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Thermal conductivity of a Brown Earth soil as affected by biochars derived at different temperatures: Experiment and prediction with the Campbell model**

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A b s t r a c t. Thermal conductivity is a significant heat transfer property of soil. However, the influence of biochar on this property is not well known. In this research, the influence of corn straw biochars prepared at 300, 500 and 700ºC on the thermal conductivity of a Brown Earth (Hapli-Udic Cambisol, FAO) soil and its prediction using a Campbell model was examined. The outcomes revealed that the bulk densities of the soil markedly decreased with increases in the biochar amendment rates of 1, 3, and 5% in linear patterns. The reduction in bulk density was mainly attributed to an increase in soil porosity and organic carbon content. With increasing volumetric water contents (10, 20, 30 and 40%), the thermal conductivity of the soils significantly increased, whereas those of soils with biochar amendment were obviously less than that of the CK and the differences increased with the biochar application rates. The pyrolysis temperature of biochar exhibited a negligible effect on the bulk density and thermal conductivity of soils at large. Combining the linear reduction of bulk density with the biochar amendment rate into the Campbell model, well-fitting results for the variation inthermal conductivity versus volumetric water content were obtained and accurate values could be predicted.

K e y w o r d s: biochar, bulk density, thermal conductivity, Brown Earth soil, Campbell model

INTRODUCTION

Biochar is a substance rich in carbon and made from biomass pyrolysis (Githinji, 2014; Lehmann and Joseph, 2015). Over nearly a decade, biochar application with the aim of mitigating the greenhouse effect (Mašek *et al*., 2013; Cayuela *et al*., 2014), soil improvement (Zhu *et al*., 2017; Guo *et al*., 2020) and remediation of soil contaminated with pesticides or heavy metals (Lu *et al*., 2015) has attracted the wide attention of the scientific community. Biochar, as a black particulate matter, can cause the soil colour to become darker and the soil component fraction to change after it is artificially added to the soil (Oguntunde *et al*., 2004; Liu *et al*., 2018), which may in turn affect the surface reflectance and temperature of the soil (Genesio *et al*., 2012). However, in relevant research conducted recently, the influence of biochar on surface reflectivity was rarely discussed (Verheijen *et al*., 2013; Zhang *et al*., 2013; Usowicz *et al*., 2016). In particular, there is not much information about the influence of biochar on soil thermophysical performance (Usowicz *et al*., 2016; Liu *et al*., 2018).

Soil thermal conductivity, an essential indicator of soil thermal properties, is an important heat transfer property that is connected to the ability of soil to conduct heat (de Vries, 1963; Ghuman and Lar, 1985; Meyer *et al*., 2012). It is likewise a prerequisite for studying other soil physical processes, such as water-heat coupled transport, gas diffusion and material transport (Shiozawa and Campbell, 1990). For a certain biomass material, the pyrolysis temperature determines the structure and property of the biochar (Mimmo *et al*., 2014; Zhao *et al*., 2017), which directly affects the application range of the biochar. Soil thermal conductivity depends upon soil structure and composition. The artificial application of biochar into soil could inevitably change the composition ratio of gas, liquid and solid in

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soil, which might affect thethermal conductivity of the soil. Therefore, the influence of biochar on the thermal conductivity of soil has been included (Usowicz *et al.*, 2016; Zhao *et al.*, 2016; Humberto, 2017; Liu *et al.*, 2018).

Besides, the accurate estimation of soil thermal conductivity has become the basis and premise for analysing the soil thermal regime using models, such as the Campbell, Côté-Konrad, and Lu models (Campbell, 1985; Côté and Konrad, 2005; Lu *et al.*, 2007). However, the physical indexes of soil such as bulk density, organic carbon content, and soil component fraction will inevitably change due to the biochar amendment, which will greatly affect the thermal conductivity model parameters. To date, there has been no report concerning the prediction of soil thermal conductivity using these models in the presence of biochar.

Based on this, the aims of the research with disturbed soil column tests are: i) to study the influence of biochars derived at different pyrolysis temperatures and their application rates on soil bulk density; ii) to clarify the effect of water content on soil thermal conductivity in the presence of biochar; iii) taking the Campbell model as a case, to propose an improved prediction for soil thermal conductivity in the presence of biochar. The results could supply a reference for the biochar effect on soil thermal properties.

