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The molecular properties of biochar carbon released in dilute acidic solution and its effects on maize seed germination

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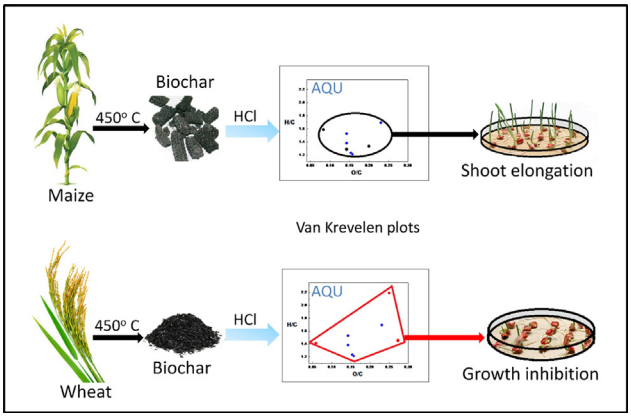
HIGHLIGHTS

- Acidic aqueous biochar extract (AQU) used to simulate soil rhizosperic conditions.
- Wheat biochar AQU inhibited maize seeds germination test.
- Maize biochar AQU promoted shoot elongation of maize seeds germination.
- Advanced characterization of AQUs revealed heterocyclic nitrogen molecules (HN).
- Difference in germination is related to the C/N ratio or the HN molecules in AQU.

GRAPHICAL ABSTRACT



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ABSTRACT

It is not yet clear whether the carbon released from biochar in the soil solution stimulates biological activities. Soluble fractions (AQU) from wheat and maize biochars, whose molecular content was thoroughly characterized by FTIR, ^{13}C and ^{1}H NMR, and high-resolution ESI-IT-TOF-MS, were separated in dilute acidic solution to simulate soil rhizospheric conditions and their effects evaluated on maize seeds germination activity. Elongation of maize-seeds coleoptile was significantly promoted by maize biochar AQU, whereas it was inhibited by wheat biochar AQU. Both AQU fractions contained relatively small heterocyclic nitrogen compounds, whose structures were accounted by their spectroscopic properties. Point-of-Zero-Charge (PZC) values and van Krevelen plots of identified masses of soluble components suggested that the dissolved carbon from maize biochar behaved as humic-like supramolecular material capable to adhere to seedlings and deliver bioactive molecules. These findings contribute to understand the biostimulation potential of biochars from crop biomasses when applied in agricultural production.

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1. Introduction

The production of biochar by controlled pyrolysis of biomass wastes has become of interest to numerous sectors of Agriculture: 1. the storage of stabilized carbon in soil presumed to contribute to climate change mitigation (Spokas et al., 2012), 2. the possible improvement of soil physical properties by favoring soil aggregation (Dong et al., 2016), aeration (Case et al., 2012), and water retention (Sun and Lu, 2014), 3. the potential enhancement of crop productivity by facilitating the growth of soil microbial populations and their activity (Chen et al., 2013, 2015; Domene et al., 2014), and releasing possibly bioactive hormone-like compounds (Spokas et al., 2010), and 4. the presumed capacity to assist soil remediation (Bereket et al., 1997; Biederman and Harpole, 2013; Kuppusamy et al., 2016; Mohan et al., 2016; Sohi et al., 2010).

The increasing tendency to largely dispose biochars into agricultural soils calls for an improved specification of their long-term persistence and bioavailability, as well as for an assessment of the potential beneficial or hazardous behavior of biochar components when released in the soil solution (Dutta et al., 2016; Sohi et al., 2010). It has been reported that biochars may increase plant growth (Rogovska et al., 2012; Zhang et al., 2012; Zhang et al., 2016) by providing nutrients (Glaser et al., 2002; Wu et al., 2016), or influencing soil pH, electrical conductivity (EC) and cation exchange capacity (CEC) (Atkinson et al., 2010). However, some types of biochar may have adverse effects due to the possible presence of heavy metals (Freddo et al., 2012; Van Wesenbeeck et al., 2014; Wu et al., 2016), polycyclic aromatic hydrocarbons (Freddo et al., 2012; Liao et al., 2014) and other phytotoxic compounds (Dutta et al., 2016; Rogovska et al., 2012). In order to understand the effects of bulk biochar materials, a large body of literature works has already covered a wide range of analytical and spectroscopical techniques, such as SEM (Lin et al., 2012), thermal desorption (TDS) GC–MS (Rogovska et al., 2012), FTIR (Lou et al., 2016), and solid state NMR (Ngunen et al., 2010).

