < 0.05

SB straw biochar, WCB woodchip biochar, WSB wastewater sludge biochar

Incubation of amended soils over an extended period may facilitate the formation of stable aggregates, which consequently affects the water retention and porosity characteristics.

#### 3.4 Effects of biochar on soil consistency limits

The effect of biochar application on soil consistency is illustrated in Table 5. Biochar applications significantly (p<0.05) increased the liquid limits (LL) of the soils. Increases in the LL values of soil increase with the application doses of biochar. As compared with the control, the application of 6 % biochar increases LL by 8 % for WCB, 22 % for SB, and 8 % for WSB, respectively. The plastic limit (PL) is a useful index of soil physical quality. The effect of biochar application on PL is

 Table 5
 Effects of biochar application on liquid limit (LL), plastic limit (PL), and plasticity index (PI) of soil (mean±SD)

Treatment	LL (%)	PL (%)	PI (%)
Control	36.9±0.4c	25.8±0.8a	11.1±1.2b
2 % SB	41.1±0.7b	24.68±0.6a	16.5±1.3ab
4 % SB	42.7±0.1ab	24.1±1.2a	18.6±1.3a
6 % SB	45.0±0.9a	22.8±1.0a	22.2±2.0a
Control	$36.9 \pm 0.4 b$	25.8±0.8a	11.1±1.2c
2 % WCB	38.7±0.7ab	26.2±0.0a	12.5±0.7bc
4 % WCB	37.9±0.5ab	23.2±0.1ab	14.7±0.4ab
6 % WCB	39.7±0.6a	22.0±1.3b	17.7±0.7a
Control	$36.9 \pm 0.4b$	25.8±0.8a	11.1±1.2ab
2 % WSB	35.8±0.6b	26.5±0.4a	9.3±0.2b
4 % WSB	36.8±1.0b	24.9±0.6a	11.9±1.6ab
6 % WSB	39.7±0.4a	23.8±1.4a	15.9±1.8a

The columns with the same letter are not significantly different at p < 0.05 *SB* straw biochar, *WCB* woodchip biochar, *WSB* wastewater sludge biochar

not significant while the 6 % WCB-amended soil is significant (p < 0.05). In biochar-amended soils, as compared with the control, PL has a decreasing trend with an increase in the application rate. In general, PL decreases with an increase in application doses, but no significant differences are obtained. The lowest value is obtained from the 6 % WCB-amended soils.

The plasticity index (PI) reflects the range of moisture content, over which the soil is susceptible to compaction by external forces. The higher the PI value, the greater the range of moisture over which the soil is susceptible to compaction. Biochar application significantly (p<0.05) increases the plastic index (PI) value of the soil (Table 5). As compared with the control, SB increases the PI value more than the WCB and WSB. The SB application increases PI by 48, 67, and 99 % with 2, 4, and 6 % application rates, respectively, as compared to the control. Based on the above result, we may conclude that biochar application can extend the range of optimum and workable water content for tillage operations without undue effort and with minimum risk of structural damage.

# 3.5 Changes in soil mechanical properties

The application of biochar significantly (p < 0.01) decreases the tensile strength of soils (Fig. 3). The tensile strength of original Ultisol is 466 kPa, which is reduced to 233, 164, and 175 kPa at the rate of 6 % WCB, SB, and WSB application (Fig. 3a). The reduction in tensile strength is greater in WSBamended soils than in SB- and WCB-amended soils.

The shear strength of soil is described by parameters, cohesion (c) and angle of internal friction ( $\varphi$ ), obtained from direct shear tests. Variations in c and  $\varphi$  for the biocharamended soils are shown in Fig. 3. It is observed that the cohesion of all biochar-amended soils is lower than that of



Fig. 3 Effect of biochar application on the tensile strength (a), soil cohesion (b), and internal friction angle (c) of Ultisol. *Vertical error bars* indicate  $\pm 1$  standard deviation of the mean values. Different *letters* over each column indicate significant (p < 0.05) differences among biochar treatments. *SB* straw biochar, *WCB* woodchip biochar, *WSB* wastewater sludge biochar

