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Oxidation of black carbon by biotic and abiotic processes

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Abstract

The objectives of this study were to assess the relative importance of either biotic or abiotic oxidation of biomass-derived black carbon (BC) and to characterize the surface properties and charge characteristics of oxidized BC. We incubated BC and BC–soil mixtures at two temperatures (30 °C and 70 °C), with and without microbial inoculation, nutrient addition, or manure amendment for four months. Abiotic processes were more important for oxidation of BC than biotic processes during this short-term incubation, as inoculation with microorganisms at 30 °C did not change any of the measured indicators of surface oxidation. Black C incubated at both 30 °C and 70 °C without microbial activity showed a decrease in pH (in water) from 5.4 to 5.2 and 3.4, as well as an increase in cation exchange capacity (CEC at pH 7) by 53% and 538% and in oxygen (O) content by 4% and 38%, respectively. Boehm titration and Fourier-transform infrared (FT-IR) spectroscopy suggested that formation of carboxylic functional groups was the reason for the enhanced CEC during oxidation. Analysis of surface properties of BC using X-ray photoelectron spectroscopy (XPS) indicated that the oxidation of BC particles was initiated on the surface. Incubation at 30 °C only enhanced oxidation on particle surfaces, while oxidation during incubation at 70 °C penetrated into the interior of particles. Such short-term oxidation of BC has significance for the stability of BC in soils as well as for its effects on soil fertility and biogeochemistry.
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1. Introduction

Annual production of biomass-derived black carbon (BC in this contribution) by vegetation burning is significant and is estimated to be 50–270 Tg C year^{-1} (Kuhlbusch and Crutzen, 1995). Compared to non-BC, BC produced during forest fires or for bio-char production has lower biological availability in soils, but actual determined rates of mineralization are still scarce (Bird et al., 1999; Baldock and Smernik, 2002). Due to the resulting long residence time, BC is an important stable C pool in soils and sediments (Schmidt and Noack, 2000). Although BC is often considered to be biological "inert", it is clear that it is oxidized and finally mineralized to CO_2 over long periods of time (Goldberg, 1985).

High-temperature aerobic oxidation (Morterra et al., 1984; Toles et al., 1999) reactions with strong chemical oxidants (Moreno-Castilla et al., 2000), or ozone oxidation (Sergides et al., 1987; Kawamoto

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et al., 2005) have shown that BC can be abiotically oxidized over short periods of time. However, short-term oxidation under ambient temperature and atmosphere has not yet been recognized and sufficiently quantified, and the extent of both abiotic and biotic oxidation is unclear. Some research has indicated that oxidation may occur through abiotic chemisorption of oxygen (O) by aging processes (Puri, 1963, 1970; Billinge and Evans, 1984; Adams et al., 1988). On the other hand, microbial oxidation may also play a role in short-term oxidation of BC, but few results that have investigated controls on its decomposition in incubation studies (Shneour, 1966; Baldock and Smernik, 2002; Hamer et al., 2004) or in the soil environment (Shindo, 1991; Petsch et al., 2001) are available. In general, such oxidation processes can lead to an oxygenated surface on BC (Boehm, 1994), forming carboxylic, phenolic, hydroxyl, carbonyl, or quinone C forms, and change the amphoteric characteristics (Lau et al., 1986).

As BC in soil is present as particles, albeit of very small size of mostly below <53 μm (Skjemstad et al., 1996), oxidation may first begin on particle surfaces (Lehmann et al., 2005). Oxidation of such particles may lead not only to mineralization of this highly stable form of organic C in soil, but may create negatively-charged surfaces, consequently leading to greater cation exchange capacity (CEC) and nutrient retention in soil (Glaser et al., 2002; Liang et al., 2006). The factors controlling this surface oxidation are important for the biogeochemistry of soil ecosystems, but have not been studied.

The objectives of this study were to quantify the relative importance of biotic or abiotic oxidation of BC and to characterize the surface properties of oxidized particulate BC. The hypotheses to be tested were: (1) oxidation is affected to a greater extent by biotic than by abiotic processes, and (2) oxidation is more pronounced on surfaces than in the interior of BC particles.

2. Materials and methods

2.1. Experimental

Biomass-derived BC was produced from black locust (*Robinia pseudoacacia* L.). The bark was removed from the air-dried logs and the wood was cut into pieces 3 cm by 2 cm. These were put into tin containers, which were loosely sealed with a lid and combusted in a muffle furnace at 350 °C for 16 h. The average recovery of BC was 33.2% by mass (SE 1.7; $N = 65$). It was then ground to pass a 2 mm sieve. To reduce the ash and tar contents, the particles were repeatedly leached with deionized water until the electric conductivity of the leachate (1:3 w/v) was below 50 μS dm^{-1}. Subsequently, the particles were dried at 60 °C for 24 h and stored in a desiccator.

The BC was incubated at two temperatures (30 °C and 70 °C), with and without microbial inoculation (mic; only for 30 °C), with and without inorganic nutrient addition (F), and with and without manure amendment (man). The experiments were conducted using only BC in comparison to a BC–soil mixture with 2 g BC and 50 g soil in 250 mL bottles. The microbial inoculum was a commercial product (BIOMEX OM-X, a pro-biotic soil restorer from Biomex Inc., Melbourne, Australia) to provide sufficient microbial activity during incubation. We pre-incubated the inoculum with water and then transferred the filtered cultures to the treatments receiving microbial inoculation. The fertilizer solution included: 4 mM NH_4NO_3, 4 mM $CaCl_2$, 2 mM KH_2PO_4, 1 mM K_2SO_4, 1 mM $MgSO_4$, 25 μM $MnSO_4$, 2 μM $ZnSO_4$, 0.5 μM $CuSO_4$ and 0.5 μM Na_2MoO_4, of which 2 mL were added to each incubation jar. The manure was obtained from a local dairy farm and 2 g were added. All bottles with the materials to be incubated were sterilized using γ irradiation before microbial inoculation in order to avoid an experimental artifact through irradiation. The soil was a subsoil horizon taken from an Anionic Acrustox from the Brazilian Cerrado savanna (Martinez et al., 2001). The BC and BC–soil mixtures were kept at 50% water holding capacity and were incubated for 4 months using a randomized complete block design with 4 replicates.