MATERIALS AND METHODS

The corn (*Zea mays* L.) straw was obtained from Longnan City, Gansu Province, China. The straw was cleaned with water to remove impurities, dried in a desiccator (DZF - 6020A, Shanghai Lichen Instrument Technology Co., Ltd, China) at 80°C for 12 h, and crushed with a kibbler (10B, Changzhou Qianjiang Drying Equipment Engineering Co., Ltd, China). The segments were put into a furnace (HWL-12XC, Shandong Huawei Luye Company, China) and pyrolysed at 300, 500 and 700°C for 6 h under oxygen-limiting and temperature-controlled conditions. The biochars were referred to as CS300, CS500 and CS700, respectively. The basic physicochemical properties of biochars are listed in Table 1, where the pH values were determined using a PHS-3C meter (Shanghai TecFront Electronics Co., Ltd. China); the total contents of O, C, N, and H in biochar were measured using an elemental analyser (Vario EL, Elementar, Germany); the particle density was determined using the pycnometer method; and the Brunauer-Emmett-Teller (BET) surface area and the pore volume were obtained from N_2 adsorption at 77 K on a physical adsorption instrument (Autosorb-1, Quantachrome, USA).

The tested soil was collected from the 0-20 cm soil layer at a vegetable farmland (104°48′30.647″E, 33°24′57.402″N) in Longnan City, China, which was classified as Brown Earth (Hapli-Udic Cambisol, FAO Classification) soil. The soil sample was air-dried, crushed and then sieved through a 2-mm sieve. The fundamental physical and chemical parameters of the soil are listed in Table 2, where the soil texture was measured with a laser particle meter (MASTERSIZER3000, Malvern, UK), the bulk density was measured using the core method; the particle density was obtained using the pycnometer method (Githinji, 2014), the porosity was calculated according to the particle density and bulk density, the organic carbon content was measured according to an agricultural standard (NY/T 85-1988, China) and the pH value was determined with a pH meter.

The soil (100 g) was mixed with CS300, CS500 and CS700 uniformly at the rates (w/w) of 0, 1, 3 and 5% (*i.e.* 0, 1, 3 and 5 g of biochar), respectively and packed into plastic columns (inner radius of 5 cm, volume of 100 cm^3), where the soil with 0% of biochar amendment was set as the control treatment (CK). The CK bulk density was 1.38 g cm^{-3}. The filling process was divided into three layers of uniform filling of soil columns. In this case, the filling process of the other treatments was consistent with the compaction times and compaction pressure of CK. In this way, the bulk density under different treatments could be obtained. The volumetric water content levels were set at 0, 10, 20, 30, and 40%. A syringe was used to inject different

Table 1. Basic physicochemical properties of biochars

Sample	Elemental composition (%)				Particle density (cm^3 g^{-1})	BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	pH
	C	H	N	O				
CS300	64.46	3.98	0.64	21.62	0.910	1.284	0.001	8.50
CS500	74.00	2.36	0.42	11.43	1.18	60.87	0.033	9.46
CS700	76.92	1.05	0.65	5.98	1.34	378.4	0.187	10.18

Table 2. Basic physicochemical properties of soil

Sample	Texture (%)			Bulk density (g cm^{-3})	Particle density (g cm^{-3})	Porosity (%)	Organic carbon (g kg^{-1})	pH
	Sand	Silt	Clay					
Soil	78.44	20.4	1.52	1.38	2.69	48.69	20.75	6.89

amounts of water into the column to control the volumetric water content. The columns were sealed and preserved at 20°C for 72 h in order to achieve equilibrium (The pre-experiments indicated that the thermal conductivity did not change after 72 h). Then the soil thermal conductivity, porosity and organic carbon content were measured.

The determination methods of soil porosity and organic carbon content were the same as those mentioned above. Soil thermal conductivity was determined using a KD2Pro portable soil thermal property analyser (METER Group, Inc., USA) (Zhang *et al*., 2013; Liu *et al*., 2018).

Campbell (1985) put forward an empirical formula of soil thermal conductivity calculation taking into account soil texture, volumetric water content and bulk density:

$$\lambda = A + B\theta - (A - D)\exp(-C\theta^E), \tag{1}$$

where: the coefficients A, B, C, and D may be computed in the light of clay content and soil bulk density; E equals constant 4. λ means the thermal conductivity of the soil (W m^{-1} K^{-1}); and θ means the volumetric water content (cm^3 cm^{-3}). The specific calculation is as follows:

$$A = 0.65 - 0.78\rho_b + 0.60\rho_b^2, \tag{2}$$

$$B = 1.06\rho_b, \tag{3}$$

$$C = 1 + \frac{2.6}{m_c^{0.5}}, \tag{4}$$

$$D = 0.03 + 0.1\rho_b^2, \tag{5}$$

$$E = 4, \tag{6}$$

where: ρ_b means the bulk density of soil (g cm^{-3}); m_c means clay content of soil (%).

