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NEXAFS and XPS characterisation of carbon functional groups of fresh and aged biochars

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ABSTRACT

The oxidation of surface functional groups on biochar increases its reactivity and may contribute to the cation exchange capacity of soil. In this study, two Eucalyptus wood biochars, produced at 450 °C (B450) and 550 °C (B550), were incubated separately in each of the four contrasting soils for up to 2 years at 20 °C, 40 °C and 60 °C. Carbon functional groups of the light fraction (< 1.8 g/cm^3) of the control and biochar amended soils (fresh and aged for 1 and 2 years at 20 °C, 40 °C and 60 °C) were investigated using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy and X-ray photoelectron spectroscopy (XPS). The spectra of biochar and light fractions of the control and biochar amended soils showed two distinct peaks at ~285.1 eV and 288.5 eV, which were attributed to the C1s-$\pi^*_{C=C}$ transitions of aromatic C and C1s-$\pi^*_{C=O}$ transitions of carboxylic C, carboxyamide C and carbonyl C. The proportion of aromatic C was substantially greater in the light fraction of the biochar amended soils than the corresponding light fraction of the control soils. Also, the proportion of aromatic C was much higher in the light fraction of the B550 amended soils than in the corresponding B450 amended soils. Neither NEXAFS nor XPS results show any consistent change in the proportion of aromatic C of biochar amended soils after 1 year ageing. However, XPS analysis of hand-picked biochar samples showed an increase in the proportion of carboxyl groups after ageing for 2 years, with an average value of 8.9% in the 2 year aged samples compared with 3.0% in the original biochar and 6.4% in the control soil. Our data suggest that much longer ageing time will be needed for the development of a significant amount of carboxyl groups on biochar surfaces.

1. Introduction

There has been growing interest in the soil application of biochar for long term C storage and other multiple potential benefits. In addition to the long term C storage, biochar has the potential to reduce greenhouse gas emissions, improve soil properties, enhance agricultural productivity and adsorb organic and inorganic contaminants in soils (Lehmann, 2007a,b; Yu et al., 2009; Namgay et al., 2010; Singh et al., 2010; Kookana et al., 2011). Biochar comprises highly aromatic and chemically stable components of C, along with some easily degradable aliphatic structures (Lehmann, 2007a,b). The composition of C forms in biochars depends on biomass type and pyrolysis conditions, such as heating temperature, heating rate and conditions. (Czimczik et al., 2002; McBeath and Smernik, 2009; Keiluweit et al., 2010; McBeath et al., 2011). Furthermore, the stability of biochar in soils is dependent on soil properties and environmental conditions (Cheng et al., 2006, 2008; Keith et al., 2011; Fang et al., 2014a,b). However, determination of changes in the molecular structure and chemical properties of biochars applied to soil remains a major challenge.

Despite having a significant proportion of recalcitrant C, some of the biochar C applied to soil is mineralised, particularly high soil temperature and moisture facilitate rapid abiotic and biotic oxidation of biochar in soils (Cheng et al., 2006, 2008; Liang et al., 2006; Keith et al., 2011; Fang et al., 2014a,b). The creation of surface functional groups on biochar is important for its increased reactivity and contribution to the cation exchange capacity of soils (Liang et al., 2006). Furthermore, the interaction of biochar with clay minerals in soils and consequent entrapment within newly formed aggregates may stabilize biochar in soil (Glaser et al., 2000; Brodowski et al., 2005; Fang et al., 2014a).

Spectroscopic techniques including solid state ^{13}C nuclear magnetic resonance (NMR), XPS and Fourier transform infrared (FTIR) have been widely used for the characterisation and monitoring of biochar in soils (Cheng et al., 2006, 2008; Liang et al., 2008; McBeath et al., 2011). Among the spectroscopic methods, NMR spectroscopy has been most commonly used for the structural

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characterisation of black carbon and biochar in soils (Baldock and Smernik, 2002; Czimczik et al., 2002; McBeath et al., 2011). However, the technique has some drawbacks, such as the poor detection limit of biochar C with cross polarisation ^{13}C NMR, poor signal to noise ratio for biochars produced at high temperatures and loss of NMR signal in the presence of paramagnetic and ferromagnetic minerals (Freitas et al., 1999, 2002; Hedges et al., 2000; Begaudeau et al., 2012).

NEXAFS spectroscopy is an element specific technique that has been successfully employed for the characterisation of heterogeneous and complex environmental C materials including black carbon particles (Lehmann et al., 2005; Schumacher et al., 2005; Liang et al., 2006, 2008). More recently Keiluweit et al. (2010) employed C-Is NEXAFS to relate C speciation to the degree of structural order in biochar produced at charring temperature ranging from 100–700 °C. Heymann et al. (2011) characterised a range of C rich materials including black carbon reference materials using C-Is NEXAFS and they found a reasonable correlation between aromatic C obtained by NEXAFS and ^{13}C NMR.

XPS is a surface specific quantitative technique (depth of analysis < 10 nm) which can also determine relative abundance of different species of an element (Briggs and Seah, 1990). It has been used for the characterisation of surface functional groups and to determine changes in the element composition of biochar with ageing (Cheng et al., 2006; Cheng and Lehmann, 2009; Nguyen et al., 2009; Lin et al., 2012). For example, Cheng et al. (2006) observed oxidation of C groups and formation of carboxylic C in black carbon particles incubated at high temperature (70 °C). Similarly, Nguyen et al. (2009) reported an increase of O content and a decrease of C content on biochar surface or entire particles after decades of ageing in soil.

