Science of the Total Environment 613–614 (2018) 969–976

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Effects of aging under field conditions on biochar structure and composition: Implications for biochar stability in soils

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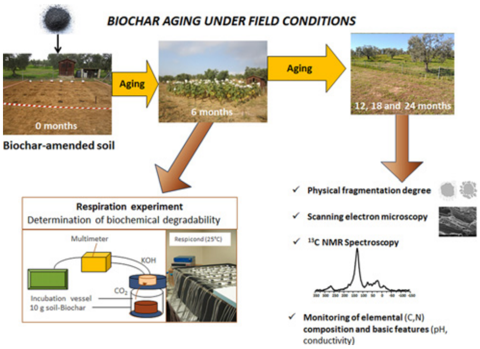
## HIGHLIGHTS

- Biochar aging grade is influenced by feedstock nature.
- Physical fragmentation of biochars increased during aging.
- Increase of *O*-alkyl C and alkyl C in aged biochars at expenses of aromatic-C ($^{13}$C NMR)
- Mean residence times of C from biochars were much lower than expected, in the range of decades.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 29 June 2017
Received in revised form 7 September 2017
Accepted 13 September 2017
Available online 26 September 2017

Editor: Ajit Sarmah

*Keywords:*
Organic amendment
Mediterranean climate
Physical and chemical parameters
Soil properties
Carbon sequestration, pyrogenic carbon

## ABSTRACT

The effects of aging on biochar (BC) properties, composition and carbon sequestration are still under debate. This study aimed at illustrating the qualitative alterations of five different BCs aged during a 24-month field experiment located in Southwest Spain. To determine the recalcitrance of each BC, physical fragmentation test, scanning electron microscopy, $^{13}$C NMR spectroscopy and $CO_2$-respiration experiments were performed.

The physical fragmentation values of all types of BC increased significantly over time at field conditions. FESEM examinations of aged BCs showed collapsed structures and the presence of entrapped soil material and microbial mats into the BC pores. The $^{13}$C NMR spectroscopy demonstrated an increase of the relative abundance of *O*-alkyl C and alkyl C at expenses of aromatic-C in aged BCs. The C losses of all BCs ranged from 27% to 11% of the initial C. In contrast, the nitrogen (N) content of wood-derived BCs significantly increased probably due to the sorption of nitrogen containing compounds into these highly-porous weathered chars. With the exception of that for the sewage sludge-BC, the pH of all aged BCs decreased from $>$9 to the soil pH, indicating a short lasting of the liming effect caused by BC addition.

The respiration experiment revealed that BC recalcitrance was much lower than expected and, within the range of decades. Only wood-derived BCs significantly increased the mean residence time of the slow C pool of the Cambisol by factors between 3.4 and 7.7. Mediterranean climate conditions and the characteristics of the Cambisol used probably accelerated the microbial degradation of BCs.

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*Abbreviations:* BC, biochar; CPMAS, cross-polarization magic angle spinning; EC, electrical conductivity; EDS, energy dispersive spectroscopy; FESEM, field emission scanning electron microscopy; KWB, vineyard wood biochar pyrolyzed in kilns; $MRT_1$, mean residence time of labile organic carbon; $MRT_2$, mean residence time of slow turning organic carbon; ms, millisecond; MWB, mix of wood chips biochar; NMR, nuclear magnetic resonance; OC, organic carbon; PSB, paper sludge biochar; PWB, pine wood biochar; PyC, pyrogenic carbon; SE, secondary electron; SOM, soil organic matter; SSB, sewage sludge biochar.

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https://doi.org/10.1016/j.scitotenv.2017.09.124
0048-9697/

## 1. Introduction

Biochar (BC) is the carbonaceous solid residue produced through the pyrolysis of organic residues and used as soil ameliorant. It offers a sustainable tool for agriculture management (De la Rosa et al., 2014) and soil remediation (Lehmann and Joseph, 2015). Numerous research studies pointed out that BC can act as a soil conditioner enhancing plant growth by retaining nutrients and improving soil physical and biological properties (Lehmann and Joseph, 2015; Lehmann et al., 2010). In addition, BC can act as an agent for carbon sequestration (Goldberg, 1985a, 1985b; Lehmann, 2007), due to its highly aromatic nature which turns it less available to microbial degradation (Sohi et al., 2010). Thus, BC is often referred to as a material of high chemical and biochemical stability, which may persist over long periods of time (Kuzyakov et al., 2009). Nevertheless, there are evidences that the paradigm of recalcitrant pyrogenic carbon (PyC), including BC, has to be revised, since newer results (Knicker et al., 2013a; Watzinger et al., 2014) indicate a much lower biochemical stability of PyC as formerly assumed. This could explain why, at a global scale, the content of PyC stored in soil is low with respect to the annual production rate by wildfires. Masiello and Druffel (2003) demonstrated that a substantial fraction of the annually produced PyC from biomass burning must be mineralized or the accumulation of PyC in the environment over time would be sufficient to perturb global atmospheric oxygen levels. However, regardless microbial decomposition (Wengel et al., 2006), a considerable loss of PyC from soil (Santín et al., 2016) is caused by erosion (Rumpel et al., 2006) or dissolution and transport by water fluxes (Jaffé et al., 2013). Evidences of PyC degradation were obtained by solid-state $^{13}$C and $^{15}$N NMR spectroscopy (De la Rosa and Knicker, 2011). This study revealed that already after two months of incubation the chemical structure of grass char was significantly altered, including partial oxidation of aryl structures and degradation of N-heterocyclic constituents. Once deposited in the environment, a range of reactions occur, which also induce changes to physical and chemical properties of BC. Aging of BC was suggested to consist mainly of oxidation of exposed C rings with a high density of π electrons and free radicals (Joseph et al., 2010), which creates a high density of O-rich functional groups at the BC surface. It was further proposed that oxidation starts at the surface and propagates to the core of particles over time (Lehmann et al., 2005; Sorrenti et al., 2016), promoting further physical, chemical and microbial degradation (Hammes and Schmidt, 2009).