In this work, we combined the biochar amendment rate (x, %) and the linear reduction of the bulk density (ρ_b, g cm^{-3}) to correct the Campbell model:

$$\rho_b = -ax + b. \tag{7}$$

Relative error (R_e) and coefficient of determination (R^2) were used to evaluate the simulation precision of the uncorrected and corrected Campbell models:

$$R_e = \sqrt{\sum_{i=1}^{n}(O_i - S_i)^2 / \sum_{i=1}^{n} O_i^2}, \tag{8}$$

$$R^2 = 1 - \sum_{i=1}^{n}(O_i - S_i)^2 / \sum_{i=1}^{n}(O_i - \bar{O})^2, \tag{9}$$

where: S_i is the fitted value of the model, O_i is the measured value, n is the sample size, and $\bar{O}$ is the sample mean value.

The research data were preliminarily managed by Excel 2007. SPSS 17.0 software was used for the variance analysis of the data. The least significant difference (LSD) method was used to investigate the differences between the treatments, where lowercase letters were used to indicate the differences between treatments within groups while uppercase ones indicated differences among groups. The significance level was given as $p < 0.05$.

RESULTS AND DICUSSION

The influences of biochar amendment on the bulk density of soil. The influence of the biochar amendment rate (x) on the bulk density (ρ_b) of soil is displayed in Table 3. The influence of the pyrolysis temperatures at which the biochars were prepared on the soil bulk density was not significant, but the biochar application rate affected soil bulk density markedly. Soil bulk density decreased linearly along with the increased usage of biochar. Table 3 shows the linear regression results with R^2 values being larger than 0.986. When the biochar was applied at 1, 3 and 5%, the bulk density of the soil was 1.36, 1.23 and 1.13 g cm^{-3}, decreasing by 1.45, 10.87 and 18.12%, respectively, compared with CK.

Soil bulk density decreased along with the increased usage of biochar. This is primarily attributed to the lower intrinsic particle density of biochar (Herath *et al*., 2013), increased organic carbon and porosity due to biochar amendment (Bilgili *et al*., 2019). Figure 1 shows the influence of biochar amendment on soil porosity. When the biochar usage was 5%, the porosity of soils with CS300, CS500 and CS700 was 54.4, 54.4 and 55.1%, and the soil porosity increased by 11.9, 11.9 and 13.4%, compared to that of CK, respectively. And when the biochar usage was 3%, the soil porosity in the presence of CS300, CS500 and CS700 was 52.6, 51.7 and 51.9%, increasing by 8.23, 6.38 and 6.79%, compared to that of CK, respectively. The results are consistent with those of previous studies (Ventura *et al*., 2012; Githinji *et al*., 2014). Glaser *et al*. (2002) noted that the reduction in soil bulk density was due to the increase of total porosity and macroporosity of the soil through the application of biochar. However, when

Table 3. Effect of biochar amendment rate (x) on bulk density (ρ_b) of soil

Biochar	Bulk density (ρ_b, g cm^{-3})				Linear regression	
	x (%) 0	1	3	5	Equation	R^2
CS300		1.35 ± 0.010aB	1.23 ± 0.014aC	1.13 ± 0.010aD	ρ_b = -5.223x + 1.392	0.992
CS500	1.38±0.014A	1.36 ± 0.013aA	1.23 ± 0.011aB	1.13 ± 0.011aC	ρ_b = -5.286x + 1.396	0.986
CS700		1.36 ± 0.019aA	1.24 ± 0.012aB	1.13 ± 0.011aC	ρ_b = -5.239x + 1.396	0.988

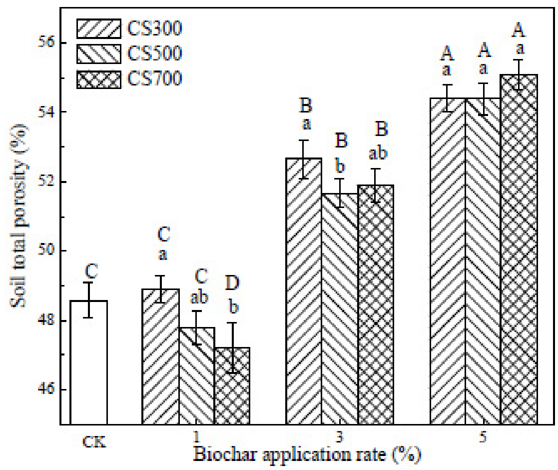

Fig. 1. Effect of biochar amendment on the porosity of soil.

