Biomass and Bioenergy 119 (2018) 346–353

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: www.elsevier.com/locate/biombioe

Research paper

How and why does willow biochar increase a clay soil water retention capacity?

Kimmo Rasa[a,*], Jaakko Heikkinen[a], Markus Hannula[b], Kai Arstila[c], Sampo Kulju[a], Jari Hyväluoma[a]

[a] Natural Resources Institute Finland, Luke, FI-31600, Jokioinen, Finland
[b] BioMediTech Institute and Faculty of Biomedical Sciences and Engineering, Tampere University of Technology, FI-33101, Tampere, Finland
[c] University of Jyvaskyla, Department of Physics, P.O. Box 35, FI-40014, Finland

ARTICLE INFO

Keywords:
Biochar
X-ray tomography
3D image analysis
Helium ion microscopy
Soil water retention
Plant available water

ABSTRACT

Addition of biochar into a soil changes its water retention properties by modifying soil textural and structural properties. In addition, internal micrometer-scale porosity that is able to directly store readily plant available water affects soil water retention properties. This study shows how precise knowledge of the internal micrometer-scale pore size distribution of biochar can deepen the understanding of the biochar-water interactions in soils. The micrometer-scale porosity of willow biochar was quantitatively and qualitatively characterized using X-ray tomography, 3D image analysis and Helium ion microscopy. The effect of biochar application on clay soil water retention was studied by conventional water retention curve approach. The results indicate that the internal pores of biochar, with sizes of at 50 and 10 μm (equivalent pore diameter), increased soil porosity and the amount of readily plant available water. After biochar addition, changes in soil porosity were detected at pore size regimes 5–10 and 25 μm, i.e. biochar pore sizes multiplied by factor 0.5. The detected pore size distribution of biochar does not predict directly (1:1 compatibility) the changes observed in the soil moisture characteristics. It is likely that biochar chemistry and pore morphology affect biochar-water interactions via e.g. surface roughness and contact angle. In addition, biochar induced changes in soil structure and texture affected soil moisture characteristics. However, the approach presented is an attractive pathway to more generalized understanding on how and why biochar internal porosity affects soil moisture characteristics.

1. Introduction

While biochar is considered as a potential measure to sequester carbon into soil [1], its secondary effects on soil properties are often controversial [2]. Biochar has been shown to increase soil water holding capacity (WHC), but no solid understanding exists on the effects of, e.g., soil type, biochar quality or climate. Addition of biochar into a given soil changes soil textural and structural properties. These changes modify soil moisture characteristics in a specific manner depending on biochar type and soil properties (indirect mechanism). However, biochar as a highly porous material also directly affects soil water holding capacity via its internal porosity. The aim of this paper is to study how this internal porosity and pore size distribution are related to the amount of plant available water in a clay soil.

A large number of papers describe biochar effect on soil hydraulic properties and water holding capacity [3–6] with heterogeneous descriptions of biochar physical quality. Physical characteristics of biochar is most commonly studied by gas adsorption techniques accompanied by the Brunauer-Emmett-Teller (BET) modelling to determine the specific surface area [7] or Barrett-Joyner-Halenda (BJH) modelling to determine pore size distribution [8]. However, pore space analysis based on gas adsorption measurements is limited to pores smaller than 300 nm, whereby it does not tell much about the porosity in the size range that is important for plant water uptake (i.e. micrometer-scale pores).

The inadequacy of gas adsorption studies and drawbacks related to porosity measurements using mercury porosimetry have been addressed in earlier studies [9,10]. NMR Cryoporometry have also been used to study porous materials at nanometer length-scale, however, resolution in the upper end is limited to few micrometers [11]. Kinney et al. [4] addressed the need for quantitative techniques to characterize micrometer-scale pores within the biochars due to their expected importance on soil WHC. All these studies support theory that large internal micrometer-scale pores of biochar may have remarkable direct

---

[*] Corresponding author. Natural Resources Institute Finland, Luke, Production systems, Biorefinery and Bioproducts, Finland.
E-mail address: kimmo.rasa@luke.fi (K. Rasa).

https://doi.org/10.1016/j.biombioe.2018.10.004
Received 21 December 2017; Received in revised form 28 September 2018; Accepted 2 October 2018

effect on soil moisture characteristics (indirect effect refers to changes in soil texture and formation of soil aggregates through bindings between biochar and soil particles, see Ref. [12]). However, the effect of biochar micrometer-scale porosity on soil moisture characteristics has not been quantitatively analysed.

We anticipate that the way forward in increasing understanding of biochar-water interactions goes through fundamental research on internal pore structure of biochars. Lately, X-ray tomography and 3D image analysis methods have been adapted to biochar research. This approach is able to visualize the internal pore structure of biochar, and to directly determine pore characteristics such as pore size distribution and pore continuity. In recent studies X-ray tomography has been used to characterize pore structure of biochars derived from various raw materials (e.g. *Pinus sylvestris*, *Miscanthus, Populus spp. L.,* cottonseed hull, hay) with resolution ranging from 0.74 to 21 μm [13–17]. Hyväluoma et al. imaged various types of biochars and hydrochars with ca. 1 μm resolution and found that considerable part of the biochar volume consist of pores in size range relevant to hydrological processes and storage of plant available water [18]. In addition, they found high variation in porosity, pore size distribution and structural anisotropy between different biochars. Also aggregates of biochar-amended soil have been imaged with X-ray tomography, although at this length-scale X-ray tomography resolution cannot capture the internal porosity of biochar [19].

