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The role of biochar particle size and hydrophobicity in improving soil hydraulic properties

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Abstract

The physical properties of biochar have been shown to dramatically influence its performance as a soil amendment. This study assessed the role of biochar particle size and hydrophobicity in controlling soil water movement and retention. Softwood pellet biochar in five particle size ranges (>2 mm, 2–0.5 mm, 0.5–0.25 mm, 0.25–0.063 mm and <0.063 mm) was used for the experiment. These particle sizes were tested on two soil types (sandy loam and loamy sand) at four different application rates (1, 2, 4 and 8%) in the laboratory. Soil water suction at wet range and dry range were measured using the Hyprop and WP4-T, respectively. From this, the moisture content at field capacity (θ_{fc}), permanent wilting point (θ_{pwp}) and plant available water (θ_{awc}), were determined. Saturated hydraulic conductivity (K_{sat}) was measured using the KSAT device and biochar hydrophobicity was determined using the ethanol drop test method. Our results showed that biochar hydrophobicity increased with decreasing biochar particle size, leading to a reduction in its water retention capacity. The highest θ_{fc} (0.087 cm^{-3} cm^{-3}) and θ_{awc} (0.064 cm^{-3} cm^{-3}) were observed for soils amended with >2 mm biochar. The soil hydraulic conductivity increased with decreasing biochar particle sizes, with the exception of <0.063 mm biochar, which showed a significant ($p \leq 0.05$) decrease in soil hydraulic conductivity compared to the larger particle sizes. The results clearly showed that both biochar intraporosity (pores inside biochar particles) and interporosity (pore spaces between biochar and soil particles) are important factors affecting amended soil hydraulic properties. Biochar interpores affected mainly hydraulic conductivity; both interpores and intrapores controlled soil water retention properties. Our results suggest that for a more effective increase in soil water retention of coarse soils, the use of hydrophilic biochar with high intraporosity is recommended.

Highlights

- Biochar increases soil water retention and reduces hydraulic conductivity.
- Hydrophobicity of biochar increased with decreasing particle size.
- Coarse biochar particles increased soil water retention due to hydrophilic surfaces and increased intraporosity.

- Fine biochar particles decreased hydraulic conductivity due to reduced macropores.

1 | INTRODUCTION

Biochar is a carbon-rich material obtained from the pyrolysis of organic biomass. Its recalcitrant nature makes it a unique soil amendment because it can store carbon for hundreds to thousands of years (Wang, Xiong, & Kuzyakov, 2016). The importance of biochar goes beyond carbon sequestration and includes improvement of soil structure (Juriga & Šimanský, 2018), hydraulic properties (Li, Zhang, Yang, Zhang, & Xie, 2018b; Omondi et al., 2016), chemical properties (Ajayi & Horn, 2016), increasing soil fertility and plant growth (Obia, Mulder, Hale, Nurida, & Cornelissen, 2018), and reducing pollutants in soil (Kong, Liu, & Zhou, 2014).

Water movement and storage in soils are crucial for successful intensification of agriculture and maintaining productivity in the face of a changing climate. Biochar application, especially in coarse-grained soils, has been shown to alter water retention properties; however, results vary greatly. Although some have found that biochar increases soil water retention (de Duarte, Glaser, de Lima, & Cerri, 2019b; Kameyama, Miyamoto, & Shiono, 2014; Obia, Mulder, Martinsen, Cornelissen, & Børresen, 2016; Villagra-Mendoza & Horn, 2018), others have not observed any significant difference in soil water retention with addition of biochar (Hardie, Clothier, Bound, Oliver, & Close, 2014; Jeffery et al., 2015; Wiersma, van der Ploeg, Sauren, & Stoof, 2020). These variations in observed results are largely due to the differences in biochar properties (Bouqbis et al., 2018; Mašek, Brownsort, Cross, & Sohi, 2013; Schnee, Knauth, Hapca, Otten, & Eickhorst, 2016; Sun, He, Pan, & Zhang, 2017). A meta-analysis by Edeh, Mašek, and Buss (2020) showed that the biochar properties of great importance with respect to improvement of soil hydraulic properties are specific surface area, particle size and porosity. Understanding the roles these properties play, and the underlying mechanisms, will enable informed selection and engineering of biochar for specific soil types and applications.

Generally, biochar improves soil water retention by modifying the shape and sizes of soil pores, increasing total porosity, and increasing aggregate formation and stability. Biochar particle size is likely to play a key role in controlling water storage in soils because it affects both intrapores (pores inside of the biochar particle) and interpores (pore spaces between biochar particles and soil particles) (Liu, Dugan, Masiello, & Gonnermann, 2017). Biochar has pores inside the particles which can hold additional water and thus increase water retention when it is added to soils. Addition of biochar to soils can also alter soil pore size distribution (Blanco-Canqui, 2017), thus affecting water movement and storage. Biochar particles can fill the large pore spaces that exist in coarse-grained soils, reducing the rate of water flow and increasing retention. Several published studies reported the impact that biochar particle sizes have on soil water retention; however, with conflicting results. Although some studies reported an increase in soil water retention with the use of fine biochar (0.5–0.06 mm) (de Duarte, Glaser, & Cerri, 2019a; Liao & Thomas, 2019), another study by Liu et al. (2017) reported a reduction in soil water retention with the use of fine biochar (<0.25 mm). These contrasting results suggest that particle size alone does not explain the mechanisms influencing how biochar controls water movement and storage in soil.

Another key property of biochar affecting its interactions with water, and therefore impact on soil water retention, is hydrophobicity (Gray, Johnson, Dragila, & Kleber, 2014; Kameyama, Miyamoto, & Iwata, 2019). Hydrophobic biochar can have water-repellent properties due to the presence of organic materials on its surface or within pores (Blanco-Canqui, 2017). Fahmi, Samsuri, Jol, and Singh (2018) showed that different biochar particle sizes obtained by grinding and sieving biochar from the same feedstock can have varying surface functional groups and thus have varying hydrophobicity. None of the studies by de Duarte, Glaser, and Cerri (2019a), Liao and Thomas (2019) and Liu et al. (2017) determined the hydrophobicity of the biochar after grinding and sieving, which may also have played a role in the results obtained. Therefore, more information on the combined role that both particle size and hydrophobicity play in modifying soil hydraulic properties is needed.