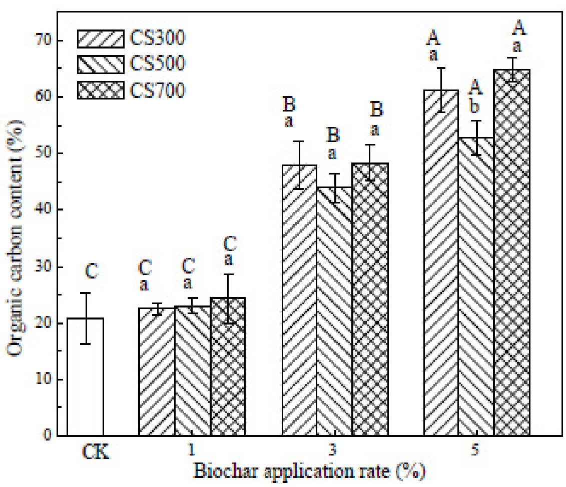

Fig. 2. Effect of biochar amendment on the organic carbon of soil.

the biochar application rate was 1%, the soil porosity in the presence of CS500 and CS700 decreased somewhat compared with CK. It is highly probable that the higher pyrolysis temperature led to tinier particles in CS500 and CS700. These particles could have the effect of blocking some soil pores and reducing soil porosity. Devereux *et al.* (2012) also found that some biochar prepared from herbaceous plants could cause soil pore blockage when applied at a rate less than 1.5%. In addition, Masiello *et al.* (2015) indicated that after soils and biochars are mixed, interparticle pore space can be lost. Immediately post amendment, the resultant interparticle pore space is controlled by the grain size and shape of the biochar and the soil.

The influence of pyrolysis temperatures at which the biochars were prepared on soil organic carbon content is shown in Fig. 2. The soil organic carbon content went up along with increased biochar usage. When the CS300, CS500 and CS700 application rates were 3 and 5%, significant increments in soil organic carbon content by 112-133 and 154-212% were observed, respectively. And when the biochar usage was 1%, increments of 8.38-17.6% were obtained. Glaser *et al*. (2000) considered that the amount of organic carbon in soils treated with biochar were 10 times higher than those in other kinds of soils at the Amazon region. With the increase in the application amount of CS300, CS500 and CS700, the increase in soil organic carbon content becomes more and more obvious. At the same application, the pyrolysis temperature of biochar exhibited a weaker effect on organic carbon content.

The influence of biochar on the thermal conductivity of soil. The soil thermal conductivity variation versus volumetric water content with or without biochar amendment