control soil, indicating that biochars can reduce the shear strength of Ultisol. The extent of decrease depends on the nature and the application rate of the biochar. The *c* of soil amended with WCB show a significant decrease as compared with the control, whereas no significant difference is observed from the SB- and WSB-amended soils. No significant effects of biochars on internal friction angle ( $\varphi$ ) are found (Fig. 3c). Significant increase in  $\varphi$  can be only observed at the higher rate of WCB. These different mechanical behaviors of soils amended with different biochars are probably due to the different initial pore structure and degree of pore water saturation of the soils. As shear strength within a soil matrix is the result of resistance to movement at interparticle contacts, physical bonds formed across the contact areas and chemical bonds, any mechanism and interaction that hinder or promote the cohesive and frictional forces between adjacent particles invariably affect the shear strength. Thus, the shear strength is probably linked to some of the same bonding mechanism as those involved in aggregation. Until now, data on the effect of biochar on shear strength are not available. More research is needed for understanding the role of biochar in altering the soil chemical bonds and interparticle contacts, thus effecting shear strength.

# 3.6 FESEM/EDS analysis

FESEM images and EDS spectra of biochar-amended soils are shown in Figs. 4, 5, and 6. FESEM images clearly show that soil mineral particles are incorporated not only into the pores of biochar but also onto the surfaces of biochar. Figure 4 shows that application of SB to soils creates porous structure with fine mineral particles inserted inside the pores of the biochar. The large continuous pores among the soil matrix provide a large portion of the total porosity. The interaction between biochar and soil mineral particles results in an aggregation effect, leading to the formation of bigger particles and an increase in the pore size area. EDS analysis indicates that the mineral matter attached to the SB surfaces contains mainly O, Al, Si, and Fe elements with trace amounts of Mn, Mg, Ca, K, Na, and P. The EDS elemental mapping (Fig. 4) indicates the presence of carbon-rich and Si, Al-rich regions on the SBamended soil. The carbon contents in the carbon-rich region are much higher than those in the mineral regions of similar areas. The mineral grains incorporated into the pores of biochar are mainly composed of Al-, Si-, and Fe-rich phases (presumably oxides). FESEM image and elemental mapping of SB-amended soil indicate that the soil clay particles are settled in the pore spaces of biochar and covered on the surface of biochar in significant ratios, which leads to a significant improvement in pore structure of soils.

FESEM images from WCB-amended soil (Fig. 5) clearly show a typical woody cellulosic porous structure with some fine mineral particles with a scale of several micrometers attached on the surface of biochar and inserted inside the pores of biochar. EDS analysis indicates that the composition of elements is consistent with that arising from biochar (point b in Fig. 5). EDS analysis on the mineral particles attached to the biochar indicates the presence of Al, Si, O, and Fe elements, presumably in the mineral form (point a in Fig. 5). Figure 6 indicates that the mineral phases are in intimate contact with the biochar particles in the WSB-amended soil. EDS analysis indicates that the mineral matter attached to the biochar surfaces contain mainly O, Al, Si, Fe, and K elements with trace amounts of Mg, Ca, P, and Ti.





◄ Fig. 4 FESEM image and EDS spectra of SB-amended soil. Four spots (a, b, c, and d) were chosen for EDS analysis. The region denoted by the *white box* on image represents the location of SEM-EDS mapping of C, O, Si, Fe, and Al. SB straw biochar

# 4 Discussion

# 4.1 Direct effect of biochar on soil chemical properties and fertility

Incubation experimental results indicate the effectiveness of biochar in improving the chemical properties and fertility status of strongly acidic Ultisol. The application of biochar significantly increases soil pH, total C, available K and P, and exchangeable K and Ca, and reduces soil acidity. These results are in agreement with previous studies (Lehmann et al. 2003; Steiner et al. 2007; Novak et al. 2009; Yuan et al. 2011; Yuan and Xu 2011; Xu et al. 2012). Our results confirm that the improvement by biochar can be attributed to the chemical properties and nutrient contents of biochar itself. During pyrolysis, most of the Ca, Mg, K, P, and plant micronutrients and about half of N and S in the biomass feedstock are partitioned into the biochar fraction. Table 1 indicates that biochars contain large amounts of soluble and accessible nutrients, particularly P and K. The application of biochar adds directly these nutrient elements to the soil, which increases the nutrient content of soils. The base cations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, and Na<sup>+</sup> in the biochar (Table 1) can exchange with  $Al^{3+}$  and  $H^+$  on the soil negative-charge sites, which as a result decreases soil

Fig. 5 FESEM image and EDS spectra of WCB-amended soil. Two spots (**a** and **b**) were chosen for EDS analysis. *WCB* woodchip biochar

exchangeable acidity and increases soil exchangeable base cations. Therefore, biochar can improve the exchangeable cation status in the soil, especially for calcium, which is in agreement with the results of Lehmann et al. (2003), who believed that original nutrients in the biochar supplied the exchangeable cations in degraded soils. The alkaline metal ( $Ca^{2+}$ ,  $Mg^{2+}$ , and  $K^+$ ) oxides in biochar have positive liming effect when being applied to low pH soils, thereby the application of biochar to acidic soils increases the soil pH and decreases the exchangeable acidity. The increased pH towards neutral has the effect of alleviating Al toxicity in Ultisols and can improve the soil nutrient availability.

