



Quantification and characterization of dissolved organic carbon from biochars

Cheng-Hua Liu^{a,b}, Wenying Chu^c, Hui Li^a, Stephen A. Boyd^a, Brian J. Teppen^a, Jingdong Mao^c, Johannes Lehmann^d, Wei Zhang^{a,b,*}

^a Department of Plant, Soil and Microbial Sciences, Michigan State University, East Lansing, MI 48824, United States

^b Environmental Science and Policy Program, Michigan State University, East Lansing, MI 48824, United States

^c Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, United States

^d Soil and Crop Sciences Section, School of Integrative Plant Science, Cornell University, Ithaca, NY 14853, United States

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ABSTRACT

Dissolved organic carbon (DOC) in biochars is critical to carbon dynamics and contaminant transport in soils. This study aimed to develop a robust and easy method to characterize and quantify the biochar-DOC, using water-, acid-, and base-extractable DOC samples (WEOC, AEOC, and BEOC respectively) from 46 biochars produced from diverse feedstocks and pyrolysis conditions. BEOC concentrations were the highest (2.3–139 mg-C/g-biochar), followed by WEOC (0.5–40 mg-C/g-biochar) and AEOC (0.2–23 mg-C/g-biochar). Fast-pyrolysis biochars generally had higher DOC concentrations than slow-pyrolysis biochars. DOC concentrations in slow-pyrolysis biochars decreased exponentially with increasing pyrolysis temperature from 300 to 600 °C. The solid-state ¹³C NMR showed that biochar-DOC had abundant small fused-ring aromatics, aliphatic C, and carboxyl C. Biochar-DOC included an acid-precipitated (AP) fraction of higher molecular weight and aromaticity and an acid-soluble (AS) fraction of lower molecular weight and aromaticity. BEOC generally had a greater AP fraction than WEOC and AEOC. Molecular weight, aromaticity and composition of AEOC and BEOC differed from those of more environmentally-relevant WEOC, suggesting that the acid- and base-extraction may not produce the DOC released in real soils. Finally, a quick, easy and robust UV-vis spectrometric method was developed to measure the composition and concentrations of WEOC in diverse biochar samples ($R^2 = 0.96$, $n = 46$).

1. Introduction

Biochars are carbonaceous porous materials co-produced with syngas and bio-oil from pyrolysis of biomass, and have been promoted as soil amendments for agronomic and environmental benefits (Jeffery et al., 2011; Kookana, 2010; Laird, 2008; Lehmann et al., 2006). The potential benefits of biochar amendment in soils include increased soil carbon (C) storage, improved soil characteristics (e.g., improving soil structure, reducing bulk density, and enhancing water and nutrient retention), decreased greenhouse gas emission, and in-situ immobilization of contaminants such as excess nutrients, organic pollutants, and trace metals (Ahmad et al., 2014; Beesley et al., 2011; Kookana, 2010; Laird et al., 2010; Lehmann, 2007; Peake et al., 2014). During the last several years, dissolved organic C (DOC) in biochars has sparked a strong research interest (Fu et al., 2016; Jamieson et al., 2014; Lin et al., 2012; Mukherjee and Zimmerman, 2013; Qu et al., 2016; Smith et al., 2016; Uchimiya et al., 2013), because it plays an

important role in controlling biochar persistence and mobility (Bird et al., 2015; Fu et al., 2016; Jaffe et al., 2013; Norwood et al., 2013), contaminant fate and transport (Uchimiya et al., 2010; Wang et al., 2017), microbial activities (Bruun et al., 2012; Smith et al., 2016; Smith et al., 2013), and plant growth (Deenik et al., 2010; Joseph et al., 2013; Korai et al., 2018; Wu et al., 2018) in agroecosystems. Once applied in the field, biochars could release DOC into soil water, and directly alter physicochemical properties of soil DOC (Dittmar et al., 2012; Hockaday et al., 2006). The released DOC from the biochars (hereafter termed as biochar-DOC) could be rapidly transported from soils into receiving surface and ground waters via surface runoff and leaching (Major et al., 2010; Wang et al., 2013a; Wang et al., 2013b), thus contributing to soil C loss and the transport of DOC-associated contaminants. More broadly, the release of DOC from pyrogenic C contributes approximately 10% of total DOC in surface water globally (Jaffe et al., 2013). Furthermore, the DOC fraction in the biochars is labile and more susceptible to photo- and bio-degradation than bulk biochars (Fu et al., 2016; Norwood et al.,

* Corresponding author at: 1066 Bogue ST RM A516, East Lansing, MI 48824, United States.