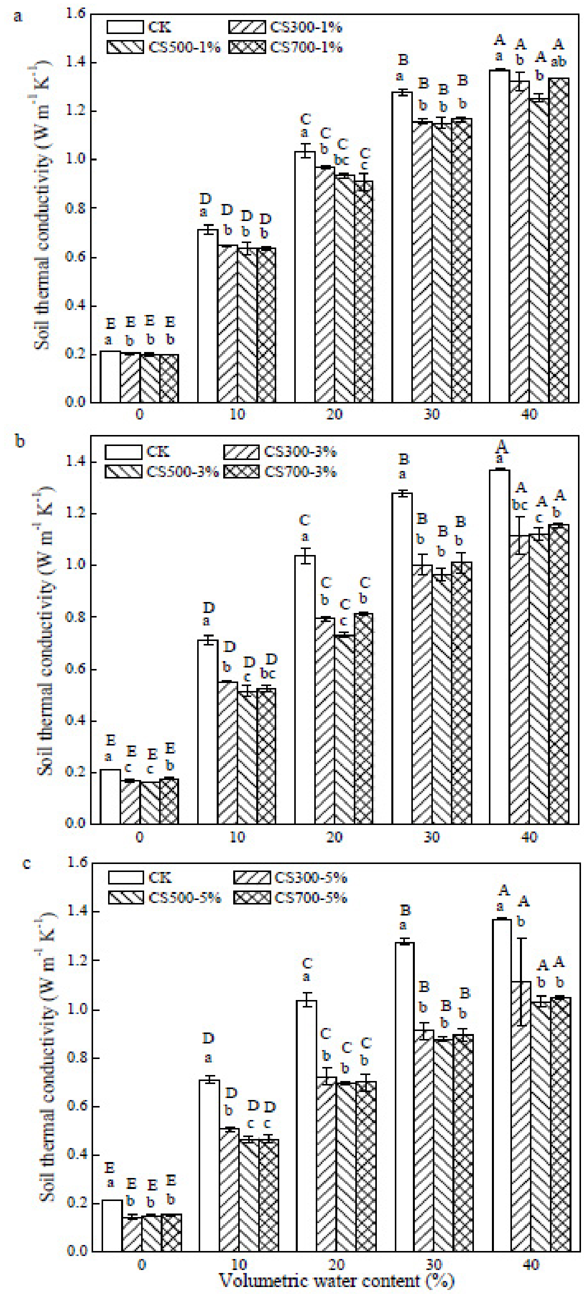

Fig. 3. Effect of volumetric water volume on the thermal conductivity of soil: a – 1%, b – 3%, c – 5%.

is shown in Fig. 3. Soil water is one of the most significant elements which can affect the thermal properties of soil (de Vries, 1963; Usowicz *et al*., 1996; Lu *et al*., 2007). Figure 3 shows that soil thermal conductivity significantly increased with water content. At a given water content level, biochar usage in soil could reduce thermal conductivity ($p < 0.05$) to a remarkable extent. However, at most water contents, the influence of the pyrolysis temperatures at which the biochars were prepared did not make a significant difference to soil thermal conductivity. The specific surface of biochar increases with the pyrolysis temperature, as shown in Table 1. The surface composition and polarity of biochar also change with the pyrolysis temperature. In general, a low pyrolysis temperature results in a biochar with a polar surface and plenty of oxygen-containing functional groups (-COOH, -OH, *etc*.) on the biochar surface, where hydrophilicity increases and water retention may be enhanced. On the contrary, a high pyrolysis temperature results in a larger surface but more hydrophobicity of the biochar, which could reduce the water retention of the soil (Kinney *et al.*, 2012; Zhang *et al.*, 2011). However, in the present study, the water contents were kept. Thus, the effects of pyrolysis temperatures on soil thermal conductivity did not differ significantly.

Besides, the amount of biochar applied influenced the soil thermal conductivity significantly. When the biochar application rate was 1, 3 and 5%, the soil thermal conductivity was reduced by 2.48-12.4%, 15.6-29.3% and 18.7-34.8%, respectively, compared with those of CK at different volumetric water content levels.

The bulk density of biochar was about 0.1 g cm^{-3}, while the thermal conductivity of CS300, CS500 and CS700 were 0.060, 0.057 and 0.058 W m^{-1} K^{-1}. These values are considerably lower than those of quartz (7.7 W m^{-1} K^{-1}) and water (0.594 Wm^{-1} K^{-1}) at 20ºC (Lu*et al*., 2007). Therefore, the application of biochar to the soil can directly reduce the soil thermal conductivity by replacing the soil particles. Soil thermal conductivity increases significantly along with the reduction in porosity and bulk density increment (Potter *et al*., 1985; Arshad and Azzoz, 1996; Abu-Hamdeh and Reeder, 2000; Dec *et al*., 2009). It has been shown that the higher the compactness of a soil, *i.e.* the lower the porosity and the larger the bulk density, the higher the soil thermal conductivity, where the particles of soil are packed more tightly, thus increasing the soil thermal conductivity (Qin, 2003). Therefore, when the biochar application rates increase, the porosity increases and the bulk density decreases (Fig. 1), the reduction in soil thermal conductivity increases, respectively, compared with the CK at different volumetric water content levels (Fig. 3).This influence is more obvious for soils which have more moisture (Horn, 1994; Usowicz *et al*., 1996). In the present study, the bulk density of soil decreased linearly along with biochar usage. A reduction in soil bulk density will lead to air filling between soil porosity, resulting in the contact segregation among the solid particles in soil, and between solid particles and water. As a result, the thermal conductivity of soil decreases along with the bulk density decreasing. When the biochar application rate was 1%, although soil porosity decreased compared to the CK, the thermal conductivity of the soil decreased significantly. The mechanism may be that biochar directly reduced soil thermal conductivity by replacing soil solid particles (Liu *et al*., 2018).