#### 4.2 Direct effect of biochar on soil physical properties

Our results confirm the addition of biochar to soil can cause a substantial and significant change in the soil physical characteristics of the strongly acidic Ultisol, namely a significant increase in LL and PI, higher water-holding capacity, and reduction in mechanical strength. These changes are undoubtedly associated with the particular properties of biochar and in particular with its high porosity and low bulk density (Manyà 2012; Mukome et al. 2013). The beneficial effect of biochars on soil physical properties is mainly due to the dilution effect of biochar with higher porosity and lower density. When the biomass is heated, volatile matters may release out of the biomass to create micropores on the surface, and meanwhile those trapped inside the biomass are evaporated to expand the



Fig. 6 FESEM image and EDS spectra of WSB-amended soil. Three spots (**a**, **b**, and **c**) were chosen for EDS analysis. *WSB* wastewater sludge biochar



microstructure. Thus, the resulting biochar has much higher surface area and porosity. These properties are particularly useful for soil application of biochar especially for enhancing soil water-holding capacity, reducing mechanical strength, and increasing soil aggregation. The dilution effect can be attributed to the increased volume of pores as well as the decreased particle density in soil amended with biochar. The effectiveness of different biochars in improving the soil physical properties can be explained by their porosity and bulk density.

The observed overall improvement of soil physical properties is mainly attributed to the increased pore volume of soils caused by the dilution effect of biochar, although the contribution of macroaggregate formation cannot be disregarded. MIP analysis (Fig. 1) indicates that pore size distribution (PSD) of biochar is highly variable, varying from nano-, micro- to macropores (>75  $\mu$ m). The total porosity for SB, WCB, and WSB is 78, 53, and 45 %, respectively (Table 1). Macroporosity (>75 µm) accounts for 35 % for SB, 4 % for WCB, and 9 % for WSB, respectively. Figure 2 indicates that application of biochar significantly (p < 0.05) increases the macroporosity of soil. It is shown that macropores of the soils have been increased from 14 % in the control to 19 % in the 6 % SB-amended soil. This finding is similar to that by Lei and Zhang (2013) who indicated a 5-35 % increase of macroporosity in sandy loam soil by an application of 5 % wood biochar. Meanwhile, micropores are also obviously increased after incorporation of biochar (Fig. 2). Soil water retention capacity is dependent on the distribution of soil pores, which is largely regulated by soil particle size (texture),

structural characteristic (aggregation), and soil organic matter (SOM) content (Lal and Shukla 2004). Application of biochar to soil has been shown to have an effective effect on the waterholding capacity of soil. Compared to the control treatments, the observed increase in  $\theta v$  at any matric potential in biocharamended soils is to a large extent related to the increase of porosity caused by the dilution effect of biochar. At a specific matric potential, the SB-amended soil has always greater values of  $\theta v$  than the WCB- and WSB-amended soils, which can be attributed to the presence of higher volume of pores, lower bulk densities, and higher surface areas in SB. The greater  $\theta v$  at permanent wilting point of soils amended with biochar can be attributed to the increased biochar microporosity. Lei and Zhang (2013) indicated that biochar application directly increased the WHC through the inner surface area of the biochar and indirectly increased the WHC by facilitating the formation of soil aggregates and macropores. Therefore, biochar can better improve water storage by modifying the soil pore size distribution.

Only few studies have so far been devoted to the modification of mechanical strength of soils by the biochar amendment. The physical dilution through the increased total pore volume and total organic carbon by the addition of biochar may cause the reduction in mechanical strength. Previous studies reported that the dilution of dense soil matrix with the less dense biochar would lead to a decrease in the bulk density of soil. Therefore, the low mechanical strength of soil is likely due to the additional pore space induced by the addition of porous biochar. Biochars can also physically modify interparticle contacts in soil through the loosening effects. Being similar to the effects of biochar on the water-holding capacity, the impact of biochar on soil mechanical strength is attributed to its highly porous structure.