2.2. Chemical analysis

The pH in water and 1 N KCl solution was measured at 1:20 (w/v) ratio for BC samples and 1:2.5 (w/v) ratio for BC–soil mixtures after occasionally stirring over 1 h. The exchangeable acidity was analyzed with 1 N KCl extraction for 1 h and titrated with 0.005 and 0.025 N NaOH solution for BC and BC–soil mixtures, respectively. The exchangeable Al was determined in the KCl extract by adding 1 N KF to react with the Al and Al-hydroxides and then back titrating with 0.01 N HCl solution. The potential CEC was measured by saturating the

exchange sites of 0.8 g BC or 2.5 g BC–soil mixtures with 40 mL 1 N ammonium acetate at pH 7 twice and by consecutively replacing the adsorbed ammonium ions by 2 N KCl. The ammonium was measured using a segmented flow analyzer (Technicon Auto Analyzer, Chauncey, CT, USA).

Analyses of C, hydrogen (H) and O and stable isotopes were done at the Stable Isotope Facility, University of California, Davis, CA. Carbon isotopes were measured for CO_2 using dry combustion analysis coupled to an on-line isotope ratio mass spectrometer (PDZ Europa ANCA and 20–20 mass spectrometer, Sercon Ltd., Crewe, UK). Hydrogen and O stable isotopes (δD and $\delta^{18}O$, respectively) were measured after sample conversion to H_2 and CO at 1400 °C over glassy C (Hekatech TCEA, Hekatech GmbH, Wegberg, Germany; and PDZ Europa 20–20 isotope ratio mass spectrometer, Sercon Ltd., Crewe, UK).

Boehm titration (Boehm, 1994) was used for quantifying various surface functional groups on BC particles. Boehm titration depends on the reaction of basic solutions having different pK_b values with functional groups having different pK_a values. A weak basic $NaHCO_3$ solution was used to neutralize strong acidic functional groups with pK_a values of less than 6.37, and a NaOH solution was used to neutralize all acidic functional groups with pK_a values of less than 15.74 (Laszlo et al., 2004). The amount of $NaHCO_3$ solution used for titration corresponds to the amount of carboxylic groups ($pK_a < 6.37$), whereas the titration with NaOH solution quantifies total acidic functional groups. The difference between neutralization of NaOH and $NaHCO_3$ was defined as phenolic and lactonic groups ($6.37 < pK_a < 15.74$). A sample weight of 0.3 g BC was suspended in 15 mL 0.1 N standard basic solution and shaken in a closed container for 30 h. The slurry was filtered with a Whatman No. 42 filter paper to remove BC particles. An aliquot of 5 mL was transferred to a 10-mL 0.1 N HCl solution that neutralized the unreacted base and prevented further reaction between atmospheric CO_2 and the bases. The solution was back-titrated with 0.1 N NaOH. The base uptake by BC was converted to the content of surface functional groups (mmole g^{-1}). The determination of surface functional groups by the Boehm titration is affected by the presence of metal oxides or other organic matter (Boehm, 1966) and titrations were therefore only performed on BC particles and not on BC–soil mixtures.

2.3. FT-IR

FT-IR absorbance spectra were recorded between 400 and 4000 cm^{-1} with a Matteson Model 5020 FT-IR Spectrometer. KBr pellets were prepared containing 0.3% wt of finely ground BC powder from both the BC and BC–soil mixtures as well as the control soil without BC amendment. One hundred scans were averaged with a resolution of 4 cm^{-1} by subtracting values obtained for pure KBr pellets.

2.4. Solid-state nuclear magnetic resonance spectroscopy (NMR)

Solid-state ^{13}C nuclear magnetic resonance (NMR) spectra were conducted at the Wiley environmental molecular sciences laboratory (EMSL) using an Infinity CMX 300-MHz spectrometer (Varian Inc., Palo Alto, CA, USA). Variable amplitude cross-polarization (vacp) magic angle spinning (MAS) experiments were run using a 7.5 mm MAS HX Chemagnetics probe. The sleeves of the pencil design rotors were made from zirconia and used Kel-F drive tips and low carbon background spacers. The experiments were run using a speed of 7 kHz, the contact time was 0.5 ms and the delay time was 3 s. Carbon chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. Approximately 4000 transients were recorded for each sample.

2.5. X-ray photoelectron spectroscopy (XPS)

Surface analysis of the BC particles was conducted using XPS. The XPS measurements can probe a maximum sampling depth of approximately 10 nm and therefore provide information about surface properties. XPS measurements were conducted at the Wiley Environmental Molecular Sciences Laboratory using a physical electronics quantum 2000 scanning ESCA Microprobe (Physical Electronics GmbH, Ismaning, Germany, a division of ULVAC PHI), which used a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The 98-W, 107-μm diameter X-rays had a rastered pattern over a 1.4 by 0.2 mm rectangle on the sample. Survey scan spectra in the 1000–0 eV binding energy range were recorded with a pass energy of 117.4 eV. High-energy resolution scan spectra of C1s and O1s were recorded in 0.2 eV steps with a pass energy of 46.95 eV. Low energy electrons and Ar ions were

conducted for specimen neutralization in each measurement.