The key objectives of the study reported in this paper were to: (a) understand the hydrophobicity of various biochar particle sizes, (b) provide further insights into how biochar particle sizes affect its efficacy in relation to

TABLE 1 Basic properties of LUFA 2.1 and 2.2 soils and softwood biochar (mean values ± standard deviation)

	pH	C_{org} %	TN	Sand	Silt	Clay	Texture	BD $g^{-1}\,cm^{-3}$	H %	O	Ash	TSA $m^{-2}\,g^{-1}$
2.1	4.7 ± 0.1	0.67 ± 0.08	0.06 ± 0.02	86.1 ± 0.7	10.2 ± 1.3	3.7 ± 0.8	Loamy sand	1.43 ± 0.04	—	—	—	—
2.2	5.6 ± 0.4	1.71 ± 0.30	0.18 ± 0.03	78.3 ± 1.0	13.7 ± 1.0	8.0 ± 1.5	Sandy loam	1.23 ± 0.94	—	—	—	—
Biochar	8.44 ± 0.69	90.21 ± 0.39[a]	<0.1	—	—	—	—	—	1.83 ± 0.15	6.02 ± 0.74	1.89 ± 0.43	162.3

Abbreviations: BD, bulk density; BET, brunauer-emmett-teller; C_{org}, organic carbon; H, hydrogen; O, oxygen; TN, total nitrogen; TSA, total surface area.

[a]value for total carbon.

soil hydraulic properties, and (c) discuss the relative contributions of biochar particle size and hydrophobicity to the mechanisms behind biochar's effect on soil hydraulic properties. The study hypothesis was that smaller biochar particle size will have a greater effect on increasing soil water retention than larger particle size. This is because it would have greater surface area, can easily fit into the large pores of sandy soils, and can increase meso-porosity (soil pore size ranges of 5–30 μm), thus it is likely to have a bigger effect even at lower application rates. Findings from this study will provide information on how biochar particle sizes and hydrophobicity drive changes in soil water retention of biochar–soil mixtures. This will be important in enhancing biochar low-dose–high-efficiency benefits specific to increasing soil water retention.

2 | METHODOLOGY

2.1 | Soil and biochar

Standard soils (LUFA 2.1 and 2.2) were collected from the Landwirtschaftliche Untersuchungs und Forschungsanstalt (LUFA) at Speyer, Germany ("Use of standard soils", n.d). The advantages of using standard lufa soils include that tests from different years can be compared because of its long-term availability, they are natural soils under organic agricultural use, and they are easy to procure and prepare. The lufa soils used in this study were sampled in 2018 from uncultivated and meadow field for 2.1 (loamy sand) and 2.2 (sandy loam), respectively, from a depth of 0–20 cm. Basic soil properties for the two soil types are provided in Table 1. Soil samples were air-dried and sieved through a 2-mm sieve. The biochar used (SWP700) was one of the standard biochars developed by the UK Biochar Research Centre (UKBRC), produced from mixed softwood pellets at a pyrolysis temperature of 700°C (Mašek et al., 2018). The basic properties for the biochar used are given in Table 1.

2.2 | Sample preparation and soil water properties measurement

We ground and sieved the biochar into five sizes: >2 mm, 2–0.5 mm, 0.5–0.25 mm, 0.25–0.063 mm and <0.063 mm. Then the biochar was mixed with the two soils at four application rates (1, 2, 4 and 8 wt% of biochar corresponding to 26.6, 53.2, 106.4 and 212.8 t/ha, assuming a depth of 20 cm and using an average soil density of 1.33 $g^{-1}\,cm^{-3}$). To measure the water content of soils and soil + biochar mixtures at higher suctions, we used the Dew point potentiometer WP4-T (Decagon Devices,

Inc., Pullman, WA, USA). The WP4-T is a quick and accurate method for measuring soil water suction above 1,000 kPa (Campbell, Smith, & Teare, 2007). To prepare samples for measuring water suction using the WP4-T, approximately 5 g of biochar–soil mixture was placed into an AquaLAb sample cup (≈4 cm in diameter) with a lid, and drops of de-aired distilled water were added to the samples (from 1 to 20 drops, to achieve the desired humidity). The samples were thoroughly mixed, sealed, and left to equilibrate at room temperature for 24 h. We placed the sample into the WP4-T and measured the suction after the equilibration period. The samples were thereafter oven-dried (105°C), weighed and values for water content (θ) obtained. From the data collected, we derived the value for permanent wilting point (θ_{pwp}) as θ at 1,500 kPa (Rai, Singh, & Upadhyay, 2017). This was carried out in triplicate and the mean and standard deviations were calculated.

To measure soil water suction in the wet range (>1,000 kPa), we used the Hyprop (Decagon Devices, Inc., Pullman, WA, USA). The Hyprop measures soil water retention with the evaporation method (Schindler, Durner, von Unold, Mueller, & Wieland, 2010). Each biochar–soil mixture was poured into the Hyprop sample ring without intentional compaction and saturated using de-aired water for 24 h, by placing the soil sample in a water pan and filling the pan with water. The soil was allowed to saturate from the bottom without pouring water on the top of the sample to avoid trapping air. The samples were fixed to the Hyprop unit with two tensiometers of heights 1.75 and 3.75 cm, measuring suction while simultaneously measuring sample mass change using a connected Hyprop balance during the evaporation process. The tensiometers reached suction limits at pF 3.0 and measurements were stopped at this point. The duration of measurements varies depending on the soil type. For our samples, this was approximately 20 days. Due to the length of time it took for each sample measurement (∼20 days), we only measured moisture retention curves by Hyprop for the 2.1 soil, with addition of >2, 2–0.5 and <0.063 mm biochar at 0 and 2 wt% application rates. Each soil and soil + biochar mixture was measured in triplicate and mean values for each suction with corresponding weight were recorded. From the collected data, we calculated water content at saturation (θ_{sat}) and field capacity (θ_{fc}) as θ at 0 and 33 kPa, respectively (Rai et al., 2017). With data from WP4-T and Hyprop we were then able to calculate the plant available water (θ_{awc}) as $\theta_f - \theta_p$.

