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Research article

Biochar feedstock and pyrolysis temperature effects on leachate: DOC characteristics and nitrate losses from a Brazilian Cerrado Arenosol mixed with agricultural waste biochars

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A B S T R A C T

Dissolved organic carbon (DOC) leached from Brazilian Cerrado Arenosols can lead to carbon (C) losses and lower soil fertility, while excessive nutrient, e.g. nitrate (NO_3^-), leaching can potentially cause water contamination. As biochar has been shown to stabilize C and retain soil nutrients, a greenhouse experiment was conducted to test different biochars' contributions to DOC and NO_3^- leaching from a sandy soil. Biochars were made from four local agricultural waste feedstocks (cotton residue, swine manure, eucalyptus sawmill residue, sugarcane filtercake) pyrolysed at 400, 500 and 600 °C. Biochar was mixed with soil at 5% weight in pots and maize seeds planted. Leachate was collected weekly for six weeks and analyzed for DOC and NO_3^- concentrations, while fluorescence spectroscopy with parallel factor analysis (PARAFAC) was used to interpret DOC characteristics. Cotton and swine manure biochar treatments had higher DOC and NO_3^- losses than eucalyptus biochar, filtercake biochar, and control treatments. Cotton and swine manure biochar treatments at high temperatures lost mostly terrestrial, humified DOC, while swine manure, filtercake, and eucalyptus biochars at low temperatures lost mostly labile, microbially-derived DOC. Through the practical use of fluorescence spectroscopy, our study identified filtercake and eucalyptus biochars as most promising for retaining DOC and NO_3^- in a Cerrado Arenosol, potentially reducing stable C and nutrient losses.

1. Introduction

Arenosols (sandy soils) account for 13% of the area of the state of Mato Grosso, Brazil, (about 11.7 million ha), and their use as cultivated soils is increasing, particularly for growing maize (SEPLAN, 2008). However, Arenosols are low in organic matter, and their high sand content causes low water retention (da Costa et al., 2013). Carbon (C) in the form of dissolved organic carbon (DOC) and nutrients, such as nitrogen (N) in the form of nitrate (NO_3^-), are easily leached from these soils. As their use for agriculture (in particular crops such as soybean and maize) is of increasing importance to the economy of Mato Grosso, sustainable management practices such as adding organic matter are necessary to improve the Arenosol's physico-chemical properties. Among the various types of organic amendments that can be added to soil, biochar is one that is considered efficient and stable in the long-term (Clough and Condron, 2010; Lehmann, 2007). Biochar refers to charcoal derived from waste biomass by pyrolysis, which has been shown to improve fertility, carbon sequestration, and water-holding capacity in soils (Lehmann and Joseph, 2009). Its potential use in strategies for improving the agronomic performance of

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sandy soils in Mato Grosso could thus be beneficial, as observed in other tropical soils (Jeffery et al., 2017). Less is known, however, about the effects of biochar use in tropical Arenosols, and more specifically, its role in retaining C and N in these soils.

Furthermore, examining the chemical reactivity of DOC can be useful to understand its contribution to ecosystem dynamics (Weishaar et al., 2003). Over the past few decades, fluorescence spectroscopy has proven to be a fast and relatively inexpensive method for characterizing DOC. Three-dimensional excitation-emission matrices (EEMs), produced by the combination of emission spectra with excitation wavelengths, can be used to produce fluorescence indices and intensities (Fellman et al., 2010). Several indices are used to determine different fluorescence characteristics. These include the fluorescence index (FI) which indicates whether the DOC is of terrestrial or microbial sources (Cory and Mcknight, 2005; McKnight et al., 2001), the biological index (BIX) described as "the index of recent autochthonous contribution" (p.716, Huguet et al., 2009), and the humification index (HIX), which measures the extent of humification (Zsolnay et al., 1999). Parallel factor (PARAFAC) analysis (Murphy et al., 2013) helps further characterize DOC composition (e.g. humic, protein-like, etc.) using data derived from EEMs (Fellman et al., 2010).

Besides its contribution to soil physical and chemical properties, biochar offers an alternative way to reduce agricultural waste compared to other organic amendments. Converting animal and crop waste to biochar significantly reduces the volume and weight of the waste, and requires fewer applications than fertilizers which need to be applied annually (Lehmann and Joseph, 2009). However, as Joseph et al. (2010) notes, the effect of biochar on the soil is "biochar- and site-specific". Thus in this study, a variety of agricultural wastes readily found in the region were transformed into biochar pyrolized at different temperatures to identify the influence of both feedstock and pyrolysis on the agroecological performance of biochar when applied to a Brazilian Arenosol. The objectives were to: 1) observe the effect of biochar type (feedstocks and temperatures of pyrolysis) on bulk leaching dynamics of DOC and NO_3^-, and 2) examine fluorescence characteristics of DOC leached from soil-biochar mixtures using fluorescence spectroscopy to infer DOC reactivity and fate. The hypotheses were that eucalyptus biochars would retain DOC more than the other biochars since it would increase soil C levels due to its feedstock's high C/N ratio, while higher temperature biochars would reduce DOC losses particularly of humic DOC because of their greater recalcitrance.

