



Effect of clay and iron sulphate on volatile and water-extractable organic compounds in bamboo biochars



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ABSTRACT

Improved plant disease resistance, seed germination and plant productivity have recently been associated with mineral-enhanced biochars. This has generated interest in characterizing those biochar organic compounds which may contribute to their favorable properties. This study builds on recent physico-chemical characterization of a series of mineral-enhanced bamboo biochars produced between 350 and 550 °C. Here, these biochars are subjected to aqueous extraction followed by liquid chromatography organic carbon detection (LC-OCD) and thermal desorption gas chromatography mass spectrometry (TD-GC/MS). These techniques provide a structural insight into their more bio-available organic compounds and how they vary with pyrolysis temperature. In comparison to neat biochar, their mineral-enhanced composites produce at least three times the water-extractable organic carbon, nitrogen and VOCs, and this increase is further amplified at pyrolysis higher temperatures. However, the biochar carbon fraction that is mobile is low, with total TD-GC/MS compatible VOCs reporting approximately 0.2% and LC-OCD solubles approximately 1–2%. Prior mineral impregnation of bamboo enhances the release of oxygenated compounds including humics and phenolics from its biochars. This increase in mobile oxygenates occurs at higher pyrolysis temperatures despite these minerals catalyzing lignocellulose condensation and carbonization. This anomaly is explained by oxygenates relatively small contribution and the self inerting batch pyrolysis conditions producing different biochar surface and bulk molecular properties. By describing the impact of mineral amendments on the yield and structure of mobile organic compounds that may be released from biochar, this work contributes to our understanding of biochar efficacy in soils.

1. Introduction

Enhancing biochars with macro and micro-nutrients has become a commercial reality in jurisdictions such as China, Japan, Australia, Europe and North America. In China and Australia, bentonite clay, Fe/O, FeSO₄, rock phosphate, ash, basalt dust, ilmenite and phosphoric and citric acid have been added either to biomass before pyrolysis or added to the biochar after pyrolysis and then blended with chemical fertilizer and/or manures to produce a compound fertilizer [1–3]. Field trials and pot trials undertaken with a range of biochar, mineral, organic and

inorganic fertilizer blends have shown improved productivity, a reduction in greenhouse gas emissions, and changes in the microbial processes in soil [1,4,5]. Rawal et al. [6] recently carried out a series of experiments to determine how pretreating bamboo with different clays and FeSO₄ changed its biochar physicochemical properties. Ye et al. [7] showed that the surfaces of these biochars impregnated with clay and FeSO₄ enriched certain types of bacteria compared to untreated biochar. These bacteria are able to oxidize iron or reduced sulfur compounds and use the derived reductive power to fix carbon dioxide. This illustrates how the properties of composite biochars can drive specific

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microbial processes that have beneficial outcomes for the soil environment.

Those microbial processes are likely to be related to the surface properties of the composite biochars tested. Rawal et al. [6] reported that quantitative ^{13}C nuclear magnetic resonance (NMR) revealed the presence of clay and FeSO_4 at pyrolysis temperatures of 350 °C and above, promoted biomass degradation. This resulted in an increase in aromatic condensation and acidic and phenolic species. The presence of the clay also increased biochar pore volume, as measured by NMR cryoporosimetry, during torrefaction at 250 °C. In contrast, clay reduced biochar pore volume during pyrolysis at 550 °C. Microbial processes could also be influenced by organic compounds available within the biochar, produced during pyrolysis, which have been shown to increase plants resistance to disease, germination rates and nutrient uptake [8–13]. Other compounds inherently present in biochars and typically isolated using organic solvent extraction or flash pyrolysis include paraffins, alkyl benzenes, phenol derivatives, furans and PAHs [16–18]. These relatively low molecular weight (LMW) are also likely to have both positive and negative impacts on soil health and horticultural outcomes [14–19]. However, soils are unlikely to be in contact with strong organic solvents or undergo flash pyrolysis and therefore, the compounds that are easily extracted from biochars using conditions that have some relevance to natural conditions (eg, aqueous extraction or gentle thermal desorption) are also of interest. Structural information on these more “labile” organic compounds and how pyrolysis conditions influence them, is relatively scarce.

Organic compounds in soil have been associated with changes in plant, bacterial, fungal and nematode activity. For example, organic acids (including acetic, malic citric, gluconic, lactic, propionic, succinic acids) have been associated with increased phosphorus uptake in plants [20] as well as restricting bacterial, fungi and protozoa growth [21–23]. Nitrogen containing organic compounds such as acetamide, benzothiazole, butanamine, methanamine and aldehydes such as phenylacetaldehyde and benzaldehyde are likely fungal growth limiters [24]. Alcohols (including phenol, octanol, terpineol, benzeneethanol), aldehydes (benzaldehyde, benzeneacetaldehyde and decanal) ketones (e.g. nonanol and undecanone, propanone, phenylethanone), nonane, cyclohexene and dimethyldisulfide have shown nematicidal activity [25].