We measured the saturated hydraulic conductivity of each sample in triplicate using the KSAT device (Decagon Devices, Inc., Pullman, WA, USA). This instrument uses both the falling head and constant head methods on a soil core and is completely automated. The

sample preparation follows a similar process to the Hyprop. After saturation, the soil core was set up on the KSAT device and measurement taken with the falling head technique. The saturated hydraulic conductivity (K_{sat}) was determined using the Darcy equation:

$$K_{sat} = (L-V)/(H-A-T),$$

where L = length of sample, V = percolated volume of water, H = height of the water column, A = area of probe and T = time.

2.3 | Measurement of soil moisture curves, unsaturated hydraulic conductivity curves and soil pore size distribution

To obtain the moisture and unsaturated hydraulic conductivity curves, combined measured data from Hyprop and WP4-T were fitted for each treatment using the van Genuchten model (van Genuchten, 1980) with the Hyprop fit software ver. 4.2.1 (Pertassek, Peters, & Durner, 2011). This model is given by the equation:

$$\theta = \theta_r + (\theta_s - \theta_r)\left[1 + (\propto h)^n\right]^{-m},$$

where θ_r is residual water content, θ_s is saturated water content, $\propto$ is the inverse of the air entry pressure, n and m are empirical shape parameters and h is tension potential.

The unsaturated hydraulic conductivity is calculated according to the Darcy-Buckingham law (Schindler et al., 2010):

$$K\left(\Psi_{mean}\right) = \frac{\Delta V}{2A\Delta ti_m},$$

where Ψ_{mean} is the mean tension from the upper tensiometer (positioned at 3.75 cm above the bottom of the sample) and the lower tensiometer (positioned at 1.25 cm above the bottom), averaged over a time interval of Δt, ΔV is the total evaporated water volume of the complete sample, A is the cross-sectional area of the sample and i_m is the mean hydraulic gradient in the time interval.

We calculated bulk density as M_d/V for each sample using measured oven dry mass (M_d) and volume of the Hyprop soil core ($V = 248.5\,cm^3$). Soil pore size distribution data were computed from the soil water retention data for tensions of approximately −3, −6 and −33 kPa using the procedure outlined in Hernandez-Ramirez et al. (2014). These tensions correspond to pore diameters of 100, 50 and 9 µm. Pore volume fractions were quantified from the change in volumetric water content using these pore diameters as class boundaries. Macroporosity,

mesoporosity and microporosity were defined as the fractional volume of pores with radii >100, 100–50 and 50–9 μm, respectively.

2.4 | Biochar hydrophobicity measurements

Hydrophobicity of the different biochar particle sizes was determined using the ethanol drop test. This method uses the known surface tensions of ethanol solution at different molarities to determine water repellency (Letey et al., 2000). Ethanol solutions of 0 to 6 M were prepared at increments of 0.2 M; 10 g of each biochar sample was weighed into an aluminium foil dish (diameter 5 cm × 3 cm depth) and 40-μL droplets of each solution added to the smoothed surface using a pipette (Figure 2). The time taken for each droplet to be absorbed was recorded using a stopwatch. The lowest concentration to be absorbed in <10 s (molarity of ethanol droplet [MED]) was reported for that sample and hydrophobicity categorized as hydrophilic (<1 M), hydrophobic (1–2 M), strongly hydrophobic (2–3.5 M) and extremely hydrophobic (>3.5 M) (Kinney et al., 2012).

2.5 | Statistical analysis

The mean of the water retention curve and K_{unsat} was reported for soil and soil + biochar samples (Figures 1 & 4). To evaluate soil hydraulic properties, θ_{sat}, θ_{fc}, θ_{awc}, θ_{pwp} and K_{sat} were compared among the treatments. We assumed full saturation for the soil and soil + biochar samples at pF 0, with the total porosity defined as the corresponding water content. We performed statistical comparisons of θ_{sat}, θ_{fc} and θ_{awc} between soil and soil + biochar mixtures by one-way analysis of variance (ANOVA), whereas θ_{pwp} and K_{sat} were compared between treatments by two-way ANOVA to account for rate of application. This was followed by Tukey's range test to test for significant differences between means at the 5% probability level. All analysis was carried

FIGURE 1 Comparison of soil moisture retention curve for control soil, and >2 mm, 2–0.5 mm and <0.063 mm biochar-amended soil [Color figure can be viewed at wileyonlinelibrary.com]
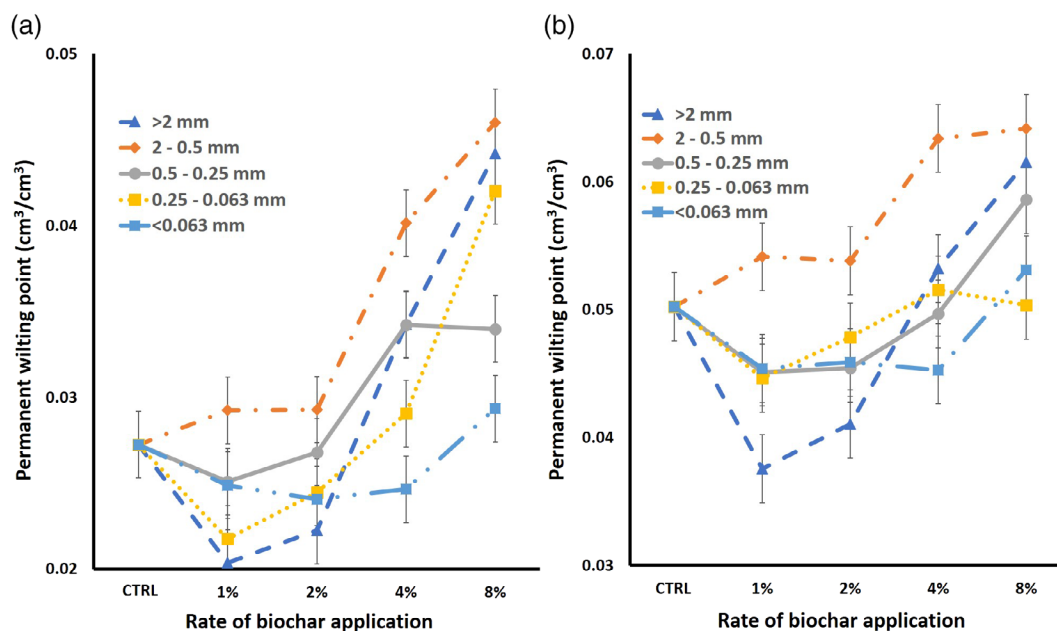