The lack of precise data on micrometer-scale porosity might be one reason that the importance of biochar internal porosity directly affecting the soil water holding capacity has been overlooked. In this study we used X-ray microtomography, 3D image analysis and Helium ion microscopy to study structural properties of willow biochar with emphasis on micrometer-scale pores contributing to storage of plant available water. Further, we conducted an incubation experiment to study the effect of this specific biochar on soil moisture characteristic and to identify pore regimes altered by biochar amendment. The relationship between biochar pore system and its specific effect on soil moisture characteristics is an attractive pathway towards development of precisely tailored biochars aimed to enhance water use efficiency.

2. Materials and methods

2.1. Experimental soil

Soil for incubation experiment was taken from Kotkanoja long-term drainage experiment site [20] located in Jokioinen in southern Finland (N 60.82°, E 23.51°). The study material was collected from the topmost 10 cm layer of an annually ploughed plot in spring 2016. The heavy clay soil had 64.8%, 30.5% and 4.7% of clay, silt and sand, respectively (mass fractions determined by pipette method [21]). Soil organic matter content was 9.2% (loss of ignition at 550 °C), carbon content 2.9% (Leco analysator), pH 6.3 and electrical conductivity 63.1 $\mu S\,cm^{-1}$ (soil to water ratio 1:5).

2.2. Biochar

The biochar used in the experiment was pyrolysed in an indirectly heated pilot-scale batch-type pyrolysis facility using Willow stem wood (Salix sp, with bark) as raw material. Temperature profile of pyrolysis process consisted of two steps. First, the temperature was raised to 280 °C, and then further to 320 °C with rates of 2.2 and 0.2 $K\,min^{-1}$, respectively.

The elemental analysis (CHNSO) of biochar was carried out using FLASH 2000 series analyser and the results were used to calculate O:C and H:C atomic ratios. The biochar was analysed for pH (SF EN 13037, 1:5 char to water ratio), electrical conductivity (EC, SF EN 13038, 1:5 char to water ratio), nutrients and heavy metals (SFS-EN 13650 Aqua Regia extraction and ICP-measurement), BET surface area (ISO 9277:2010(E) Brunauer–Emmett–Teller (BET) Surface Area) and Ash content (SFS 3008, loss of ignition at 550 °C).

The BET surface area of biochar produced was 6.8 ± 0.43 $m^2\,g^{-1}$. The elemental mass fractions of C, H, N, S and O were 74.0 ± 0.0%, 4.1 ± 0.1%, 0.4 ± 0.0%, 0.0 ± 0.0% and 15.8 ± 0.3%, respectively. The ash mass fraction of the biochar was 3.13 ± 0.15%. The corresponding mole ratios of H:C and O:C were 0.66 and 0.16, respectively. Biochar had low content of main nutrients (1.5 $g\,kg^{-1}$, 3.6 $g\,kg^{-1}$, 9.1 $g\,kg^{-1}$ of P, K, Ca respectively) and heavy metals Cd, Cu and Pb (0.79 $mg\,kg^{-1}$, 6.8 $mg\,kg^{-1}$, < 3 $mg\,kg^{-1}$, corresponding limits are 1.5, 600 and 100 $mg\,kg^{-1}$, respectively) contents were below limits set for soil amendments in Finland.

2.3. X-ray tomography

The X-ray computed microtomography imaging was conducted with Zeiss Xradia MicroXCT-400 (Zeiss, Pleasanton, CA, USA) device. Source voltage was 40 kV and source current was 250 μA. The pixel size was 1.14 μm. A 20× objective was used with 2 binning. 1600 projections were taken in full 360°. Each projection was exposed with X-rays for 3 s. No filters were used in the imaging process. Zeiss XMReconstructor software with the filtered back projection algorithm was used in the reconstruction of the image stacks.

For quantitative structural analysis the original grey-scale image was de-noised and segmented into solid and void phases. Details of these image processing steps have been described by Hyväluoma et al. [18] and reviewed in Appendix A. The subvolume used in the further image analysis consisted of $1.9 \cdot 10^8$ voxels (sample size ca. 0.5 mm).

The porosity of the sample was calculated by dividing the number of void voxels by the total number of voxel in the analysed volume. The pore-size distribution was determined using an approach based on mathematical morphology [22] by successively applying morphological opening operations (sphere with radius r was used as the structuring element) on the pore space [23]. The pore size based on morphological opening closely relates to the stationary distribution of wetting and nonwetting fluids in pore space and the related capillary pressure via the Young-Laplace equation

$$p_c = \frac{2\gamma cos\theta}{r} \tag{1}$$

where γ is the surface tension, θ the contact angle, and *r* the pore radius defined as the radius of the structuring element used in the morphological opening [24]. This method is particularly suitable for our purposes where the pore-size distribution determined from imaged pore space is linked to measured soil moisture characteristic curve. The structural anisotropy of the sample was quantified by calculating the degree of anisotropy using the method based on grey-scale gradient tensor [25].

2.4. Helium ion microscopy

Helium ion microscopy (HIM) is a novel development within the family of scanning beam microscopes. Instead of using electrons for beam particles, as in conventional scanning electron microscopes (SEM), helium ions are used. Helium ions have a focal depth that is 5–10 times larger than electrons in SEM, a beam spot size below 0.5 nm, and very small interaction volume producing secondary electrons, resulting in images with very high resolution. Another important advantage of HIM is its capability to image insulating materials without charging effects (no metal coating is needed) as the positive surface charging from helium ions and secondary electrons can be neutralized with an electron flood gun. A Zeiss Orion NanoFab Helium ion microscope was used in this work.

2.5. Soil sample preparation

Experimental soil was air-dried in room temperature and sieved