Rovdan *et al*. (2002) considered that soil thermal conductivity changed markedly when only a small amount of organic substance was added to the soil. Abu-Hamdeh and Reeder (2000) determined the thermal conductivity of soil after mixing with peat soil, and discovered that the soil thermal conductivity reduced with peat soil addition. Therefore, they attributed the thermal conductivity reduction to organic carbon content additionin soil. In this research, the soil organic carbon content increased after the application of biochar. The thermal conductivity of the soil declined gradually with organic carbon content addition, which was similar to the outcomes recorded by Abu-Hamdeh and Reeder (2000). Although the soil organic carbon content does not change dramatically under the balance of natural ecosystems, farming, organic fertilizer and other man-made activities could significantly change the soil organic carbon content over a short period of time (Lal, 2004). Therefore, the effect of soil organic carbon content on the thermal conductivity of soil cannot be ignored.

The influence of biochar amendment on the prediction of thermal conductivity using the Campbell model. The fitting results for variations in soil thermal conductivity versus volume water content using the Campbell model with uncorrected and corrected bulk density of soil are shown in Table 4. The determination coefficient R^2 of the uncorrected Campbell model changes from 0.60 to 0.73, the relative error R_e changes from 0.224 to 0.275, while R^2 of the corrected one changes from 0.919 to 0.945, and R_e from 0.10 to 0.13. The calculated $\lambda(\theta)$ data using uncorrected and modified Campbell models and those derived through measurements were listed in Fig. 4. The modified model may provide a more accurate prediction over the whole range of water content, while the uncorrected one produced relatively large errors.

Table 4. Fitting results for variation of soil thermal conductivity versus volume water content using uncorrected and corrected Campbel models

Sample	Campbel			
	corrected		uncorrected	
	R^2	R_e	R^2	R_e
CS300	0.944	0.103	0.737	0.224
CS500	0.919	0.125	0.606	0.275
CS700	0.930	0.117	0.679	0.250

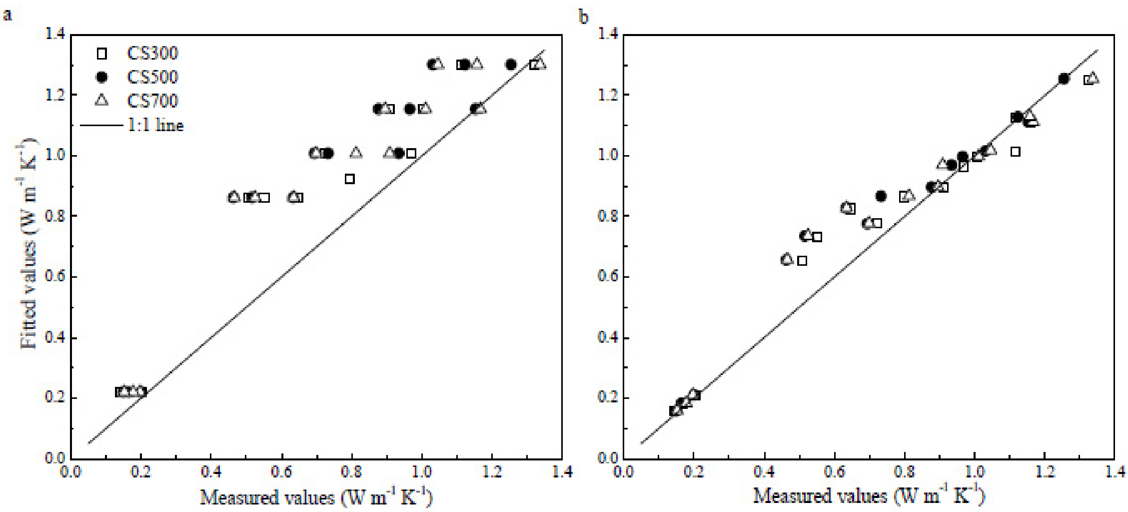

Fig. 4. Comparison between thermal conductivity values measured and fitted using uncorrected (a) and corrected (b) Campbell models.

CONCLUSIONS

1. Biochar application in soil may reduce soil bulk density to a remarkable extent, enlarge soil porosity and increase organic carbon. The pyrolysis temperature of biochar had no significant effect on these indexes.

2. At different water content levels, biochar application could drastically abate soil thermal conductivity. However, no significant differences between the applications of biochar prepared at different pyrolysis temperatures were found.

3. The corrected Campbell model had a better fitting effect ($R^2 > 0.919$, $R_e < 0.123$) and provided a more accurate prediction for soil thermal conductivity.

Conflict of interest: The authors do not declare any conflict of interest.

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