Based on recently published work it appears that both XPS and NEXAFS spectroscopy are ideally suited for characterising C functional groups of soil organic carbon (SOC) and biochar (Cheng et al., 2006, 2008; Lehmann et al., 2009; Keiluweit et al., 2010, 2012; Heymann et al., 2011). Considerable research has been conducted to understand the mineralisation of biochar C in different soil types and under different conditions (Hamer et al., 2004; Cheng et al., 2006, 2008; Liang et al., 2008; Zimmerman, 2010; Keith et al., 2011; Fang et al., 2014a,b). However, little is known about the changes in C functional groups of biochars after ageing in soils under different conditions. Therefore, this study was conducted with the specific objectives: (i) to investigate the chemistry of C of the light fraction of unamended and biochar amended soils after ageing at different temperatures; and (ii) to identify changes in the molecular structure of biochar C (and native organic C) with ageing in contrasting soils at three temperatures. A number of reference organic compounds relevant to soils were also analysed in order to compare the performance of the soft X-ray beamline at the Australian Synchrotron, where these experiments were performed, and to identify the C functional groups. We hypothesised that the proportion of carboxylic carbon will increase on biochar after ageing in soils, and the increasing incubation temperature will further increase the development of carboxylic functional groups.

2. Materials and methods

2.1. Biochar and reference samples

The aged biochars were obtained by incubating two biochars, produced from a woody biomass of 2 year old Sydney blue gum (*Eucalyptus salinga* Sm.) by slow pyrolysis at 450 °C (B450) and 550 °C (B550), with four contrasting soils from Australia at 70% of the maximum water holding capacity and at three temperatures, i.e. 20 °C, 40 °C and 60 °C, for up to two years. High temperatures in the incubation experiment were used to increase the mineralisation of biochar C in soils. The light fractions were isolated using a density separation procedure after dispersing the control soils and soil–biochar mixtures in sodium polytungstate solution, 1.8 g/cm (Golchin et al., 1994). The four soils are referred to as NSW (an Oxisol), WA (an Inceptisol), Qld (a Vertisol) and SA (an Entisol) soil in the manuscript; the description of the experimental soils, two biochars and the incubation experiments are given elsewhere (Fang et al., 2014a,b). The light fractions were isolated from the four soils immediately after mixing (day 0) and after ageing for 1 yr and 2 yr at 20 °C, 40 °C and 60 °C. The recovery of the biochars in the light fraction of soil–biochar mixtures was generally good (average > 80%) for the WA, Qld and NSW soils. However, in the SA soil the recovery was very poor (average = 28%); the presence of calcite might have contributed to the poor recovery of biochar from the soil. The isolated light fraction was washed thoroughly with deionized water and dried at 70 °C before analysis.

Ground samples were used for the NEXAFS analysis. The XPS analysis was done only for the light fraction isolated from the WA soil with and without the addition of the B450. The samples were analysed in a powdered form (similar to NEXAFS) and additionally hand-picked biochar particles were analysed to observe the surfaces (~10 nm) of biochar and native SOC particles.

Fifteen reference compounds (as listed in Supplementary Table 1) of C (analytical grade reagents), sourced from the Agricultural Chemistry Laboratory at the University of Sydney, were included in the C-1s NEXAFS analysis.

2.2. Near edge X-ray absorption fine structure spectroscopy

Carbon 1s-NEXAFS spectra were obtained at the soft X-ray spectroscopy beamline of the Australian Synchrotron in Melbourne (Cowie et al., 2010). The beam was operational in top-up mode at the time of analysis and the storage ring beam current ranged between 150 and 200 mA. The soft X-ray beamline is equipped with a plane grating monochromator that is capable of providing between 10^{11} and 10^{12} photons/s at 200 mA at the K-edge of the required element with a resolving power better than 10^4. The photon energy for C 1s-NEXAFS was calibrated using photoemission of the gold 4f7/2 peak at 83.96 eV that was obtained from a reference foil available on the standard manipulator.

Ground samples of the reference organic compounds, original biochars and isolated light fractions of soil and soil–biochar mixtures were mounted on to the sample disc using a double sided adhesive C tape. We compared a few spectra obtained for samples mounted on the C tape and indium foil and did not find any C signal from the tape in the samples mounted on the C tape. The samples were loaded into a vacuum chamber (2×10^{-10} mbar) for the analysis. C-1s K-edge spectra were obtained in the 275–315 eV range using a step size of 0.1 eV and the dwell time of 0.5 s. The spot size of the beam under the operating conditions was approximately 0.75×0.50 mm. Beam damage was judged to be negligible as no deterioration in the signal was observed in repeated measurements (up to five) at the same spot with the dwell time of 0.5 s.

The C-Is NEXAFS signal was simultaneously recorded in fluorescence yield (FLY), total electron yield (TEY) and auger electron yield (AEY) modes, however, only the AEY data are presented here. The AEY signal was recorded using a SPECS Phoibos 150 Hemispherical Analyser, set to a kinetic energy of 230 eV, positioned at an angle of 45° with respect to the beam. Spectra were normalised using I_0 reference gold foil prior to peak assignments and peak fitting (Fig. S1). The reference gold foil spectra were previously normalised using an argon sputtered clean gold surface; and raw AEY and I_0 data were also corrected for the dark current