Unaltered BC particles were measured in comparison with finely-ground BC powder. The spectra from the BC particles were assumed to represent the properties of the real surface of the particles, whereas the spectra of the finely-ground powder were assumed to be representative of the bulk BC sample, including both exterior and interior properties. Samples were mounted on to stainless steal sample holders and were gently pressed on to adhesive tape using a propanol-washed spatula. The samples were verified to cover the entire tape by stereomicroscopy.

A non-linear least squares curve fitting program (XPSPEAK Version 4.1 software, programmed by R. Kwok, Chinese University of Hong Kong) with a Gaussian–Lorentzian mix function and Shirley background subtraction was used to deconvolute the XPS spectra. The C1s binding energy of graphitic or aromatic C and hydrocarbon was assigned at 284.6 eV. The shifts of the C1s binding energy were defined for 1.6 eV as C–O, for 3.0 eV as C=O, and for 4.5 eV as COO (Proctor and Sherwood, 1982). The deconvolution of O1s was done by separating O with a double C bond (O=C) with a binding energy at 531.3 eV, and O with a single C bond (such as hydroxyl or ester in O–C or O–H bonds) with a binding energy at 533.1 eV. The deconvolution of C1s and O1s spectra in BC particles or finely ground powder was set to the same FWTH values and Gaussian–Lorentzian ratios.

2.6. Statistical analysis

Data were analyzed using SAS Version 8 (SAS Institute Inc., Cary, NC, USA). Separation of the means was performed using Duncan differences calculated with the ANOVA procedure.

3. Results

3.1. Chemical properties

The pH values of the BC before incubation were 5.3 and 4.0 in water and KCl solution, respectively, exchangeable acidity was 52 mmole kg^{-1} and the potential CEC (P-CEC) was 140 mmole kg^{-1} (Table 1). These values for P-CEC were significantly higher than those of the soil (25 mmole kg^{-1}). After the 4-month incubation, P-CEC of BC significantly increased with all additions at both temperatures. Consequently, P-CEC of soil significantly increased by 90% after addition of BC (Table 1). The presence of microbial activity did not further increase P-CEC, while additions of manure led to an additional 64% and 39% increase compared to the BC and BC–soil mixtures, respectively, without further applications. Nutrient addition (+F in Table 1) did not improve P-CEC in any combinations. The largest increase in P-CEC was observed when BC and BC–soil mixtures were incubated at 70 °C (by 538% and 285%, respectively), while P-CEC of the soil alone did not increase.

The pH in water was greater in BC than in soil, while the pH in KCl was lower in BC than in soil (Table 1). In contrast to P-CEC, the pH of BC particles slightly decreased after the incubation at 30 °C. Manure addition significantly increased pH, whereas nutrient addition did not induce any change in pH. Incubation at 70 °C of BC and BC–soil mixtures significantly decreased the pH and pH in KCl of BC alone dropped to a very low value of 2.3.

The changes in exchangeable acidity reflected the trends seen for the pH in BC, but the absolute values were much higher in BC compared to soil (52 versus 3.6 mmole kg^{-1}, respectively). In BC–soil mixtures, the changes in acidity were more pronounced than for BC alone. Both exchangeable acidity and Al of soil alone doubled after incubation at 70 °C, whereas exchangeable Al was entirely absent from BC. When BC was incubated with soil at 70 °C, the exchangeable Al significantly increased by 75% over unamended soil. Manure addition did not significantly decrease exchangeable Al in soil–BC mixtures incubated at 70 °C, whereas exchangeable Al was absent when the mixtures were incubated at 30 °C.

3.2. Elemental and isotopic composition

Incubation at 30 °C both with and without the presence of microorganisms did not affect C and O contents of BC particles (Table 2). Manure addition decreased the C and increased the O concentrations. The BC incubated at 70 °C had the lowest C and the highest O content among all treatments. The H/C atomic ratio did not show much difference, while the O/C atomic ratio increased through incubation at 70 °C from 0.19 to 0.29.

The incubation did not change the δ^{13}C value, except for the BC to which manure was added. However, incubation led to an increase in the δD value and a decrease in the δ^{18}O value. In general,

Table 1
The chemical properties of BC and BC–soil mixtures under different incubation treatments