Despite BC is increasingly used as soil amendment and the properties of freshly produced BCs are well documented (De la Rosa et al., 2014; Kim et al., 2013), its biochemical stability and alteration during aging in the soil environment are still unclear (Ameloot et al., 2013). Amazonian dark earths, which triggered interest in BC, probably comprise the best-documented long-term case study of BC in soil. Nevertheless, results from *terra preta* are difficult to extrapolate to other soil, climatic and agronomic contexts (Hardy et al., 2017). Alternatively, studies dedicated to BC aging in agricultural soils have been conducted. Yet, they have been frequently performed using artificially accelerating aging methods, including drying or wetting and chemical oxidants (Sultana et al., 2011; Ascough et al., 2011; Cross and Sohi, 2013; Wang et al., 2015). Others promoted the aging of BC with the aid of microorganisms whose activity was enhanced through supplementation of labile organic compounds such as glucose or fresh biomass (Hamer et al., 2004; Keith et al., 2011). In general, they agreed that with progressive aging, BC is reduced in size, and functional groups such as carboxyl and carbonyl or hydroxyl are formed on the BC surface. Functionalized (aged) BCs can potentially increase interactions between BC, SOM, soil minerals, nutrients, and contaminants (Mia et al., 2017). Spokas (2013) reported that aging greatly alters the greenhouse gas response of the soil systems to BC amendments. Unfortunately, taking into account the complex interactions within the soil matrix, the extrapolation of these impacts to BCs added as agricultural soil ameliorant is very uncertain. As soil amendment with BC targets mainly agricultural soils, a better assessment of the effect of climate and soil characteristics on the fate of BC is crucial for predicting the long-term dynamics of BC in soil. It is well known that intensive tillage disrupts soil aggregates and exposes SOM to physical and microbial degradation (Panettieri et al., 2015). Such soil treatments may also accelerate BC aging. The environmentally more sustainable conservation agriculture enhances not only soil quality but also favours soil aggregation and prevents increasing SOM loss due to enhanced microbial activity. We hypothesize that in spite of the conservation agriculture and the hot Mediterranean clime, BC ages, once it has been applied to soils. Thus, for this study a no-tillage field experiment was conducted during 24 months in an agriculturally used Calcic Cambisol (SW Spain) to determine the alterations induced by the environmental conditions, soil properties and native microbiota to physical and chemical characteristics of five different types of BC. For that purpose, weathered BC particles were collected 6, 12 and 24 months after soil amendment and sunflower sowing. Subsequently, they were analyzed by a multidisciplinary approach which combined the analysis of basic properties (pH, electrical conductivity and physical fragmentation degree), elemental composition (C and N), field emission scanning electron microscopy (FESEM) and $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. In addition, the biochemical recalcitrance of the field-aged BCs was assessed through a laboratory-based respiration experiment in which the collected BCs were mixed with the same soil and incubated for 110 days. To the best of our knowledge, this is the first study on the effects of aging at field conditions on BC properties involving qualitative analyses (composition, physical and chemical characteristics) and quantitating the microbial degradation potential of field-weathered BCs, without applying additional chemical, physical or microbiological procedures for aging acceleration.

## 2. Materials and methods

### 2.1. Biochars aging experiment at field

The field experiment was carry out at the experimental farm “La Hampa” of the Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS), located 13 km southwest of the city of Seville (Spain) in the Guadalquivir river valley (SW Spain; 37° 21.32′ N, 6° 4.07′ W) from February of 2014 to March of 2016. The soil of the plots used for this experiment is a Calcic Cambisol (IUSS Working Group WRB, 2007). This is a calcareous soil (Mudarra-Gómez, 1988), with a sandy clay loam texture (240 g kg$^{-1}$ clay, 180 g kg$^{-1}$ silt and 580 g kg$^{-1}$ sand) which contained 20 g C kg$^{-1}$ soil (7 g organic C kg$^{-1}$ soil) and 1 g N kg$^{-1}$ soil., Its pH$_{(H2O)}$ was 7.8 and the electrical conductivity was 68 μS cm$^{-2}$ (Panettieri et al., 2015). The climatic conditions are typical Mediterranean with mild rainy winters (496 mm mean annual rainfall) and very hot and dry summers. The mean annual daily temperature at the experimental site is around 21 °C, with maximum and minimum mean monthly temperatures of 33.5 °C and 5.2 °C registered in July and January, respectively (Panettieri et al., 2015). Five types of BCs, produced from pine wood (PWB), paper sludge (PSB), sewage sludge (SSB), old vineyard wood pyrolyzed in traditional kilns (KWB) and a mix of wood chips (MWB) were homogenized, moistured (biochar:water, 1:1) and subsequently applied to the first 5 cm of the topsoil at a dose equivalent to 15 t ha$^{-1}$. Additionally, KWB was crushed and sieved (<2 cm) before application. Table 1 comprises a complete description of the production conditions of the used BCs.

Certified seeds of *Helianthus annuus* L. (sunflower) were planted on the 20th of February 2014. Detailed descriptions of the experimental conditions and of the effects of BCs addition on sunflower productivity are described in Paneque et al. (2016). No tillage operations were performed, except for the crumbling of the sunflower stalks, and the sowing was performed by direct drilling. Sunflower plants were harvested 6 months after sowing. During that initial period weeds were removed manually. Subsequently, the plots were kept fallow at the field from month 7 until the end of the experiment (month 24). Soil samples