FIGURE 2 Effect of biochar particle size on permanent wilting point of a loamy sand (a) and sandy loam (b) at different application rates [Color figure can be viewed at wileyonlinelibrary.com]
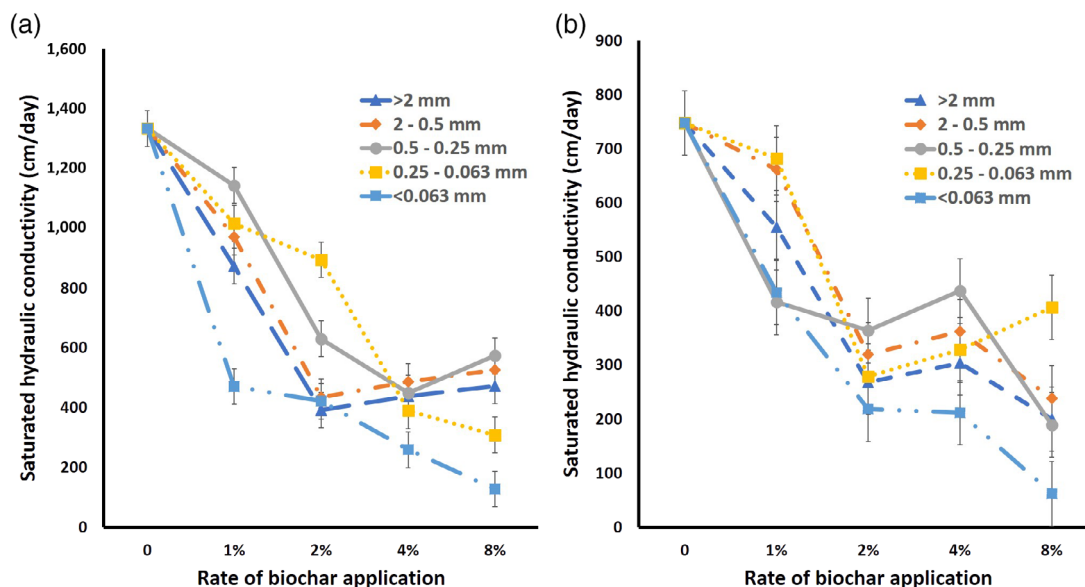
FIGURE 3   Effect of biochar particle size on saturated hydraulic conductivity of a loamy sand (a) and sandy loam (b) at different application rates [Color figure can be viewed at wileyonlinelibrary.com]

out using Minitab 17 (State College, PA; Minitab, Inc. (www.minitab.com)).

3 | RESULTS

3.1 | Soil water retention properties

The results presented in Figure 1 clearly show that biochar particle size influenced water retention at different soil water potential levels. This suggests that biochar particle size has a role to play in controlling the storage of water in soils. At soil water potential 0–1 kPa, the difference in water content (θ) between biochar soil mixtures and the control was larger for 2–0.5 mm (Figure 1), whereas for >2 mm and <0.063 mm (Figure 1) there were no clear differences between the θ of biochar-amended soils and the control. The curve for >2 and 2–0.5 mm starts to separate again at soil water potential of ≈1,000 kPa. At this point, the difference in θ between biochar–soil mixtures and the control was larger for soil with biochar particles >2 mm compared to that with particles in size range of 2–0.5 mm. Soil with biochar particles smaller than 0.0063 mm showed no clear difference in θ compared to the control.

Water content at permanent wilting point (θ_{pwp}) for the biochar-amended soils increased with increasing rate of biochar application (Figure 2). For both soil types, looking at soil–biochar mixtures with 2–0.5 mm biochar, there was an increase in θ_{pwp} with increasing rate of application to the tune of 4% (0.034 and 0.063 cm^{-3} cm^{-3}

for loamy sand and sandy loam, respectively). There was, however, no significant difference between the θ_{pwp} of 4% and 8% application rates. For loamy sand at 2% application rate, the θ_{pwp} of soils with 2–0.5 mm biochar (0.029 cm^{-3} cm^{-3}) was significantly greater than the θ_{pwp} of soils with <0.063 mm biochar at 4% application rate (0.025 cm^{-3} cm^{-3}). It took the application of 8% <0.063 mm biochar to get the same results (θ_{pwp} = 0.029) that were observed for 2–0.5 mm biochar at 2%. These results were also observed for sandy loam soils. This shows that modification of particle sizes of biochar can help enhance low-dose–high-efficiency benefits.

Compared to the control, the main effects of biochar particle size on θ_{pwp} were significantly higher ($p \leq 0.05$) for biochar particle sizes of 2–0.5 mm, with a 24.7 and 14.7% increase for loamy sand (Figure 2a) and sandy loam (Figure 2b), respectively, whereas the other particle sizes showed no statistical difference compared to the control for the two soil types. For loamy sand, at 1% (0.029 cm^{-3} cm^{-3}) and 4% (0.04 cm^{-3} cm^{-3}) biochar application rates, the θ_{pwp} of soil amended with 2–0.5 mm biochar was greater than that of all other particle sizes, whereas there were no statistical differences between the θ_{pwp} of soils with 2–0.5 mm and 0.5–0.25 mm biochar at 2% application rate and between >2, 2–0.5 and 0.25–0.063 mm at 8% biochar application rate.