Treatment	pH in Water	pH in 1N KCl	Ex-acidity (mmole kg^{-1})	Ex-Al[a] (mmole kg^{-1})	P-CEC[b] (mmole kg^{-1})
Black carbon					
Original BC[c]	5.35c ± 0.03[d]	4.00c ± 0.02	52e ± 5	n.d.[e]	140f ± 10
30 °C C	5.22cd ± 0.07	3.70d ± 0.11	54e ± 3	n.d.	214e ± 14
C + F	5.12d ± 0.02	3.74d ± 0.06	47e ± 4	n.d.	224e ± 8
C + Mic	5.21d ± 0.01	3.78d ± 0.01	52e ± 1	n.d.	186e ± 10
C + Man	6.88a ± 0.07	6.61a ± 0.12	90d ± 4	n.d.	350d ± 40
C + F + Mic	5.19d ± 0.10	3.80d ± 0.04	50e ± 2	n.d.	206e ± 11
C + Mic + Man	6.71b ± 0.11	6.62a ± 0.11	90d ± 17	n.d.	356d ± 24
C + F + Mic + Man	6.93a ± 0.11	6.73a ± 0.08	85d ± 4	n.d.	383d ± 30
70 °C C	3.41f ± 0.06	2.25f ± 0.03	202b ± 5	n.d.	893a ± 66
C + F	3.46f ± 0.05	2.41e ± 0.05	170c ± 2	n.d.	759b ± 116
C + Man	4.85e ± 0.09	4.34b ± 0.12	243a ± 31	n.d.	601c ± 64
Black carbon and soil mixtures					
30 °C Soil	4.33fg ± 0.07	4.12f ± 0.01	3.6d ± 0.1	1.9c ± 0.1	25.0e ± 4.2
Soil + C[c]	4.48ef ± 0.04	4.13f ± 0.01	3.9d ± 0.3	1.5cd ± 0.2	47.4d ± 3.6
Soil + C + F	4.48ef ± 0.06	4.21e ± 0.03	2.9de ± 0.8	1.1de ± 0.2	46.1d ± 5.7
Soil + C + Mic	4.83d ± 0.09	4.37d ± 0.02	2.2e ± 0.1	0.7e ± 0.1	44.5d ± 4.4
Soil + C + Man	6.3c ± 0.032	5.59c ± 0.08	0.8f ± 0.1	n.d.	65.9c ± 7.6
Soil + C + F + Mic	4.61e ± 0.08	4.27e ± 0.04	2.2e ± 0.3	1.1de ± 0.4	42.6d ± 2.7
Soil + C + Mic + Man	6.71a ± 0.02	6.15a ± 0.02	0.6f ± 0.1	n.d.	61.3c ± 5.9
Soil + C + F + Mic + Man	6.50b ± 0.05	5.85b ± 0.10	0.5f ± 0.3	n.d.	62.2c ± 3.7
70 °C Soil	4.14h ± 0.01	3.94g ± 0.02	7.2c ± 0.3	4.0b ± 0.1	22.8e ± 1.4
Soil + C	4.17h ± 0.03	3.68h ± 0.04	19.1a ± 1.8	7.0a ± 0.4	87.8a ± 11.2b
Soil + C + F	4.17hg ± 0.08	3.58i ± 0.07	14.5b ± 1.8	6.1a ± 0.7	92.4a ± 5.8
Soil + C + Man	4.59e ± 0.03	4.12f ± 0.05	14.1b ± 0.8	6.7a ± 0.9	79.8b ± 7.3

Values in one column inside either BC or BC–soil mixture groups followed by the same letter are not significantly different at $P < 0.05$.
[a] Ex-Al: exchangeable aluminum.
[b] P-CEC: potential CEC.
[c] BC sample before incubation.
[d] Means ± standard deviation.
[e] n.d.: not detected.

the changes were more pronounced with a higher incubation temperature and were found to be less for δD than for $\delta^{18}O$. Microbial activity did not change the H and O stable isotopic composition.

3.3. Boehm titration

Boehm titration showed that incubation of BC at 30 °C did not significantly change surface functional groups compared to original BC, except for the carboxylic functional groups when incubated with

microbial activity (C30 mic). The incubation at 70 °C significantly increased acidic functional groups. The amount of carboxylic groups increased to a greater extent than phenolic and lactonic groups as a proportion of the amount in the original BC.

3.4. FT-IR analysis

The most prominent absorptions for BC included O–H bonds at 3400 cm^{-1} (Fig. 1; Table 4), aliphatic

Table 2
Elemental composition and stable isotope values of BC under different incubation treatments and the atomic H/C and O/C ratio based on elemental analysis (means ± standard deviation or pooled samples from $N = 4$)

	C (%)	$\delta^{13}C$ (‰)	H (%)	δD (‰)	O (%)	$\delta^{18}O$ (‰)	H/C	O/C
Original BC	74.3a ± 0.2	−24.9b ± 0.0	1.9	−110.7	19.2	20.3	0.30	0.19
C30	74.1a ± 1.5	−24.9b ± 0.0	2.1	−93.6	19.9	18.5	0.33	0.20
C30 mic	75.7a ± 1.4	−25.0b ± 0.0	2.0	−89.3	19.3	18.5	0.32	0.19
C30 man	65.1c ± 1.2	−21.9a ± 0.1	2.5	−84.7	25.2	18.1	0.47	0.29
C70	67.7b ± 1.3	−24.9b ± 0.1	1.9	−82.0	26.3	12.6	0.33	0.29
C70 F	70.8b ± 1.8	−24.9b ± 0.0	1.7	−71.4	23.5	14.1	0.28	0.25

C–H bonds at 2750–2950 cm^{-1}, carboxylic (COOH) bonds at 1700 cm^{-1}, aromatic bonds (C=C) at 1600 cm^{-1} and C–O bonds at 1260 cm^{-1}. Minor bands could also be noticed for some spectra, such as polysaccharide C–O bonds at 1035 cm^{-1} (Fig. 1a) when manure was applied (C30 man). In the BC isolated from BC–soil mixtures or the soil samples (Fig. 1b), additional O–H stretching of kaolinite at 3700–3800 cm^{-1} and Si–O vibrations at 1040 cm^{-1} could be observed.

None of the BC incubated at 30 °C (C30, C30 mic, C30 man) was different from the original BC (Original BC) with respect to spectral intensities of O–H bonds, carboxylic bonds, and C=C bonds (Fig. 1). Microbial inoculation and manure application additionally showed greater intensity for aliphatic C–H bonds and a wider C=C peak. The latter is likely a result of the contribution of other aromatic structures with greater asymmetry than for BC. Manure addition also led to a distinct poly-saccharide C–O absorbance at 1035 cm^{-1}. The most pronounced changes were observed after incubation of BC at 70 °C, which led to greater intensity for carboxylic bonds (1700 cm^{-1}), aromatic C–O bonds (1260 cm^{-1}), and a slightly lower intensity for aliphatic C–H bonds (2750–2950 cm^{-1}) and slightly increasing aromatic C–H (3050 cm^{-1}). The BC isolated from the BC–soil mixture at 70 °C (Fig. 1b) showed similar trends in shifts compared to the BC incubated alone. However, the magnitude of carboxylation was greater when BC was incubated alone and not together with soil as indicated by the 2–10% greater ratio of peak heights for carboxylic-to-aromatic C absorptions (1700 versus 1600 cm^{-1}).

