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New approaches to measuring biochar density and porosity

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ARTICLE INFO

Article history:

Received 4 October 2013

Received in revised form

25 March 2014

Accepted 26 March 2014

Available online xxx

Keywords:

Biochar

Skeletal density

Envelope density

Pore volume

Gas sorption analysis

Mercury porosimetry

ABSTRACT

It is clear that the density and porosity of biochar will impact its mobility in the environment, its interaction with the soil hydrologic cycle, and its suitability as an ecological niche for soil microorganisms. However, the wide range of biochar pore sizes complicates biochar porosity characterization, making it challenging to find methods appropriate to connect the fundamental physical properties of density and porosity to environmental outcomes. Here, we report the use of two fast, simple density measurement techniques to characterize biochar density and porosity. We measured biochar skeletal density by helium pycnometry and envelope density by displacement of a dry granular suspension. We found that biochar skeletal density ranged from 1.34 g cm⁻³ to 1.96 g cm⁻³, and increased with pyrolysis temperature. Biochar envelope density ranged from 0.25 g cm⁻³ to 0.60 g cm⁻³, and was higher for wood biochars than grass biochars—a difference we attribute to plant cell structures preserved during pyrolysis. We compared the pore volumes measured by pycnometry with those measured by nitrogen gas sorption and mercury porosimetry. We show that biochar pore volumes measured by pycnometry are comparable to the values obtained by mercury porosimetry, the current benchmark method. We also show that the majority of biochar pore volume is in macropores, and thus, is not measured by gas sorption analysis. These fast, simple techniques can now be used to study the relationship between biochar's physical properties and its environmental behaviors.

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1. Introduction

Charcoal enters the environment as a natural byproduct of fire, where it is a component of the larger black carbon pool that also includes soot. When charcoal enters soils through intentional human amendment to sequester carbon and increase crop productivity, it is called biochar. If the adoption of biochar as a climate change mitigation option is to be implemented at any significant scale [1], we must understand how the natural environment is affected by the fate, transport, and ecosystem services [2] of this biochar material.

While it has been possible to characterize the biological and chemical controls on biochar environmental residence times and ecosystem services [3], we know much less about the physical processes that determine the transport and interactions of biochar within the environment. A first step in understanding these two topics is a description of biochar physical properties beyond particle size. Density and porosity are fundamental physical properties that control how biochar moves through the landscape and how it interacts with water to alter soil hydrologic processes, particularly plant-available water holding capacity [4]. These properties likely also impact biochar's capacity to act as an ecological niche, for example, by providing growing space for microbes and shelter for mycorrhizal fungi from predators [5], and subsequently affecting the accessibility of substrates and nutrients in important biogeochemical cycles mediated by these soil microorganisms.

Density and porosity almost certainly play a role in biochar transport within the soil environment because materials with bulk densities less than water ($<1 \text{ g cm}^{-3}$) will float. There is evidence that under some circumstances, black carbon in general and biochar specifically can be transported within soils. For example, Rumpel et al. observed preferential erosion of black carbon in steeply sloped soils (46% slope) in Laos which had been subjected to slash-and-burn agriculture [6]. The concentration of black carbon was 2.2 times higher in the eroded sediments than in the corresponding bulk soils, a result that the authors attributed to the tendency of black carbon to float. In a rainfall simulator experiment on a 1% slope soil with added black carbon, Rumpel et al. also showed that up to 55% (550 g kg^{-1}) of the black carbon was transported horizontally, a result which was again attributed to charcoal's ability to float under some hydrologic conditions [7]. Similar horizontal movement was shown in a biochar amendment where the applied biochar had a traceable isotopic signal. Through subtraction, Major et al. estimated that 20%–53% (200 g kg^{-1} to 530 g kg^{-1}) of applied biochar was lost through surface runoff over a 2-year period following tillage of biochar into a soil with no visible inclination (slope $<2\%$) [8]. Higher erosion rates of black carbon, relative to other forms of terrestrial organic matter, also have implications for the composition of fluvial organic matter and long-term carbon sinks in marine sediments [9–11]. These examples highlight the importance of understanding the environmental impacts of the physical, in addition to the chemical, characteristics of biochar.

An accurate characterization of biochar pore structure and pore size distribution is challenging, because the pore sizes of

biochars range over at least five orders of magnitude, from sub-nanometer slit-shaped pores that correspond to spaces between graphite-like layers of flat aromatic carbon clusters [12–14], to pores on the order of tens of micrometers from partially preserved cellular structures [15,16]. There is no single technique that can measure pore volume precisely across these scales, and as a result, effective biochar porosity characterization has been elusive.

Gas sorption methods have been popular for characterizing the porosity of carbon materials due to their relative ease of use and demonstrated relationship to chemical sorbate–sorbent interactions [17]. The most common methods involve carbon dioxide adsorption to characterize biochar pores that are smaller than 2 nm (sub-micropores) and nitrogen adsorption with BET analysis to characterize pores in the $<2 \text{ nm}$ – 50 nm range (micro- and meso-pores). These adsorption methods do not, however, provide any information about pores larger than mesopore size (macropores), which have been shown in electron microscopy images to be present in many biochar samples [12,18–23].

Mercury porosimetry can be used to characterize pores with openings from a few nanometers to a few hundred micrometers in diameter [24]. Previous work has demonstrated that mercury porosimetry detects more biochar pore volume than gas sorption does [25]. The drawbacks of mercury porosimetry, however, include the risk of crushing the sample with the high pressures required for analysis, thereby introducing inaccuracies in the porosity measurements, and its inability to distinguish between inter-particle and intra-particle porosity, especially for powdered samples. There are further limitations with safety and handling mercury, and the destructive nature of the analysis method. Another difference of mercury porosimetry is that it determines the diameter of the pore throat, not the actual pore size [24]. Finally, the fact that biochars are granular materials with highly variable surface chemistry complicates the measurement of the contact angle between mercury and the biochar surfaces, and the relationship between pressure and pore throat size is directly dependent on contact angle [24].

Stereological methods based on sectioning, image analysis, and 3-D reconstruction techniques have been used to visualize the largest pores (typically $> 1 \mu\text{m}$) of carbonaceous materials [26,27], but are not quantitative. Techniques like scanning electron microscopy (SEM) are frequently used in biochar characterization studies [12,18,25], and are excellent at detecting biochar macropores. However, microscopy and computerized tomography (CT) face challenges including selection of representative samples and viewing orientations, definition of edges between solid and pore, and development of image analysis protocols to quantify porosity [15].

Here we report a novel approach to measure the total pore volume of biochars using two forms of density measurement: skeletal and envelope density. Both techniques measure the volume of a known mass by a displacement technique. In the case of skeletal density (ρ_s), the displaced material is helium gas; in the case of envelope density (ρ_e), the displaced material is a micro-granular suspension. Combined, these two density measurements can be used to calculate a sample's porosity. We assess biochar porosity variation across two feedstocks, a range of pyrolysis temperatures, and two reactor conditions in

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