For sandy loam, the θ_{pwp} of 2–0.5 mm biochar was greater than that of all other biochar particle sizes at all rates of application (0.0541, 0.0538, 0.063 cm^{-3} cm^{-3} for 1, 2 and 4%, respectively), except at 8%, where no statistical differences were observed between >2, 2–0.5 and
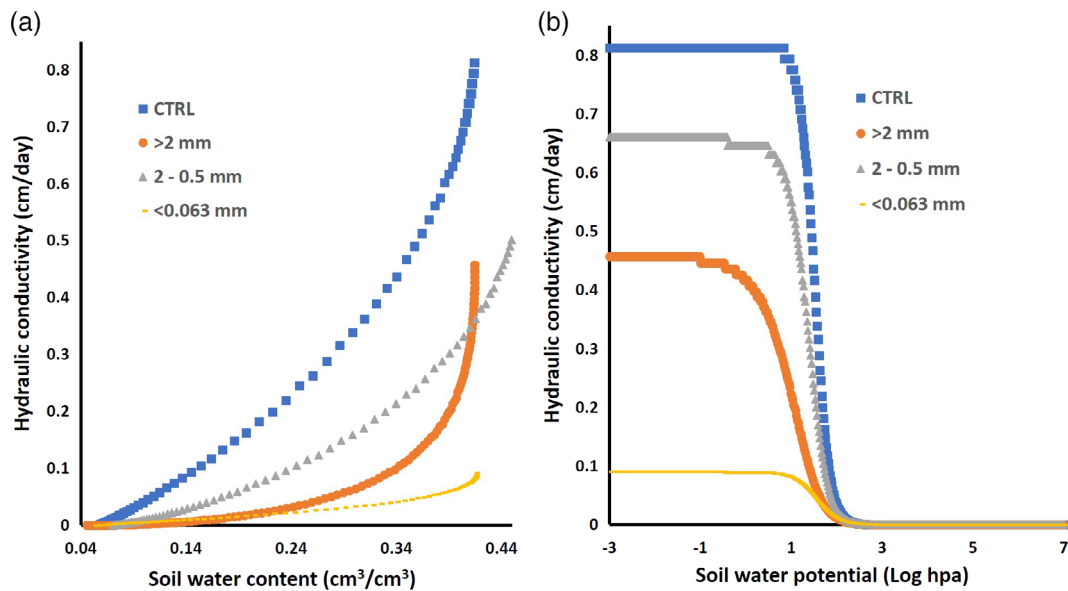
FIGURE 4 Effect of biochar particle size on hydraulic conductivity curve plotted against soil water content (a) and potential (b) for a loamy sand [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Effect of biochar particle size on soil water retention properties (mean values ± standard deviation)

	$cm^{-3} cm^{-3}$				cm	
Biochar particle size	θ_{sat}	θ_{FC}	θ_{AWC}	θ_{RWC}	α	n
Control	0.415 ± 0.001^b	0.061 ± 0.003^b	0.034 ± 0.003^d	0.059 ± 0.002	0.025 ± 0.0004	3.396 ± 0.187^a
>2 mm	0.418 ± 0.006^a	0.087 ± 0.002^a	0.064 ± 0.001^a	0.052 ± 0.001	0.032 ± 0.0001	1.907 ± 0.007^b
2–0.5 mm	0.454 ± 0.013^b	0.085 ± 0.005^a	0.057 ± 0.001^b	0.074 ± 0.005	0.026 ± 0.002	2.909 ± 0.182^b
<0.063 mm	0.415 ± 0.001^b	0.063 ± 0.003^b	0.040 ± 0.003^c	0.032 ± 0.030	0.031 ± 0.015	2.16 ± 0.812^b

Abbreviations: θ_{AWC}, available water content; θ_{FC}, water content at field capacity; θ_{RWC}, residual water content; θ_{sat}, saturated water content; α, negative inverse of the air entry potential; n, shape parameter related to the curve smoothness. Means that do not share a letter are significantly different.

0.5–0.25 mm biochar amendments. For both soil types, there was a reduction in θ_{pwp} for biochar–soil mixtures with >2 mm biochar at lower application rates of 1 and 2%.

The addition of 2–0.5 mm biochar increased θ_{sat} by 8.5%, whereas there were no statistically significant differences observed for the θ_{sat} among the other biochar particle sizes and the control (Table 2). Water content at field capacity (θ_{fc}) for >2 mm and 2–0.5 mm biochar amendment increased by 30.4 and 28.5%, respectively, whereas there was no statistically significant difference observed between the θ_{fc} of <0.063 mm biochar–soil mixtures and the control (Table 2).

With decreasing biochar particle size, its effect on plant available water content (θ_{awc}) decreased. There was a significant ($p \leq 0.05$) increase in θ_{awc} of up to 47.8, 40.8 and 16.1% for soils amended with >2, 2–0.5 and <0.063 mm biochar, respectively, compared to the control treatment (Table 2). The highest θ_{awc} occurred in the biochar–soil mixtures with >2-mm particle size (0.064 cm^{-3} cm^{-3}).

This could be attributed to its θ_{fc} increasing while its θ_{pwp} did not change or even decreased in some cases (Figure 2). None of the biochar amendments affected the soil residual water content and the α parameter (which relates to the inverse of the air-entry potential). There were also no significant differences between the various biochar particle sizes measured (Table 2).

The shapes of the water retention curves (n) were similar among biochar particle sizes but different from the control (Table 2). Generally, biochar–soil mixtures had a flatter curve, whereas the slope of the control soil was steeper, suggesting that the biochar–soil mixtures had a more uniform distribution of pore sizes.

3.2 | Hydraulic conductivity

Results from the saturated hydraulic conductivity (K_{sat}) measurements showed that biochar amendment

decreased K_{sat}, and the effect was stronger with increasing rate of biochar application for all particle sizes (Figure 3). At the same rate of application, >2 and 2–0.5 mm biochar-amended soils had similar K_{sat} for both soil type. Looking at >2 mm biochar-amended soils, increasing biochar application rate up to 2% significantly reduced K_{sat} (392 and 268 cm/day for loamy sand and sandy loam, respectively), whereas there was no significant difference observed between higher rates of application and 2%.