To address the lack of information on labile or “guest” biochar organic compounds, this study reports on their soluble and/or volatile organic molecules across a thermal sequence of bamboo biochars. It investigates how their composition is influenced by FeSO_4 addition with either bentonite or kaolinite clays. Liquid Chromatography with Organic Carbon Detection (LC-OCD) enables a broad characterization of water-extractable and hence polar components such as macromolecular humics. Thermal Desorption Gas Chromatography Mass Spectrometry (TD-GC/MS) is a complimentary technique which identifies volatile compounds with low polarity including hydrocarbons and terpenes. Both these volatile and water-extractable compounds together represent the organic biochar components most likely to interact with the surrounding soil and influence the efficacy of biochar soil application.

2. Materials and methods

2.1. Biochar samples

Biochars were subsamples of those described by Rawal et al., [6] and produced from the thermal decomposition of bamboo either neat i.e. producing (Bamboo Char BC), or as composite blends i.e. Bamboo/Kaolinite/ FeSO_4 (BKF) and Bamboo/Bentonite/ FeSO_4 (BBF) at pyrolysis temperatures of 350 °C, 450 °C and 550 °C. These temperatures are incorporated into the sample coding e.g. BKF350 is a bamboo/kaolinite/ FeSO_4 composite biochar prepared at 350 °C. The method of producing these composite biochars and their properties are detailed elsewhere [6] and Table SI-1. Batch pyrolysis involved heating the pretreated samples in an oxygen-limited static chamber (forming a self-

inerting “static” atmosphere) until the final pyrolysis temperature was reached and holding this temperature for 30 min before water quenching.

2.2. LC-OCD

Water extracts were obtained from the nine biochars using the same equipment and procedures as described by Taherymoosavi et al. [27]. Briefly, 1 g of each sample was finely ground and added to 10 mL distilled water. The solutions were regularly stirred at 50 °C for 24 h and subsequently filtered in order to separate the solid and liquid phases and the pH adjusted to approximately 7. The LC-OCD analysis was performed once for each sample with an RSD of 5% established using standards. LC-OCD is a multimode (size-exclusion and weak cation exchange) chromatography system coupled to three detectors, for organic carbon, organic nitrogen and UV absorbance for molecules containing chromophores such as humics. Details of the measurement procedure have been described by others [26–29]. In this study, a weak cation exchange Toyopearl TSK HW50S (polymethacrylate) LC column was used with a phosphate buffered mobile phase with pH 6.85 at a flow rate of 1.1 mL/min. Injection volumes were 1000 μL . Calibration of retention times and instrument response was performed using an alkaline-extractable organic matter (AEOM) standard (Suwannee river Standard II humic acid and fulvic acid from the International Humic Substances Society) that enables identification of the high-molecular weight fraction of Dissolved Organic Carbon (DOC) [29,30]. The carbon detection limit following these calibrations was observed to be 0.1–5 mg/L.

The LC-OCD instrument separates dissolved organic carbon into hydrophobic and hydrophilic fractions. Hydrophobic organic carbon is the fraction of DOC remaining on the column, implying a strong hydrophobic interaction with the stationary phase, and typically comprises longer-chain aliphatic and polycyclic aromatic material. The hydrophilic eluate fraction (known as chromatographable DOC) is then sub-divided into five categories based upon their retention time and molecular weight [29,30]. Example chromatograms from this study notated with fraction names has been provided in the supporting data (Fig. SI-1):

1. Biopolymers: Organic matter with high molecular weight, including polysaccharides, proteins and amino sugars (molecular weight > 20 kDa)
2. Humics or AEOM: Mixture of acids containing carboxyl and phenolate groups produced by biodegradation of dead organic matter (molecular weight ~1000 Da)
3. Building blocks: Molecular chains of polyphenolics/polyaromatic acids that have disaggregated, due to breakage of hydrogen bonding and electrostatic interactions (molecular weight 300–500 Da)
4. Low molecular weight acids: Representing protic organic acids (molecular weight < 350 Da)
5. Low molecular weight neutrals: Uncharged small organics, including LMW alcohols, aldehydes, ketones, sugars and LMW amino acids (molecular weight < 350 Da)

An additional parameter that can be obtained from the LC-OCD chromatogram is the aromaticity i.e. a measure of the degree of aromatic and unsaturated organic structures in the sample. Aromaticity is estimated by the ratio of the specific absorbance coefficient (SAC) at 254 nm to the dissolved organic carbon (DOC), as described in reference [29] and is expressed with units of $\text{L mg}^{-1} \text{m}^{-1}$.

2.3. TD GC/MS

Between 5 and 5.2 mg of each sample was accurately weighed into a clean quartz tube containing one quartz wool plug. A second glass wool plug was added over the sample to prevent its loss, and the tube was

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