



Research article

Field-scale fluorescence fingerprinting of biochar-borne dissolved organic carbon

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ABSTRACT

Biochar continues to receive worldwide enthusiasm as means of augmenting recalcitrant organic carbon in agricultural soils. Realistic biochar amendment rate (typically less than 1 wt%) in the field scale, and subsequent loss by sizing, rain, and other transport events demand reliable methods to quantify the remaining portions of amended biochar. This study employed fluorescence excitation-emission (EEM) spectrophotometry and parallel factor analysis (PARAFAC) to specifically target pyrogenic dissolved organic carbon (DOC) released by amended biochar during the course of a field trial at Bowling Green, KY experimental site. Toluene/methanol (1:6 v/v) extracts of surface (0–15 cm) soils amended with 21.28 t ha⁻¹ fast pyrolysis biochar afforded PARAFAC fingerprints representing different degrees of aromaticity. Compared to the control without treatments, biochar treatment (with and without poultry manure or chemical fertilizer) increased the relative contribution of PARAFAC fingerprint attributable to labile polyaromatic DOC structures. Poultry manure or chemical fertilizer alone (without biochar) did not influence the amounts of polyaromatic DOC structures. Existence of biochar could be further validated by the changes in %DOC (relative to the total carbon), fixed C content, and UV absorbance (360 nm), whereas FTIR, %O, and sorption of model agrochemical (deisopropylatrazine) did not reflect the presence of biochar in the soil samples. Developed toluene/methanol-based EEM-PARAFAC technique will provide a sensitive, rapid, and cost-competitive method to validate the long-term carbon sequestration by the biochar soil amendment.

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1. Introduction

Although biochar soil amendment continues to receive worldwide interests for carbon sequestration purposes, low amendment rate (typically <1 wt%) and transport by rain and sizing (Wang et al., 2013) pose challenges in monitoring the remaining fraction of amended biochar in the field scale. Recently, near infrared spectroscopy (NIRS) coupled with the least square fitting was proposed as a rapid and low-cost method to verify remaining biochar in amended soils from field trials (Allen and Laird, 2013). Calibration was obtained between NIRS of a large number of soil samples against the total carbon (TC) and biochar carbon contents (Allen and Laird, 2013). In addition to increasing the particulate carbon content of soil, biochar releases pyrogenic dissolved organic carbon

(DOC) having distinctively different structures from the soil organic carbon. Biochar-derived DOC has been characterized by electro-spray ionization Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) (Smith et al., 2013), size-exclusion chromatography (Lin et al., 2012), ion chromatography (Liu et al., 2015), and fluorescence excitation-emission (EEM) spectrophotometry and parallel factor analysis (PARAFAC) (Uchimiya et al., 2013a, 2015b). Previous EEM-PARAFAC analysis on the aqueous extracts of fast pyrolysis, slow pyrolysis, and flash/high-yield carbonization biochars showed polyaromatic DOC structures having different amounts of conjugated double bonds (Uchimiya et al., 2015b). Quantitative relationships were obtained between (1) the degree of aromaticity in DOC structures and (2) bulk (volatile matter) and solution (DOC content) characteristics of biochar.

The objective of this study was to utilize unique structures of pyrogenic DOC as means of validating the existence of biochar in amended soils over the course of field trials conducted at Bowling Green, KY site. The DOC samples were extracted from pre-

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treatment background and post-harvest surface (0–15 cm) soils amended with 21.28 t ha⁻¹ biochar, with and without poultry litter and chemical fertilizer. Of various extraction fluids available, toluene/methanol (1:6 v/v) was used to specifically target polycyclic aromatic structures of pyrogenic DOC. This solvent afforded the highest recovery of polycyclic aromatic hydrocarbons (PAHs) from soot, coal, and charcoal in a systematic study investigating different organic solvents (Jonker and Koelmans, 2002). To provide comparison, 10 mM CaCl₂ was used to extract labile DOC, and 125 mM Na₄P₂O₇ (pH 5) was used to release DOC complexed by Al/Fe (hydr) oxides and clays (Erich et al., 2012). The EEM-PARAFAC results were compared with the following additional methods to validate the existence of biochar in amended soils: fixed C and %O contents, Fourier transform infrared (FTIR) and UV/visible spectra, and the ability to retain a model agrochemical (deisopropylatrazine).

2. Materials and methods

2.1. Biochar field trials

Detailed description of the field experimental site and soil properties have been provided (Sistani et al., 2014). Briefly, field experiments were conducted in Bowling Green, KY on a Crider silt loam (fine silty, mixed, active, mesic Typic Paleudalfs) containing 3.1% sand, 65.3% silt, 31.6% clay, and 35 g kg⁻¹ soil organic matter (pH 5.8). Background soil samples were collected in early May, 2010 at 0–15 cm depth. Subsequently, the following 6 treatments were applied in a completely randomized block design (15 ft by 11.67 ft plots with alleys) with three replicates: (1) 21.28 t ha⁻¹ biochar (hereby denoted B), (2) poultry litter (L; 224 kg ha⁻¹ N+163 kg ha⁻¹ P+405 kg ha⁻¹ K), (3) chemical fertilizer (F; 224 kg ha⁻¹ N+67.2 kg ha⁻¹ P+112 kg ha⁻¹ K), (4) 21.28 t ha⁻¹ biochar + poultry litter (B + L; 224 kg ha⁻¹ N+163 kg ha⁻¹ P+405 kg ha⁻¹ K), (5) 21.28 t ha⁻¹ biochar + chemical fertilizer (B + F; 224 kg ha⁻¹ N+67.2 kg ha⁻¹ P+112 kg ha⁻¹ K), and (6) controls without treatments (C). All treatments (B, L, F, B + L, and B + F) were applied using a tractor mounted power-take-off rotary tiller. Subsequently, corn was planted for no-till, rain-fed production. Above-described background soil collection, treatments, and planting were performed on the same day. Total aboveground plant biomass was harvested at the physiological maturity in early August, 2010. Post-harvest soil samples were collected in late October, 2010 at 0–15 cm depth. All soil samples were air dried, mechanically ground, and sieved (<2 mm). Total carbon (TC) contents of soil samples were determined using a Vario-Max CN analyzer (Elementar, Hanau, Germany).