At the 2% rate of application, the K_{sat} of soils with >2 mm biochar for both soil types was significantly lower (392 and 268 cm/day for loamy sand and sandy loam, respectively) than that of 0.5–0.25 mm biochar (630 and 363.7 cm/day for loamy sand and sandy loam, respectively). It took twice the application rate (4%) of 0.5–0.25 mm biochar for its K_{sat} to be statistically equal to that of >2 mm at 2% application rate for loamy sand, and quadruple (8%) for sandy loam, which suggests that changing the biochar particle size can help achieve low-dose high-efficiency benefits.

The magnitude of decrease in K_{sat} due to biochar addition was higher in soils amended with larger biochar particles (>2 mm) compared to those with other particle sizes, except for the <0.063 mm. For loamy sand, the decreases were 54.2, 51, 41.2, 47.1 and 76% when compared to the control for >2, 2–0.5, 0.5–0.25, 0.25–0.063 and <0.063 mm biochar, respectively (Figure 3a). For sandy loam, the reductions were 45.4, 30.2, 34.1, 41.5 and 69.3% when compared to control for >2, 2–0.5, 0.5–0.25, 0.25–0.063 and <0.063 mm, respectively (Figure 3b).

Data from the Hyprop experiments were used to plot unsaturated hydraulic conductivity (K_{unsat}) as a function of soil volumetric water content (Figure 4a) and water potential (Figure 4b). With increasing θ, the K_{unsat} also increased, whereas the opposite was observed when plotted against water potential. The K_{unsat} was also affected by biochar particle sizes. At soil water potentials of 0–100 kPa and θ of 0.14–0.44 $cm^{-3}\ cm^{-3}$, the K_{unsat} of <0.063 mm was lower than that for other particle sizes. Both the K_{unsat} and K_{sat} of soil amended with biochar particles <0.0063 mm was lower than that of soils amended with larger biochar particles. This observation was unexpected, given that <0.0063 mm biochar amendment also resulted in comparably lower water retention. Possible explanations are explored in the Discussion section.

3.3 | Biochar hydrophobicity

The different biochar particle sizes were tested for hydrophobicity. The results showed that grinding and sieving

TABLE 3 Hydrophobicity of the different biochar particle sizes

Particle size	MED (M)	Time (s)	Category
>2 mm	0.2	<1	Hydrophilic
2–0.5 mm	0.2	4.5 ± 0.7	Hydrophilic
0.5–0.25 mm	0.4	5.0 ± 0.7	Hydrophilic
0.25–0.063 mm	1.2	7.2 ± 0.3	Hydrophobic
<0.063 mm	3.0	8.8 ± 0.3	Strongly hydrophobic

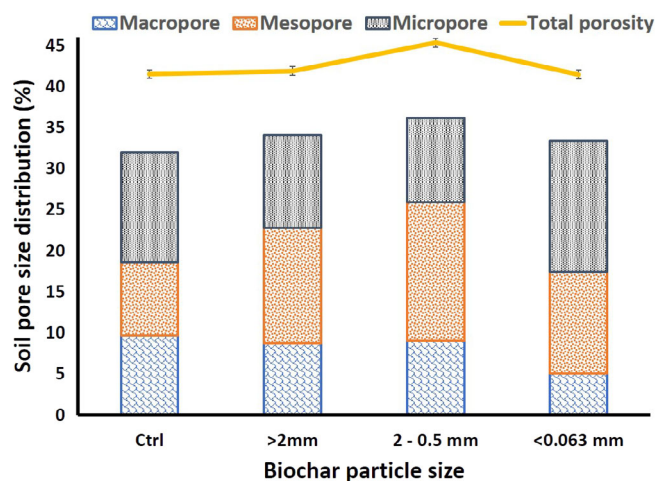Abbreviation: MED, molarity of ethanol droplet.

FIGURE 5 Effect of biochar particle size on soil pore size distribution [Color figure can be viewed at wileyonlinelibrary.com]

of biochar into smaller particle sizes increased its tendency to repel water molecules (Table 3). Biochar particle sizes of >2 mm, 2–0.5 mm and 0.5–0.25 mm were hydrophilic, whereas 0.25–0.063 mm and <0.063 mm were hydrophobic. The molarity of ethanol droplet (MED) increased as particle size decreased, with <0.063 mm having the highest MED (3 M), classified as strongly hydrophobic.

3.4 | Soil pore size distribution

The pore size distributions of soil and soil–biochar mixtures using different particle sizes are shown in Figure 5. The highest total porosity was observed for soil–biochar mixtures with 2–0.5-mm particle size (45.32%), whereas the total porosity for all other soil–biochar mixtures had no significant difference to the control. The 2–0.5 mm biochar-amended soil had a slightly higher proportion of mesopores (16.9%) compared to the >2 mm biochar-amended soil (14.05%), whereas the soils amended with the <0.063 mm biochar fraction had the least mesopores (8.92%) and most micropores (15.93%). The proportion of

macropores of soils amended with <0.063 mm was also smaller than for the other particle sizes. Control, >2 and 2–0.5 mm biochar–soil mixtures had a 48, 42.3 and 44.3% greater proportion of macropores than <0.063 mm biochar fractions.

4 | DISCUSSION

Our results showed that biochar increased soil water retention and decreased hydraulic conductivity. This could be due to an increase in soil porosity. Increased porosity and pore connectivity, especially in the meso-pore range, leads to an increase in water retention. A shift towards more mesopores, especially in sandy soils, could also lead to a reduction in macropores and a reduced hydraulic conductivity. Addition of biochar to soil usually increases its porosity, number of pores and connectivity of pores (Obia et al., 2016; Zhao, Ta, & Wang, 2017b). This effect, combined with a decrease in bulk density, and increased formation of macroaggregates and aggregate stability, can lead to a reduced flow of water in soil and more retention (Pituello et al., 2018; Speratti, Johnson, Martins Sousa, Nunes Torres, & Guimarães Couto, 2017; Wang, Fonte, Parikh, Six, & Scow, 2017). Our results are consistent with those of several previous studies (Basso, Miguez, Laird, Horton, & Westgate, 2013; Liao & Thomas, 2019; Liu et al., 2017) that also observed increased soil water retention with biochar amendment. However, some other reports have shown cases where biochar had no significant effect on soil hydraulic properties (Hardie et al., 2014; Wiersma et al., 2020). These findings highlight the importance of biochar properties matching specific soil type/texture and that they can be tailored for a better outcome.

