



Nanoscale analyses of the surface structure and composition of biochars extracted from field trials or after co-composting using advanced analytical electron microscopy



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ABSTRACT

Biochars have been recognized as an important material to improve soil properties. In a number of studies their beneficial properties have been found to increase with residence time in soil and during the composting process. The beneficial properties have been correlated with surface functional groups resulting from the interactions between char particles, inorganic and organic matter in the soil and soil biota. These interactions result in the formation of organo-mineral phases on the internal and external surfaces of the biochar. A paucity of information exists, particularly from longer-term field trials, on organo-mineral phases present on both the internal and external surfaces of the biochar. To characterize the structure of, and interface between, the carbon and mineral phases, we examined biochars recovered from two field trials and after composting from different countries using high resolution scanning electron microscopy (SEM), atomic resolution transmission electron microscopy (TEM) and scanning TEM (STEM), energy electron loss spectroscopy (EELS) and energy dispersive X-ray spectroscopy (EDS) at resolutions of 1–20 nm. The work revealed the formation of porous agglomerates of different minerals/inorganic compounds bound together with organic compounds on the surfaces of the biochar. In some cases, these agglomerates were bound together to form organo-mineral associations. The analyses also showed that the organic compounds containing both N and C functional groups and mixed valence iron oxide nanoparticles are possibly interacting with the organic compounds. The analysis also showed the formation of pores at the interface of the carbon matrix and organo-mineral aggregates.

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1. Introduction

Biochar is defined as charred organic matter applied in agriculture. It is recognized as an important material to improve a range of soil properties, by increasing the efficiency of N and P chemical fertilisers and by enhancing the properties of compost (Lehmann and Joseph, 2009). However, as soon as biochar is amended to soil or composting feedstock, it is subjected to a range of physical, chemical and biological

interactions. Biochar can be fragmented into smaller particles as soon as it interacts with water (physical disintegration), which is suggested to hardly alter the carbon speciation of the biochar (Spokas et al., 2014). Biochar will sorb a broad range of organic and inorganic compounds from soil or compost (Borchard et al., 2014; Hale et al., 2013; Hale et al., 2015) and might be involved in acid-base – reduction of biochar pH during aging in soil, cf. (Heitkötter and Marschner, 2015; Spokas, 2013) – as well as redox reactions (Klüpfel et al., 2014; Quin et al., 2015). Biochar interacts with soil fauna, microorganisms and roots (Lehmann et al., 2011), especially, it can be a habitat for microorganisms (Quilliam et al., 2013). The sum of these processes results in an alteration of the biochar. To some extent, this alteration can be characterized as an oxidation of the biochar surface (Cheng et al., 2006; Wiedner et al., 2015). A range of studies has shown that the structure and properties of biochars evolve in a complex, spatially heterogeneous manner beyond the oxidation of carbon. This involves the interaction (sorption) with non-biochar organic and inorganic matter (Araujo et al., 2014; Joseph et al., 2010; Singh and Cowie, 2014) and complex biotic and abiotic redox reactions (Joseph et al., 2015; Kappler et al., 2014; Pagano et al., 2016). Thus, (electron) microscopy and related techniques are important tools to identify the spatial distribution of these processes on the biochar surface, and also can be used to identify the nature of these alterations.

Detailed evaluation of biochar after incorporating into the soil for more than one year has been carried out using a range of techniques including transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Chia et al. (2012) characterized the interfaces between carbon-rich and mineral-rich regions of particles collected from the *Terra Preta* soils from the Amazon. A key finding was the appearance of Fe and Mn nanoparticles around the surface of the carbon-rich regions and the high concentration of Ca in the amorphous carbon that surrounded mineral phases. These nanoparticles were shown to be redox-active (Joseph et al., 2015).

Archanjo et al. (2014 and 2015) and Jorio et al. (2012) examined the carbon-rich core as well as the organo-mineral shell around these *Terra Preta* particles. They were able to map the distribution of carbon functional groups around sub-micron carbon particles using monochromated electron energy-loss spectroscopy (EELS). These studies showed that the carbon matrix is not homogenous throughout a single particle. Also, using energy dispersive X-ray spectroscopy (EDS), the carbon particles showed high concentrations of Ca. In addition, X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy both showed biochar particles to have higher carbon aromaticity in their core than at the surface.