Biochar was produced by fast pyrolysis employing a rapid heating (>1000 °C s⁻¹) and short residence time to maximize the yield of liquid-phase biooil product (Branca and Di Blasi, 2006). The biochar was produced at 500 °C from mixed sawdust by Dynamotive Energy Systems (Vancouver, BC, Canada) using an industrial-scale bubbling fluidized bed reactor designed to yield 60–75 wt% biooil, 15–20 wt% biochar, and 10–20 wt% syngas (Branca and Di Blasi, 2006). The biochar was a fine powder, and was used as received in a sealed drum. The biochar sample has been extensively characterized by FTIR, proximate analysis (Uchimiya et al., 2013b), BET surface area and the composition of volatile organic carbon (Spokas et al., 2011), DOC structure (Uchimiya et al., 2015b), and phosphorus speciation (Uchimiya et al., 2015a).

2.2. Proximate, ultimate, and FTIR analyses of soil samples

Moisture, ash, volatile matter (VM), and fixed carbon contents of selected soil samples were determined in triplicate by American

Society for Testing and Materials (ASTM) method D7582 (ASTM, 2010) using LECO thermogravimetric analyzer (TGA701, LECO, St. Joseph, MI). Moisture was determined as the weight loss after heating the sample under N₂ atmosphere in open crucible to 107 °C and holding at this temperature until sample weight stabilized. Volatile matter was determined as the weight loss after heating the sample under N₂ atmosphere in covered crucible to 950 °C and held for 7 min. Ash was defined as the remaining mass after subsequently heating the sample under O₂ atmosphere in an open crucible to 750 °C and holding at this temperature until sample weight stabilized. After the determination of moisture, ash, and VM, fixed carbon was calculated by difference. Elemental composition (CHNSO) of biochar (without soil) and selected soil samples were determined in triplicate by dry combustion using Perkin–Elmer 2400 Series II CHNS/O analyzer (Perkin–Elmer, Shelton, CT).

FTIR spectra were obtained for triplicate subsets of selected soil samples using Bruker Vertex 70 spectrometer (Bruker Optics, Billerica, MA) fitted with a Pike Technologies MIRacle attenuated total reflectance (ATR) accessory (Madison, WI) with a diamond crystal plate. The spectra were obtained at 8 cm⁻¹ resolution from 650 to 4500 cm⁻¹ with 128 scans. Second derivatives of FTIR spectra were obtained by Savitzky-Golay smoothing using MATLAB version 8.5.0.197613 (R2015a) (Mathworks, Natick, MA) with PLS toolbox version 8.0.1 (Eigenvector Research, Manson, WA).

2.3. Soil extraction and DOC characterization

Distilled, deionized water (DDW) with a resistivity of 18 MΩ cm (APS Water Services, Van Nuys, CA) was used in all laboratory procedures. All chemical reagents were obtained from Sigma–Aldrich (Milwaukee, WI) with the highest purity available. Each soil sample was extracted in duplicate using 10 mM CaCl₂, 125 mM Na₄P₂O₇ (pH 5), and toluene/methanol (1:6 v/v) independently, rather than sequentially. Pyrophosphate is traditionally utilized to release Fe and Al-bound DOC in soil samples (Erich et al., 2012). Toluene + methanol (1:6 v/v) was used to recover polyaromatic DOC structures (Jonker and Koelmans, 2002) of amended biochar.

Each extraction step employed the soil to extraction fluid ratio of 2 g:30 mL, and 24 h end-over-end rotation (40 rpm) at 25 °C. Biochar alone (without soil) was extracted by each fluid at a lower ratio of 0.3 g:30 mL. Suspension was allowed to settle overnight, and then the supernatant was carefully decanted and filtered (0.45 μm Millipore Millex-GS; Millipore, Billerica, MA); centrifugation or other artificial settling methods were not employed. Filtered CaCl₂ and pyrophosphate extracts (87 total) were analyzed for total organic carbon (in ppm C) using Torch combustion TOC/TN analyzer (Teledyne Tekmar, Mason, Ohio). The pH was determined using Sartorius Professional PP-15 meter (Sartorius, Bohemia, NY). Electric conductivity (EC) was determined using YSI 3200 conductivity meter (YSI, Yellow Springs, OH). UV/visible spectra of selected CaCl₂, pyrophosphate, and toluene/methanol extracts were obtained using a diode-array spectrophotometer (HP8452A, Hewlett–Packard, Palo Alto, CA).

Fluorescence EEM and PARAFAC analyses were conducted on all extracts. As described in detail elsewhere (Stedmon and Bro, 2008), PARAFAC models three-way data (samples, excitation wavelengths, and emission wavelengths) by minimizing the sum of squares of the residuals. In order to normalize the intensity and remove inner-filtering effects, pyrophosphate extracts were diluted by 22-fold. Raw EEM spectra of CaCl₂ and pyrophosphate were then combined to perform PARAFAC. Toluene/methanol extracts were separately analyzed by PARAFAC because of higher intensity and distinctively different peak positioning compared to CaCl₂ and pyrophosphate extracts. Fluorescence EEM of each extract was obtained using F-7000 spectrofluorometer (Hitachi, San Jose, CA) set to 220–400 nm

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