From our result, biochar effectiveness in increasing soil water retention varied in relation to its application rates and particle sizes. Generally, soil water retention increased while hydraulic conductivity decreased with increasing rate of application. Due to its porous nature, biochar can absorb and retain water. An increase in the amount of biochar added to the soil will also increase water retention properties. Other studies have also reported increasing water retention and decreasing hydraulic conductivity with increasing biochar application rates (Bruun, Petersen, Hansen, Holm, & Hauggaard-Nielsen, 2014; de Melo Carvalho et al., 2014; Lim, Spokas, Feyereisen, & Novak, 2016; Liu et al., 2016).

Using very high application rates of biochar may not be economically beneficial considering that the cost could range from US$ 222 to 584 per ton (Shackley, Hammond, Gaunt, & Ibarrola, 2011). Therefore, for soil water retention purposes, it is necessary to investigate methods that

can increase biochar's low-dose–high-efficiency benefits. Biochar application methods can help optimize its agricultural profitability. Spot and deep-banded applications can be a way to achieve high local concentration in the root zone while keeping per hectare application rates manageable (Li, Zhang, Yan, & Shangguan, 2018a; Blackwell, Riethmuller & Collins, 2009). Due to biochar's varying characteristics, it is also important to understand the mechanisms responsible for biochar's ability to enhance different soil properties. If the right biochar characteristics are enhanced to match the specific soil properties needing improvement, this would help increase low-dose–high-efficiency benefits. Our research suggests that changing the particle size of biochar can enhance low-dose–high-efficiency benefits. In contrast with finer biochar particles, larger biochar particles significantly increased soil water retention and decreased hydraulic conductivity at lower rates of application (Figures 2 & 3). This could be attributed to the modification of the intra-pore, interpore and hydrophobicity caused by changing particle sizes.

Our results suggest that biochar intrapore, interpore and hydrophobicity play fundamentally different roles in soil water movement and retention. X-ray CT scans have shown that pores exist inside biochar particles (intra-pores) that also contribute to water storage (Hyväluoma et al., 2018). A destruction of these pores would reduce the amount of water that can be held in the pore network. Liu et al. (2017) used the intraporosity of a mesquite biochar to estimate how much water a biochar intrapore could hold. They found out that mesquite biochar can store up to 0.6 m^3 of water per 1 m^3 of biochar. Additionally, they observed an increase in the skeletal density of smaller biochar particles, which is associated with a decrease in its intraporosity and thus a decreased capacity to hold water. In our results, soils mixed with <0.063 mm biochar had the lowest θ_{fc} (0.063 cm^{-3} cm^{-3}), θ_{awc} (0.04 cm^{-3} cm^{-3}) and θ_{pwp} (0.023 cm^{-3} cm^{-3}) (Table 2 & Figure 2), possibly due to damage to its intrapore caused by grinding and sieving. A reduction in the intraporosity of fine biochar could lead to a decrease in its ability to increase water retention when applied to soils.

Although our results show a general increase in water retention with larger biochar particle sizes (>2 and 2–0.5 mm), they also show that the θ_{sat} for >2 mm was not different from the control. This could be related to the total porosity of the soil. Soil pore size distribution data were computed from our soil water retention curve (Figure 5). The results showed that the total porosity was significantly greater for 2–0.5 mm, whereas other biochar particle sizes had similar total porosity to the control. This could have resulted in 2–0.5 mm biochar–soil

mixtures having higher θ_{sat} than >2 mm. As total porosity is closely related to θ_{sat}, with an increase in total porosity, the amount of water the soil can store when saturated also increases.

The differences observed among the soil pore size distributions for various biochar particle sizes could also explain why <0.063 mm had lesser K_{sat} and K_{unsat} even when the water retention was lower. X-ray CT studies have shown that addition of biochar to soils can change the shape, size and connectivity of soil pores (Quin et al., 2014). Our results also show that the macropores for <0.063 mm were smaller than for the other particle sizes. Control, >2 and 2–0.5 mm biochar–soil mixtures had a 48, 42.3 and 44.3% greater proportion of macropores than <0.063 mm biochar fractions (Figure 5). Hydraulic conductivity is largely controlled by pore sizes, continuity and distribution in soil (Amer, 2012). Macropores, also known as transmission pores, allow for movement of water in the soil. The larger the number of macropores, the greater the hydraulic conductivity, due to a reduced resistance in pores leading to an increased flow of water (Ahuja, Cassel, Bruce, & Barnes, 1989). The low proportion of macropores in the <0.063 biochar–soil mixtures is likely to be a contributing factor to the low K_{sat} and K_{unsat} observed. A similar observation was made by Liu et al. (2016), who also observed a decrease in hydraulic conductivity with fine mesquite biochar (<0.85 mm) attributed to changes in soil pore size distribution.

Because hydraulic conductivity (K), referring to both K_{sat} and K_{unsat}, is largely controlled by interporosity (pore spaces between biochar and soil particles), pore size and connectivity, when the target soil property for improvement is K, manipulating the biochar particle size to fit with the soil particle size distribution could also create the necessary interpore for decreased K. Liu et al. (2016) showed that an effective decrease in K can be obtained when the biochar particle size is finer than the sand particle. They also reported no statistically significant differences in K when sand particles and biochar particles were of comparable size. To reduce water drainage, especially for sandy soils, the use of finer biochar is more effective. However, this may pose some risks to groundwater, atmosphere and human health (Liu et al., 2016; WHO Europe, 2003) if not applied correctly. Using appropriate application methods, eliminating or reducing dust formation, can mitigate the risk of exposure to the atmosphere, and pretreatment of the biochar to remove leachable carbon can help reduce any risks of contamination of surface or groundwater.