3.5. NMR spectroscopy

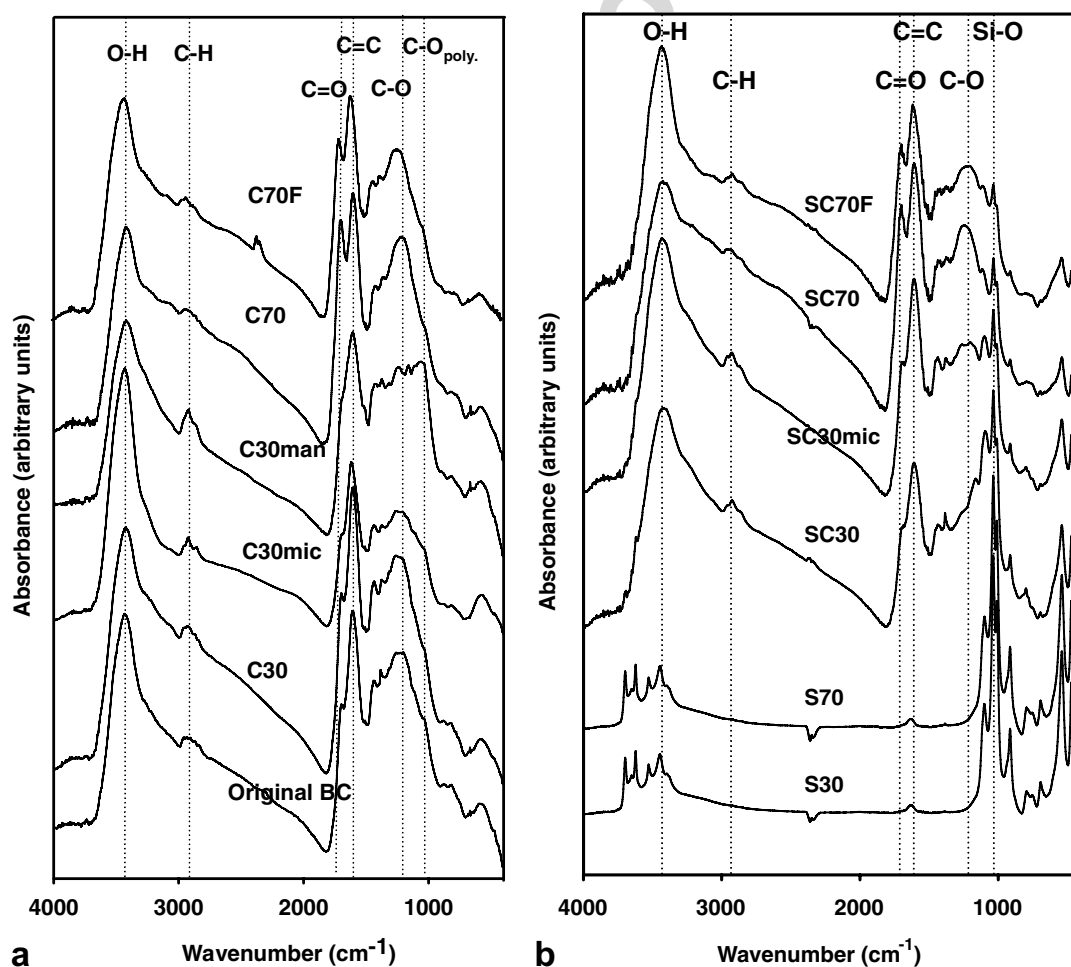Carbon forms in the original BC were dominated by aryl and O-aryl C at 90–160 ppm, with lower

Fig. 1. FT-IR spectra of BC (a) and BC–soil mixtures (b) incubated at 30 and 70 °C, with (mic) and without microbial activity, and

Table 3
Surface functional groups determined by Boehm titration

	Carboxylic groups (mmole g^{-1})	Phenolic and Lactonic groups (mmole g^{-1})	Total acidic functional groups (mmole g^{-1})
Original BC	0.16d ± 0.02	1.66b ± 0.19	1.82b ± 0.19
C30	0.21d ± 0.02	1.69b ± 0.18	1.90b ± 0.19
C30 F	0.29cd ± 0.03	1.58b ± 0.07	1.87b ± 0.07
C30 mic	0.34c ± 0.08	1.71b ± 0.26	2.06b ± 0.19
C70	0.89a ± 0.10	2.70a ± 0.34	3.59a ± 0.29
C70 F	0.73b ± 0.10	2.83a ± 0.10	3.56a ± 0.03

Values in one column followed by the same letter are not significantly different at $P < 0.05$ (means ± standard deviation).