2. Materials and methods

2.1. Soil collection and biochar production

Soils from the top 0–20 cm layer were collected from an agricultural field located within the farm Fazenda Água Azul (15°13′55.2″S, 54°57′43.4″W) managed by the agribusiness Grupo Bom Futuro, 178 km northwest of the state capital of Cuiabá in Mato Grosso, Brazil, an area within the Cerrado. The soil collected was classified as an Arenosol (FAO soil classification), with a sandy texture (91% sand, 4% silt, 5% clay). Carbon and nitrogen levels in the soil were 0.7% C and 0.08% N as determined by elemental analysis (628 Series CHN Analyzer, LECO Corp., St. Joseph, MI). The average pH_{water} was 5.8 and average CEC was 5.3 $cmol_c\ kg^{-1}$, with a bulk density of 1.6 $g\ cm^{-3}$. Over the last 10 years, the crops sown on the study site included soybean, sorghum, maize, and cotton, with the latter two crops grown in rotation with soy for the last three years (Afonso Campos da Silva, Grupo Bom Futuro, personal communication, 2014). Twelve biochars were commercially produced (SPPT Ltda., Mogi Morim, São Paulo, Brazil) from four feedstock materials: cotton husks, eucalyptus sawmill residue, sugarcane filtercake, and swine manure, slow-pyrolysed at three temperatures (400°, 500°, 600 °C). These were subsequently crushed and sieved to <2 mm in order to have similar biochar particle sizes between the different feedstocks.

2.2. Experimental design

In a greenhouse located at the Federal University of Mato Grosso (UFMT), Cuiabá campus, 9 L volume pots with one hole drilled at the bottom were filled with 8 kg of a <2 mm-sieved Arenosol. Twelve biochars (4 biochar feedstocks x 3 temperatures of pyrolysis) were applied to pots at 5% soil dry weight, mixed and compacted by hand, making a total of 52 pots (12 biochars x 4 replicates plus 4 unamended soil controls). A high biochar application rate (equivalent to 80 t ha^{-1}) was used to ensure a biochar effect was detected. The pots were divided into 4 blocks, with each block running north-south along a greenhouse bench, with a replicate of each treatment (biochar amended soil) plus a control (unamended soil) randomly assigned to locations within each block. The greenhouse temperature was controlled to 28 ± 2 °C, similar to temperatures during which the dry season maize is grown from January to June (INPE, 2012).

Water was initially added to achieve field capacity and allowed to equilibrate. Since fertilizer applications are a standard management practice in the region, fertilizer was added to the pots corresponding to the amount each maize plant requires at the rate of 150 kg NPK + S, 150 kg KCl and 200 kg urea for 60,000 plants/hectare in the field (Afonso Campos da Silva, Grupo Bom Futuro, personal communication, 2014). Fertilizer, 2.5 g NPK + S (12-46-0 + 7), was added after 1 week and four maize seeds were planted in each pot. Crushed KCl (2.5 g) and diluted urea (2.0 g in 50 mL water) were added 20 days after planting, followed by a second diluted urea application of 1.3 g 7 days later. Watering thereafter took place once a week then three times a week once the plants began to grow, adding water at 110% field capacity each time to produce sufficient leachate from each pot.

2.3. Laboratory analysis

Elemental analysis (C, H, N) of the 12 biochars was performed on a CHN Analyzer (628 Series, LECO Corp., St. Joseph, MI). Oxygen content of the biochars was calculated as O = 100-(C + H + N + ash content). Ash content was determined by placing 1 g of each biochar in crucibles and heating in a muffle furnace to 900 °C for 4 h (Fuertes et al., 2010). Biochar pH was determined from 1:2.5 biochar:water mixtures. Biochar extracts (i.e. without soil) were made by mixing 3 g of each biochar into 30 mL of distilled water, heating in an oven at 50 °C for 24 h, then centrifuging for 5 min at 5000 rpm before filtering (Lin et al., 2012). Extracts were then analyzed for DOC characteristics. Biochar properties are presented in Table S1 in the supplemental material. Additional physical properties (e.g. surface area, porosity, particle size) can be found in Speratti et al. (2017). Total C and N in soils post-experiment were also analyzed on a CHN Analyzer.

Leachate was collected once per week for 6 weeks and filtered through 0.7 μm glass fiber filters. DOC and NO_3^- concentrations were determined weekly immediately after collection using a UV–Vis spectrophotometer (Spectrolyser; S-can, Austria) (Van Den Broeke et al., 2006). Since concentrations were higher than the spectrophotometer's range, samples were diluted with ultrapure water. DOC fluorescence characteristics from weekly samples were analyzed by obtaining EEMs on an Aqualog spectrofluorometer