The effects of biochar on plant growth seem to be more complex than simple nutrients source (Güereña et al., 2013; Mukherjee and Zimmerman, 2013; Sohi et al., 2010), but they are not yet clarified (Biederman and Harpole, 2013; Shackley et al., 2011), due to the heterogeneity of biochar materials and their nutrient supplying capacity (Alburquerque et al., 2014). The readily bioavailable water-soluble components are regarded as indicators of biochars' effects on plant growth (Lou et al., 2016; Zhang et al., 2012), and were shown to potentially either inhibit or stimulate seed germination and seedling growth (Solaiman et al., 2012). Phenolic compounds holding a carboxyl group are believed to be the most likely inhibiting species (Smith et al., 2013a, 2013b), possibly because their free radicals may induce hydroxyl radicals in solution, which become toxic to both roots and bacterial cells (Liao et al., 2014). Previous research on biochar water extracts employed ICP-MS, total organic carbon detection (TOC), and liquid chromatography coupled with organic carbon detector (LC-OCD), while FTIR was used on freeze-dried biochar water extracts to identify functional groups (Lou et al., 2016). More detailed characterization was conducted at molecular level by high resolution MS techniques, such as ESI-Orbitrap-MS (Cole et al., 2012), and FTICR-MS (Podgorski et al., 2012; Smith et al., 2013a).

Seed germination tests have been recommended as simple, rapid and reliable tests to identify biochars potential toxicity or biostimulation prior to soil application (Solaiman et al., 2012; Free et al., 2010), and differentiate their bioactivity (Rogovska et al., 2012; Solaiman et al., 2012). For example, growth of maize (*Zea mays* L) seedlings was inhibited by amending soil with miscanthus biochar formed at 400 °C for 10 min, whereas biostimulation was observed when pyrolysis of the same biomass waste was conducted at 600 °C for 60 min (Kwapinski et al., 2010).

Most seed germination tests were conducted using untreated bulk biochar (Liao et al., 2014; Solaiman et al., 2012), or bulk biochar washed with distilled or deionized water (Rogovska et al., 2012). However, it is precisely the water-soluble fractions of biochar that should be more effective on plant stimulation, due to a larger availability of bioactive compounds than for the bulk biochar. Nevertheless, these types of studies are still limited and mainly restricted to application of materials solubilized from biochar by alkaline extractions or pressurized hot water at neutral pH (Lin et al., 2011, 2012; Lou et al., 2016), despite the evidence that these conditions are hardly representative of the biochars' releasing potential in the acidic rhizospheric environment (Neumann and Romheld, 2002).

The objective of this study was to assess the potential bioavailability or toxicity of carbon materials released by wheat and maize biochars in acidic aqueous conditions, which better model the soil rhizospheric conditions than alkaline water extracts. The stimulating or inhibiting effects on maize seeds germination were then related to a number of chemical functionalities and molecular properties of the carbon compounds present in the acidic aqueous extracts from biochars. With this aim the Point of Zero Charge (PZC) and proton binding were calculated to reveal the potential humic-like character of the solubilized fractions, and liquid state ^{1}H NMR was applied for the first time to characterize the structure of the functional groups in the dissolved materials, whose molecular composition was reached by high resolution ESI-IT-TOF-MS. The relation between soluble biochar components and their biological activity may provide preliminary rigorous information on which type of biochar should produce the most useful plant response.

2. Experimental

2.1. Biochar and extracts

The two biochars of this study were made of wheat and maize straw under the pyrolytic temperature of ~450 °C. Wheat straw biochar was produced by Sanli New Energy Company, Henan, China. The general properties of this bulk biochar were reported earlier (Liu et al., 2012; Lou et al., 2016; Zhang et al., 2010). Maize straw biochar was produced by Qinfeng Straw Technology Co., Ltd., Jiangsu, China. The bulk biochars were homogenized by grinding and sieving at 1-mm sieve.

The extraction of water-soluble fraction (AQU) from both maize and wheat biochars were conducted at room temperature (22 ± 2 °C) by weighing 5 g of biochar and shaking the suspension overnight in 75 ml of a 0.1 M HCl solution in a rotatory shaker at 120 rpm. The supernatant was separated from biochar by centrifugation at 10,000 rpm and filtered twice through a double 41 grade Whatman filter paper. Finally, the extracts were freeze-dried and stored for further analyses. Extraction in dilute HCl solution to solubilize bioavailable cations from soil is a common and most efficient technique applied in nutritional studies (Meers et al., 2007; Chang et al., 2014).

Elemental composition (C, H, N) of AQU samples was determined with a Fisons Instruments EA 1108 Elemental Analyzer. An aliquot (50 mg) of the freeze-dried biochar aqueous extracts was dissolved in 1 ml of HCl (37%) overnight and brought to volume with 49 ml of Milli-Q water. The solution was filtered through a 41 Whatman filter and its content of Fe, Zn, Mg, Ca, K, Na, Cd, Co, Cu, Cr, Ni, Pb, was measured by a Perkin Elmer AA700 graphite furnace atomic adsorption spectrophotometer (AAS).

2.2. Proton binding and Point of Zero Charge

Proton uptake by AQU extracts was measured by potentiometric titration, as previously reported for humics by Drosos et al. (2009). In particular, 25 mg of AQU were suspended in a titration cell containing 25 ml of Milli-Q water to reach a concentration of 1 g l^{-1}, and kept under constant purge by N_2 gas (99.999% purity). The pH was set to 3 using traces of HNO_3 and set to equilibrate for 60 min under continuous stirring prior to titration. Each AQU solution was titrated with a 0.05 M NaOH solution (Drosos et al., 2009; Schulthess and Sparks, 1986) from pH 3.0 to 10.5, at an ionic strength of either 0.001 M or 1 M KNO_3.

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