Table 4
Major band assignments for FT-IR spectra of BC (van der Marel and Beutelspacher, 1976; Morterra et al., 1984; Guo and Bustin, 1998)

Wavenumber (cm^{-1})	Band assignments
3700–3800	Stretching of OH vibration of kaolinite
3400	Stretching of OH vibration
3050	Stretching of aromatic C–H
2750–2950	Stretching vibrations of aliphatic C–H.
1690–1710	Stretching mainly of carboxyl-C and traces of ketones and esters C=O
1595–1630	Stretching of aromatic C=C
1430–1440	Deformation of CH$_2$ and CH$_3$ bending
1370–1395	Deformation of aliphatic C–H (some C–O stretching of phenolic OH)
1255–1265	Stretching of aromatic C–O and phenolic OH
1040	Si–O vibrations
1035	Stretching of polysaccharide C–O

intensities of alkyl C at 0–50 ppm and only traces of carboxylic or ketone C at 160–200 ppm (Fig. 2). The decrease in alkyl C was the most prominent change during the incubation process. The amount of carboxylic C did not show a clear increase during incubation.

3.6. XPS analysis

The XPS wide-scan spectra showed the presence of two distinct peaks in C (C1s) at 284.6 eV and O (O1s) at 533 eV and two small peaks in N (N1s) at 400 eV and Ca (Ca2p) at 350 eV (high resolution spectra for C and O in Fig. 3; for N and Ca not shown). The bulk properties of BC (BC powder, Table 5) showed the same trend in elemental content of C and O as the results obtained from dry combustion (Table 2): a negligible increase in O and no decrease in C during incubation at 30 °C. However, incubation at 70 °C led to a pronounced increase in O and a correspondingly lower C concentration. The O/C ratio of original BC of the interior (being the bulk of what was assessed through analyzing BC powder, Table 5) was similar to the O/C ratio of the surface (BC particles, Table 5). During the incubation at 30 °C, however, the O/C ratio of BC surfaces increased by more than 20% of the value of the original BC. This was not
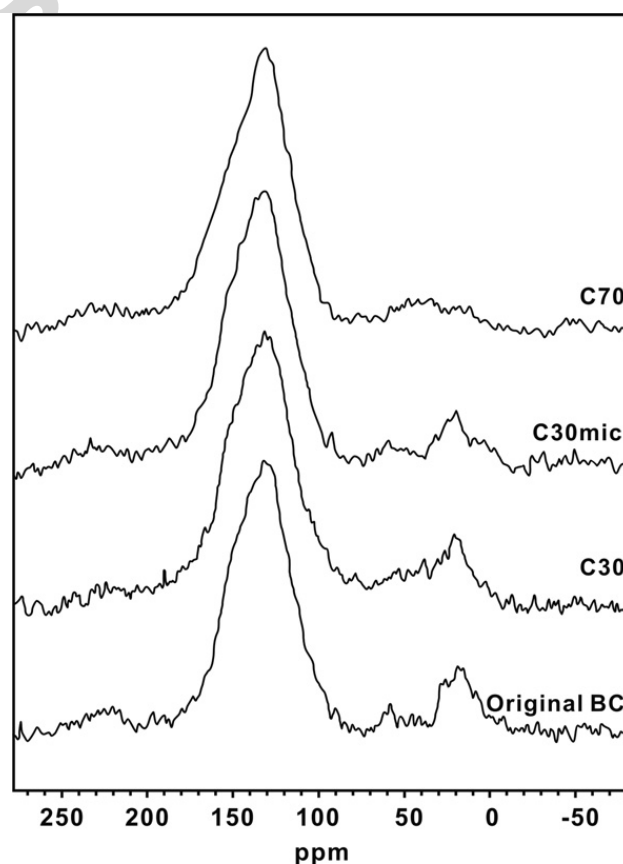

Fig. 2. NMR spectroscopy of BC incubated at 30 and 70 °C, with (mic) and without microbial activity in comparison to original BC.

observed for the bulk properties (BC powder, Table 5). If a temperature of 70 °C was used, the O/C ratios were identical both for the surface and the interior.

The spectra of high resolution XPS of C1s and O1s were used to quantify the C and O forms on surfaces (BC particles) and in the interior (BC powder) (Fig. 3, spectra were normalized on the basis of intensity). Incubation of BC at 70 °C yielded the most contrasting spectra compared to the other treatments, leading to higher intensity at C1s 289.1 eV and O1s 531.3 eV. Similar to the total elemental data obtained from XPS (Table 5), the high-resolution XPS did not show a difference in bulk properties of BC after incubation at 30 °C (Fig. 3; Table 6). BC incubated at 30 °C only enhanced the formation of oxidized C groups on surfaces. However, the incubation at 70 °C resulted in significant oxidation of both surfaces and bulk BC mainly through the formation of carboxylic C (BC particles, Table 6). As noted for all the other experiments in this study, the presence of microbial activity did also not change the degree of surface oxidation.

Table 5
Atomic elemental contents of C, N, O, and Ca and atomic O/C ratios measured from XPS widescan spectra of BC particles and finely ground powder (pooled samples from $N = 4$)

	C (%)	N (%)	O (%)	Ca (%)	O/C (%)
BC particles					
Original BC	82.9	0.7	16.3	0.1	0.20
C30	79.3	1.0	19.8	0.2	0.25
C30 mic	79.6	0.6	19.5	0.3	0.24
C70	78.2	0.5	21.2	0.2	0.27
BC powder					
Original BC	82.1	0.3	17.6	nil	0.21
C30	81.1	0.5	18.4	nil	0.23
C30 mic	82.2	0.4	17.4	nil	0.21
C70	78.3	0.3	21.4	nil	0.27