E-mail address: weizhang@msu.edu (W. Zhang).

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2013). Thus, both qualitative and quantitative characteristics of biochar-DOC are needed for better assessing the qualities of biochars and their impact on agroecosystems, as well as for developing biochar-based fertilizers (Joseph et al., 2013).

DOC is often operationally defined as the organic C fraction smaller than the pores of filter membranes (e.g., 0.45 or 0.75 μm) (Bird et al., 2015). The biochar-DOC thus includes both truly dissolved molecules and sub-micron sized biochar particles (Qu et al., 2016; Spokas et al., 2014; Wang et al., 2013a; Wang et al., 2013b). Water-soluble organic compounds can be formed by re-condensation and entrapment of volatile organic compounds into the biochar pore structure during pyrolysis, which can be later released as DOC (Antal and Gronli, 2003; Buss et al., 2015; Spokas et al., 2011). In addition, sub-micron biochar particles may initially be present or later produced from physicochemical disintegration of bulk biochars (Qu et al., 2016; Spokas et al., 2014).

Biochar-DOC is often extracted by either water or strong alkaline (i.e., sodium hydroxide [NaOH] or potassium hydroxide [KOH]) solutions (Lin et al., 2012; Qu et al., 2016; Smith et al., 2016; Uchimiya et al., 2013). The alkaline extraction is adapted from the method of organic matter extraction from soils (IHSS, 2017; Lehmann and Kleber, 2015; Swift, 1996). The extracted soil organic matter (SOM) has been traditionally perceived as primarily humic substances, i.e., stable macromolecules formed by a humification process that are resistant to microbial degradation. However, it is increasingly recognized that the humification process may not actually occur in soils, and SOM is primarily formed through microbial decomposition, biosynthesis, as well as physical protection by sorption on mineral surfaces and sequestration in soil aggregates (Kleber et al., 2011; Lehmann and Kleber, 2015; Schmidt et al., 2011). Furthermore, the alkali-extractable SOM may not truly represent organic matter released into soil water because natural soils rarely reach the extreme alkaline and high pH conditions used in the alkaline extraction (Lehmann and Kleber, 2015). Similarly, the alkali-extractable biochar-DOC may not reflect the amount and properties of DOC released into soil water from the added biochars. Indeed, Chen et al. (2015) found that the amount of DOC released from biochars increased with increasing solution pH (2–11). Thus, water extraction may produce more representative DOC released from biochars under natural soil conditions (Lehmann and Kleber, 2015). Additionally, acid washing is commonly used for de-ashing biochars before analysis (Rajapaksha et al., 2016; Sun et al., 2013) and would presumably extract certain fractions of biochar-DOC. However, studies on the difference in the quantity and characteristics of biochar-DOC extracted by water, strong acid solution, and strong base solution are rare. Such information is very relevant for biochar amendment in acidic, neutral and alkaline soils.

A number of recent studies have characterized biochar-DOC via advanced spectroscopic and mass spectrometry techniques. About 300–2400 unique molecular formulas could be assigned in the spectra of the biochar-DOC (200–800 m/z) detected by Fourier transform ion cyclotron resonance mass spectrometry (Smith et al., 2016). Many small organic compounds in the mass range of 45–500 m/z belonged to phenolic compounds, acids, and bio-oil-like compounds, as revealed by 2D gas chromatography coupled with time of flight mass spectrometer (Smith et al., 2016). Qu et al. (2016) reported that biochar-DOC was composed primarily of small aromatic clusters rich in carboxyl functional groups, based on Fourier transform infrared spectroscopy and solid-state ^{13}C nuclear magnetic resonance (NMR). Using liquid chromatography-organic C detection analysis (Lin et al., 2012) and fluorescence excitation-emission spectrophotometry with parallel factor analysis (Jamieson et al., 2014; Uchimiya et al., 2013), biochar-DOC could be characterized by several components (e.g., low-molecular-weight acids and neutrals, and high-molecular-weight compounds) differing in their individual mean molecular weight (M_w) and fluorescence features. Because these components can have distinct environmental persistence and mobility, their proportions may be used to

characterize the biochar-DOC.