Pore size distribution may also have affected the water retention properties of the soil. Compared to the other particle sizes, the <0.063 mm biochar fraction had a smaller proportion of mesopores and larger proportion of micropores (Figure 5). Plant available water is stored in the mesopores, whereas water stored in the micropores is often retained too tightly, so that it may not be available for plant use (Major et al., 2009). The larger amount of mesopores observed for >2 and 2–0.5 mm biochar–soil mixtures would have contributed to its higher θ_{awc}. The pore size distribution results also showed that the 2–0.5 mm biochar-amended soil had a slightly higher proportion of mesopores compared to the >2 mm biochar-amended soil; however, the θ_{awc} for >2 mm was greater than that of 2–0.5 mm. This further shows that biochar intraporosity plays a greater role in controlling plant available water, implying that the use of biochar with high intraporosity will be more efficient in coarse-textured soils with low water retention capacity. Feedstock and pyrolysis temperature can affect the development of biochar intrapores, with woody and crop residue biochar typically having a higher content of intrapores compared to biochar from animal wastes (Abel et al., 2013; Brewer et al., 2014; Lu & Zong, 2018; Speratti et al., 2017), and biochar produced at high pyrolysis temperatures (>500 °C) tending to have higher porosity than biochar produced at lower temperatures (Brewer et al., 2014; Tomczyk, Sokołowska, & Boguta, 2020). Some pre- and post-pyrolysis treatment methods can also be used to increase biochar intrapores. For example, the use of phosphoric acid pretreatment increased the formation of micropores and enhanced specific surface area (Chu et al., 2018; Zhao et al., 2017a). Biochar-blocked pores can be cleaned with methanol modification and alkaline post-treatment, leading to increased porosity (Wang et al., 2020). Therefore, based on such understanding, an optimum pyrolysis condition, pre- and post-pyrolysis treatment methods and feedstock can be selected to produce biochar with high intraporosity.

To understand how biochar particle sizes in connection with hydrophobicity control soil water properties, we used an ethanol drop test to determine the hydrophobicity of each biochar particle size fraction. Table 3 shows that with reduction in biochar particle size, its hydrophobicity increases. Although we do not have a definite explanation for an increase in hydrophobicity with decreasing particle size, we hypothesize that this could be a result of exposure of the inner pores, which were hydrophobic. Gray et al. (2014) proposed that hydrophobic aliphatic compounds are likely to be found only in a portion of biochar pores. Grinding and sieving could expose these surfaces in our biochar internal pores, which were absent on the external surface, with finer particle sizes more likely to contain these functional groups.

The differences in θ_{fc} and θ_{awc} between the soil–biochar mixtures of different particle size (Table 1) can be attributed to the changes in observed hydrophobicity. The presence of organic materials on the surface of hydrophobic biochar can lead to it having water-repellent properties (Blanco-Canqui, 2017). The <0.063 mm biochar was strongly hydrophobic, which could explain why it had decreased water retention ability when mixed with soil compared to other biochar particle sizes. Apart from its water-repellent properties, water can also be prevented from entering the intrapores of hydrophobic biochar because of its high intrapore entry pressure caused by hydrophobicity of the biochar particle (Gray et al., 2014; Liu et al., 2016). This could mean less water being absorbed by the biochar particle and ultimately lower water retention ability when added to soils. This could result in a reduction in soil water retention properties of biochar–soil mixtures with fine particle sizes. The efficiency of biochar with regards to increased soil water retention can be strengthened with the use of hydrophilic biochar. Hydrophobicity of biochar can be reduced by using the right pyrolysis temperature during production. Studies have suggested that the use of a high pyrolysis temperature (>500 °C) can lead to the production of biochar with less hydrophobic surfaces (Gray et al., 2014; Kameyama et al., 2019; Kinney et al., 2012). Hydrophilic biochar can also be obtained through alkaline pretreatment of feedstocks (Hina et al., 2010; Rizwan et al., 2020), and through post-pyrolysis treatments such as initial wetting and composting (Kinney et al., 2012).

It is important to note that our results were obtained after mixing biochar with soil at a laboratory timescale; however, over longer field studies' timescales soil water retention properties due to biochar application are likely to be altered due to wetting/drying and freezing/thawing conditions, and soil structure evolution. A study by Ojeda et al. (2015) suggested that initial biochar hydrophobicity may disappear after 1 year. Several other studies have also demonstrated that over time biochar application improves aggregation processes and increases aggregate stability (Herath, Camps-Arbestain, & Hedley, 2013; Pituello et al., 2018). This can alter how biochar affects soil water movement and retention over time. Consequently, it is crucial to study the effects of biochar particle sizes on soil hydraulic properties in the field over an extended period of time.

5 | CONCLUSION

In this study, we assessed the role of biochar particle size and hydrophobicity in controlling soil water movement and retention. Addition of biochar to soil generally increased soil water retention while reducing its hydraulic conductivity. The extent of this increase varied with different biochar application rates and particle sizes. Water retention increased while hydraulic conductivity decreased with increasing rates of biochar application. The use of different biochar particle sizes allowed us to better understand the role that biochar interpore, intrapore and hydrophobicity played in relation to soil water retention properties. Our results suggest that the increase of water retention of sandy soils, especially plant available water, is mainly controlled by biochar intraporosity and its hydrophobicity, whereas decrease in the hydraulic conductivity of sandy soils is controlled by biochar–soil interporosity. For an effective increase in the water retention of coarse-textured soils, the use of hydrophilic biochar with high intraporosity is recommended. It is important to note that biochar hydrophobicity changes over time as a result of wetting, drying, freezing and thawing cycles as well as aging, which changes its status. Therefore, tests with aged biochar and long-term field trials assessing the effects of biochar ageing on soil hydraulic properties are also recommended. Overall, this study showed that it is possible to achieve significant changes in soil water retention and conductivity even with relatively low application rates when the biochar particle size and properties are well matched to the target soil and application. This opens up a whole new area of research and applications.

AUTHOR CONTRIBUTIONS
Ifeoma Edeh: Conceptualization; formal analysis; methodology; writing-original draft; writing-review & editing. **Ondřej Mašek:** Conceptualization; supervision; writing-review & editing.

DATA AVAILABILITY STATEMENT
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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