4. Discussion

4.1. Biotic and abiotic oxidation of BC

Abiotic oxidation was found to be more important for the creation of negative surface charge and CEC than biotic oxidation, which is in contrast to our initial hypothesis. The presence of microbial
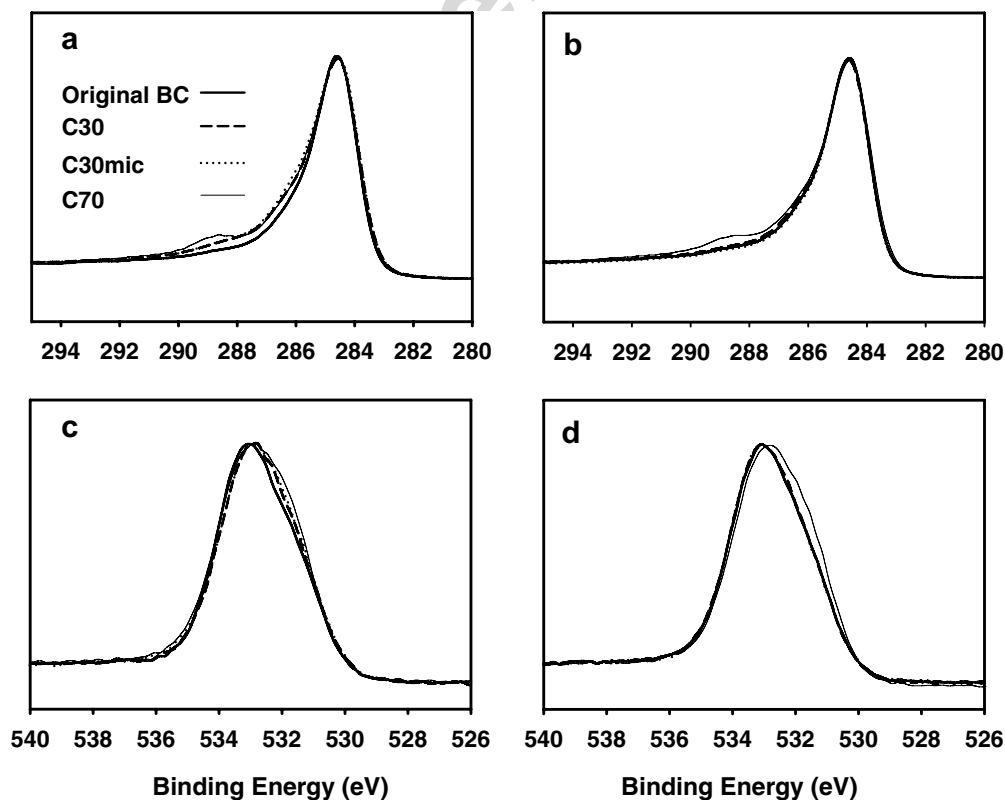

Fig. 3. XPS spectra of BC incubated at 30 and 70 °C, with (mic) and without microbial activity in comparison to original BC; C1s of BC particles (a) and powder (b) as well as O1s of BC particles (c) and powder (d).

Table 6
Chemical composition of carbon (C1s) and oxygen (O1s) from high-energy resolution XPS spectra of BC particles and finely ground powder

	C1s composition (%)				O1s composition (%)	
	C–C, C=C, or C–H	C–O	C=O	COO	O=C	OH–C or C–O–C
BC particles						
Original BC	73.5	15.2	4.4	6.9	22.6	77.4
C30	68.8	16.0	6.3	8.9	24.7	75.2
C30C mic	68.7	16.9	6.0	8.4	23.7	76.3
C70	65.9	16.3	5.2	12.6	26.7	73.3
BC powder						
Original BC	72.7	15.2	4.8	7.3	18.4	81.6
C30	71.4	15.2	5.2	8.2	17.2	82.8
C30 mic	72.8	15.2	4.6	7.4	18.0	82.0
C70	67.4	14.7	5.6	12.3	25.8	74.2

The binding energy of C1s at 284.6 eV was assigned to C–C, C=C, and C–H, at 286.2 eV to C–O, at 287.6 eV to C=O, and at 289.1 eV to COO. The binding energy of O1s at 531.3 eV was assigned to O=C and at 533.1 eV to O–C.

activity had no significant effects on oxidation of BC during the 120 day incubation period, although other studies have found significant biotic oxidation of coal or graphitic BC (Shneour, 1966; Willmann and Fakoussa, 1997; Machnikowska et al., 2002). It should be noted that the BC was washed before incubation to remove soluble salts and it is possible that most tar dissolved organic C was leached out during the cleaning process. However, the presence of microorganisms did also not increase P-CEC when labile C was added in the form of manure, suggesting that the lack of easily decomposable C or nutrients did not limit oxidation of BC. It cannot be excluded that the ability of other microbial populations could have been greater for decomposing the BC, since specialized microorganisms have been shown be effective in decomposing BC (Fakoussa and Hofrichter, 1999; Machnikowska et al., 2002).

Abiotic oxidation at high temperature may, to a certain extent, happen by chemisorption of O rather than by oxidation of reduced C forms (Morterra and Low, 1982), since $\delta^{18}O$ values decreased to a much larger extent than δD values. However, the significant increase in negative surface charge and the identification of carboxylic C with XPS and Boehm titration suggest that a large proportion of the oxygenation was actually oxidation of C. The oxidation of BC may be largely initiated by chemisorption of O at unsaturated ring sites and lead to a subsequent formation of carboxylic groups (Puri and Sharma, 1968). These reactions or aging processes of BC have been found to accelerate at higher temperature (Rideal and Wright, 1925; Bradbury and Shafizadeh, 1980; Teng and Hsieh, 1999; Chughtai et al., 2003), indicating that

the reaction between soot and ozone increased three times with an increase in temperature from −35 to +23 °C. In addition to oxidation of the BC particles themselves, adsorption of non-BC may also increase the number of oxidized groups on BC surfaces that can create CEC (Lehmann et al., 2005). This may be the case with manure addition, as the P-CEC of BC particles (Table 1) increased much more by incubation with than without manure additions. A pronounced increase in the adsorption of ammonium was also observed by coating BC particles with manure extract (Lehmann et al., 2002). A similar process may be observable in soil even without manure addition, as the P-CEC increased comparatively more in the BC–soil mixture (Table 1) than when incubated alone (Table 1), considering that the BC–soil mixture only contained about 4% BC. This is in contrast to the finding from FT-IR analysis showing that oxidation of BC was lower for soil mixtures than when incubated alone. A possible explanation may be the difference between the analysis achieved by FT-IR that captures oxidation of the entire particle in comparison to determining CEC which only captures surface properties.