# 4.3 Indirect effect of biochar on soil physical properties

The indirect effect of biochar application on the soil physical properties is related to the soil aggregation or structure improvement by biochar. Interaction between biochar and mineral phases improves micro-structure and hence soil aggregation, which is responsible for the reduction in mechanical strength of the soil. The SEM images indicate the rearrangement of soil particles in the biochar-amended soils (Figs. 4, 5, and 6), forming microaggregates and then continuing to combine with other soil-biochar complexes to form macroaggregates. A similar process has been observed by Jien and Wang (2013) when they incorporated a wood biochar into the highly weathered soil. The formation of macroaggregates probably affects soil water-holding capacity because macroaggregates retain more water than the small aggregates by their high total pore volume. FESEM observation indicates that biochar has high concentration of macropores that distribute from the surface to the interior, and that mineral and small organic particles are accumulated in the pores. Water retention at low suctions depends on the content of larger pores, which is strongly affected by the aggregation and soil structure, while water retention at high suctions is influenced more by the soil texture and surface area. Improvement of soil aggregate structure by the addition of biochar increases the total soil porosity and macropores, which as a result increases the water content at low suctions. The obvious change of macroporosity (>75 µm in diameter) may be attributed to the rearrangement of soil particles and formation of macroaggregate.

For the impacts of biochar on mechanical characteristics, there is still a lack of literature. It is expected that soil pore characteristics can affect the soil mechanical behavior, especially when tensile failure occurs, which may explain the reduction in soil mechanical properties of biochar-amended soils. A significantly negative correlation between the macroporosity and tensile strength of dry soil has been reported (Munkholm et al. 2002; Imhoff et al. 2002). The reduced tensile strength for biochar-amended soils is due to the fact that biochars possess more planes of failure, more microcracks, and weaker contact points than mineral phases. Previous studies found that the stress concentration took place in the air-filled cracks and pores and the water-filled pores had no stress concentration (Munkholm et al. 2002; Imhoff et al. 2002), indicating the strong influence of air-filled cracks and pores on soil tensile strength.

Effects of biochar on soil shear strength can also be explained partly by the increased carbon particles with the incorporation of biochar into the soil. Soil mineral particles covered by layers of organic matters with low surface free energy have weak attraction between the solid and liquid phases. It can be seen from FESEM images that some pores and cracks in the biochar-amended soils are empty, and others are partially or completely filled with very fine mineral phases. A portion of the mineral surfaces are coated by organic matters, which reduce the number of mineral-to-mineral contacts. Another source for the decrease of soil cohesion (*c*) by biochar would be the reduction in cementing force caused as a result of coating of hydrophobic carbon on the soil mineral particles.

#### 4.4 Influence of different biochar types on soil quality

Our results suggest that the influence of biochar on the soil quality strongly depends on the biochar feedstock type. The wood-derived biochar shows a better ability to increase the pH and organic carbon of the acidic Ultisol, which is attributed to its higher alkalinity and organic carbon content. The wheat straw-derived biochar possesses higher pore volume than wood-derived biochar. The wheat straw-derived biochar is better to increase soil water-holding capacity and reduce the tensile strength of soil. However, the influence of different biochars on the mechanical properties of soils remains unclear. Further research is needed to better understand the effect of biochar feedstock on soil quality. A reasonable selection of biochar feedstock can be more effective to improve soil quality.

# **5** Conclusions

Pot incubation experiments indicate that biochar application not only increases soil pH, organic carbon, exchangeable cations, and water-holding capacity but also reduces exchangeable  $H^+$  and  $Al^{3+}$ , and tensile strength in strongly acidic Ultisol. Biochar has been proven to be an effective acidneutralizing material, a potential source of nutrients, and an amendment for poor physical characteristics for Ultisols. It is shown that the biochar made from woodchips is more effective in increasing soil pH and decreasing soil exchangeable acidity than those produced from straw and wastewater sludge. The application of biochars significantly reduces the mechanical strength and increases liquid limit and plastic index. Biochars are shown to increase soil water-holding capacity in the whole matric potential range (0-1500 kPa). The ameliorations of soil physical properties, particularly the soil water-holding capacity, by biochar amendments are contributed one hand to the direct dilution of porosity and inner surface area, and on the other hand to the indirect effects on the interaction between biochar and soil mineral phases. As a whole, we show that the incorporation of biochar effectively mitigates the degradation of strongly acidic Ultisols, including the acidification and deterioration of physical properties.

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