Lin et al. (2012) examined the surface of biochar produced from chicken litter that was collected after being in the soil for one year. This work was complemented by examination of the biochar surface with XPS. They found that organo-mineral layers had been formed on the surface of the biochar and that these were characterized by formation of a range of sub-100 nm mineral particles surrounded by amorphous carbon to form micro-aggregates. Pores ranging in size from 1 to 100 nm were observed between the biochar and the organo-mineral layer and there was an increase in carboxyl (COOH) and amino (NH₂) functional groups. More detailed TEM analysis of the interfaces between poultry litter and paper sludge biochar and organo-mineral complexes, which had been in the soil for two years, was also undertaken. It has been hypothesised that the long-lasting properties of the biochars were due to the formation of this nutrient-rich functionalised layers (Joseph et al., 2013).

Although a number of studies on the characteristics of field applied biochars can be found in the literature, a detailed analysis of the interfaces between the biochar and organo-mineral phases, as well as the strengths and weaknesses of each microscopy and sample preparation methods, have not been yet undertaken. Studies using high resolution SEM or atomic resolution TEM/STEM methods with spectroscopic techniques such as EELS and EDS at resolutions of 1–20 nm can be very

useful for soil science research. In fact, such studies would provide insights into the process of stabilisation of the biochar and its long-term agronomic benefits. It will also allow an evaluation of the various sample preparation methods and imaging and analysis techniques, to understand which are best suited to characterising these complex materials.

This paper presents the results of the observations and measurements of three very different biochars produced in different continents. Two of these biochars were extracted from field trials in two different soil types and the third was extracted from a high quality mixed manure/biochar compost. The questions to be addressed by this study include:

1. Can the nanometer-scale chemical and structural information acquired by SEM and TEM provide insights into the complex reactions which take place on the external and internal surfaces of biochar in soil and compost?
2. Are there similarities between the organomineral layers formed on different biochars extracted from different soils and from compost at the nanometer scale?
3. What are the optimal microscopic techniques to obtain images and spectra at high resolution without contamination and damage of the specimen?

2. Materials and methods

Three very distinct biochars were examined. Two were derived from various soils and the third from a composting experiment. These biochars have been shown to increase plant growth (Mohammadi et al., 2016) and total soil carbon content (Slavich et al., 2013) under field conditions. Biochars extracted manually from the ground/compost pile were thoroughly washed with demineralized water on a 100 µm sieve and then dried at 50 °C in an oven for 24 h.

Mineral-rich biochar (RCBS) was produced in North Vietnam. A mixture of rice straw and husk coated in clay, along with wood and bamboo was pyrolysed in a top lit updraft gasifier drum oven (TLUD) at approximately 450 °C (Mohammadi et al., 2016) to produce a mineral-rich biochar (RCBS) which was then added to manure and composted for 45 days. This mixture was applied to rice paddies and was extracted after 2.5 years. The basic properties of the pristine biochar were pH 9.8, total C 54%; nitrogen 0.82%, ash content 23%, phosphorous 5.12 g/kg and potassium 25 g/kg. The soil was loamy sand, the pH_{KCl} (1:2.5) 5.3 and organic carbon (OC) 1.23%.

Green waste biochar (GWS) was from a field trial in Wollongbar NSW Australia (Slavich et al., 2013), after being incorporated for 9.5 years. This biochar was produced at 550 °C, it has a relatively low ash and high carbon content (76%). Details of this biochar are provided elsewhere (Slavich et al., 2013; Weng et al., 2015). The basic properties of the pristine biochar were: pH 7.8, total C 76%, nitrogen 0.61%, ash content 7.6%, phosphorous 0.19 g/kg and potassium 1.7 g/kg. The field experiment was conducted on a mixed C₃/C₄ vegetated rhodic Ferralsol. The soil was acidic (pH 4.5; 1:5 CaCl₂) with 4.5% total carbon content.

A wood biochar (WC) was produced from branches taken after the tree was pruned in a Kon-Tiki kiln (Cornelissen et al., 2016) at approximately 700 °C. It was co-composted under aerobic conditions with manure at sub-industrial scale for 63 days during a composting field experiment at the Ithaka Institute in Arbaz and St. Léonard, Switzerland. The compost windrow (20 m³) reached a maximum temperature of 65 °C. The basic properties of the pristine biochar were: pH 8.5, total C 77%, nitrogen 0.75%, ash content 18.4%, phosphorous 2.1 g/kg and potassium 4.8 g/kg.

Further basic characteristics and information on the processing and characterization techniques of these biochars are given in Table 1, which summarizes the spectro-microscopic techniques and respective sample preparation methods applied to the biochars. The microscopy was carried out in 4 different universities. Each of these centres has different microscopes and different techniques to measure the properties

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