Many of the aforementioned methods are costly and not routinely available in many laboratories, thus hampering their wide use in quality assessment during biochar production and application. Therefore, developing a quick, easy and robust method for characterizing and quantifying the biochar-DOC is critically needed. Ultraviolet–visible (UV–vis) absorption spectroscopy is commonly available and has been successfully used to characterize the biochar-DOC (Fu et al., 2016; Jamieson et al., 2014). It was thus selected for developing the new method here.

Therefore, this study aimed to: (1) investigate whether the base- or acid-extractable DOC from biochars is different with the more environmentally-relevant water-extractable DOC regarding their quantities and qualities; and (2) develop a quick, easy and robust method for quantifying biochar-DOC. To do so, we thoroughly quantify and characterize the DOC extracted with deionized (DI) water, 0.1 M hydrochloric acid (HCl), and 0.1 M NaOH from 46 biochars pyrolyzed from diverse feedstocks and pyrolysis conditions. As the quantities and qualities of biochar-DOC highly depend on pyrolysis temperature (Jamieson et al., 2014; Lin et al., 2012; Liu et al., 2015; Smith et al., 2016; Uchimiya et al., 2013) and feedstock type (Lin et al., 2012; Liu et al., 2015; Uchimiya et al., 2013), the relative importance of these factors in determining the biochar-DOC concentrations was also explored. Additionally, advanced solid-state ^{13}C NMR spectroscopy was used to provide detailed quantitative structural information of DOC and the structure change of bulk biochars after the extraction treatment. Finally, a quick, easy and robust method was developed to quantify the biochar-DOC by only using the commonly available UV–vis absorption spectroscopy.

2. Materials and methods

2.1. Biochars

Details on the feedstocks, production conditions, and sample labeling of 46 biochars used in this study are provided in Table S1 of Supplementary Material. Briefly, the feedstocks were: (1) animal manures including bull manure with sawdust bedding (BM), dairy manure with rice hulls bedding (DM), poultry manure with sawdust bedding (PM), raw dairy manure with sawdust bedding (RDM), digested dairy manure (DDM), composted digested dairy manure (CDM), and composted digested dairy manure mixed with woodchips (CDMW) (note that RDM, DDM, CDM, and CDMW were from the same manure source with various pretreatments prior to pyrolysis); (2) woody biomass including oak wood (OW), pine wood (PW), mixed woodchips (WC), mixed hardwood (HW), mixed softwood (SW), Chinese bamboo (CB), and Brazilian pepperwood (BP); (3) herbaceous residues including corn stover (CS), soybean (SB), switchgrass (SG), sugarcane bagasse (BG), and yard leaves (YL); and (4) urban wastes including food waste (FW) and paper mill waste (PMW). The feedstocks were pyrolyzed via fast pyrolysis at 500 °C or slow pyrolysis at 300–600 °C. Here fast pyrolysis had a residence time of < 30 s, whereas slow pyrolysis had a residence time > 15 min. The produced biochars were gently crushed and ground by a porcelain mortar and pestle, passed through a 74- μm (200 mesh) sieve, and then stored in glass vials before use. This particle size fraction was chosen to represent finer biochars that may have greater potential to release DOC and to be mobilized once applied to soils (Wang et al., 2013a; Zhang et al., 2010). Hereafter, the biochar samples were named by feedstock and pyrolysis temperature, e.g., BM300 for bull manure pyrolyzed at 300 °C. These biochars have previously been characterized (Enders et al., 2012; Rajkovich et al., 2011; Yao et al., 2012). Their selected physicochemical properties are summarized in Table S2.

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