4.2. Surface oxidation of BC

Oxidation of BC was initiated on the surface of particles and analysis of the oxidation of entire particles completely masked this important process. The difference between the XPS analysis of BC particles and powder exemplifies the surface-oriented nature of initial BC oxidation. The XPS analysis of particles only captures the surface properties of

the BC due to the low penetration depth of the X-ray to about 10 nm, whereas the same XPS analysis of ground particles quantifies their bulk properties. At higher temperature, the interior of BC particles was also oxidized, as demonstrated by FT-IR and XPS analyses. NMR spectra did not show much change in O-aryl or carboxylic C even at a high temperature. The lack of a clear increase in acid functional groups using Boehm titration in comparison to the significant increase in P-CEC and pH values may be explained by the lower contact time during the measurements of CEC and pH, which may therefore have preferentially captured surface properties.

Abiotic oxidative processes appeared to at first cause oxidation of BC surfaces. Longer exposure in soil may then gradually lead to an oxidation of the interior of BC particles. The oxidation of BC surfaces progressed from phenolic groups to a proportionally very large increase in carboxylic groups (Table 3); therefore, surface oxidation continued to increase with time. However, Lehmann et al. (2005) still observed the greatest oxidation of BC particles close to the surface even of BC with several hundred years of exposure in soil using near-edge X-ray spectroscopy.

The concentrations of carboxylic functional groups determined by Boehm titration (Table 3) were similar to the values of the P-CEC (Table 1) and it is possible that the adsorption of base cations is mainly controlled by the negative charge of carboxylic groups in BC. Pittman et al. (1999) reported similar observations using Ag ion adsorption on activated C and they suggested that carboxyl and phenolic groups (at pH 10) were the main adsorption sites.

4.3. Environmental significance

These results have significance for the stability of BC in soil as well as the effects of BC on soil fertility. Firstly, the disappearance of the aliphatic C observed using NMR and FT-IR, especially for BC samples incubated at 70 °C, indicates that aliphatic C compounds are more labile than aromatic C. Mawhinney and Yates (2001) also observed decomposition of aliphatic C in BC by ozone. Sergides et al. (1987) proposed an oxidation model of soot particles by ozone and indicated that stripping of aliphatic chains is the first stage of ozonation. The oxidation catalyst for soot also showed a removal of the aliphatic species from particles, and not from their graphitic part (Albers et al., 2000). This process was also observed for microbial oxidation (Willmann and Fakoussa, 1997), which was not observed in our study. Therefore, it is likely that the aliphatic C in our experiment was abiotically oxidized to CO_2, as suggested by other studies (Sergides et al., 1987; Cody and Alexander, 2005).

Secondly, the increasing acidic functional groups could increase the hydrophilicity of BC and enhance further physical, chemical, and biological weathering, such as breaking and reducing its particle size, leaching to deeper soil horizons, and dissolution or export from the soil profile (Bird et al., 1999). It is also possible that microbial oxidation would be facilitated by this initially significant abiotic oxidation due to the increase in hydrophilicity. For a long-term perspective on BC stability, a significant oxidation by microbes can therefore not be excluded.

The surface oxidation also increased CEC, which typically enhances soil fertility through greater nutrient availability as nutrients are retained in the soil against leaching. Sombroek et al. (1993) and Glaser et al. (2001) hypothesized that oxidation of BC leads to a high CEC being responsible for the high soil fertility found in BC-rich soils. The surprisingly rapid formation of CEC after only 4 months of incubation, even without microbial activity, may be important for the utilization of BC as a soil amendment for improving the fertility of highly weathered soils (Lehmann and Rondon, 2006).

At the same time as CEC increased, the pH decreased and Al saturation increased, which is a result of the oxidation and production of acidic functional groups. The magnitude of this change in soil pH by BC may largely depend on the amount of base cations contained in the BC, which can vary significantly (Tryon, 1948), as well as the production temperature of BC (Mattson and Mark, 1971). Although our data showed that soil fertility may be negatively affected by BC oxidation through a pH decrease or an increase in exchangeable Al, the net effect of BC oxidation on pH in soil may be different owing to the interaction with other organic and mineral soil materials, such as with ash or other base cations present in soil. In addition to an increase in adsorption through formation of CEC, a change of adsorption ability of both hydrophobic and hydrophilic organic pollutants through the described aging processes of BC could also be expected (Yang and Sheng, 2003) and warrants further research.

5. Conclusions

Abiotic processes were more important than biotic processes for the initial oxidation of fresh BC. This significant and rapid oxidation may have important implications for the stability of BC since further microbial decomposition may be less constrained by the recalcitrance of aromatic ring structures typical of BC. At the same time, cation retention was significantly enhanced, which would improve soil fertility. This oxidation is sufficiently rapid to make an application of fresh BC to soil feasible in order to enhance crop productivity and decrease potential off-site pollution in agricultural landscapes. Longer term laboratory and field studies are needed to characterize and quantify further oxidation of BC to answer the question whether microbial decomposition of BC is facilitated by the initial abiotic oxidation.

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