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Long-term black carbon dynamics in cultivated soil

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Abstract Black carbon (BC) is a quantitatively important C pool in the global C cycle due to its relative recalcitrance compared with other C pools. However, mechanisms of BC oxidation and accompanying molecular changes are largely unknown. In this study, the long-term dynamics in quality and quantity of BC were investigated in cultivated soil using X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) and nuclear magnetic resonance (NMR) techniques. BC particles and changes in BC stocks were obtained from soil collected in fields that were cleared from forest by fire at 8 different times in the past (2, 3, 5, 20, 30, 50, 80 and 100 years before sampling) in western Kenya. BC contents rapidly decreased from 12.7 to 3.8 mg C g^{-1} soil during the first 30 years following deposition, after which they slowly decreased to a steady state at 3.5 mg C g^{-1} soil. BC-derived C losses from the top 0.1 m over 100 years were estimated at 6,000 kg C ha^{-1}. The initial rapid changes in BC stocks resulted in a mean residence time of only around 8.3 years, which was likely a function of both decomposition as well as transport processes. The molecular properties of BC changed more rapidly on surfaces than in the interior of BC particles and more rapidly during the first 30 years than during the following 70 years. The Oc/C ratios (Oc is O bound to C) and carbonyl groups (C=O) increased over the first 10 and 30 years by 133 and 192%, respectively, indicating oxidation was an important process controlling BC quality. Al, Si, polysaccharides, and to a lesser extent Fe were found on BC particle surfaces within the first few years after BC deposition to soil. The protection by physical and chemical stabilization was apparently sufficient to not only minimize decomposition below detection between 30 and 100 years after deposition, but also physical export by erosion and vertical transport below 0.1 m.

Keywords Biochar · Black carbon · Charcoal · FTIR · Long-term agriculture · XPS

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Introduction

Black carbon (BC) is a C-rich organic material derived from incomplete combustion of fossil fuels and vegetation and from weathering of graphitic C in rocks (Schmidt and Noack 2000; Koelmans et al. 2006). BC is most likely ubiquitous in terrestrial and aquatic ecosystems as well as in the atmosphere. It is comprised of a continuum of forms, ranging from slightly charred organic material to highly condensed, refractory soot (Masiello 2004). In this study the term BC is used to describe the residual product from incomplete combustion of biomass either by land clearing or natural forest fires.

It is well known that the global C cycle is closely connected to global climate change largely through anthropogenic emissions of carbon dioxide originating from fossil fuel use and land use change (IPCC 2007). An increase in temperature of about 0.8 K was related to increases in carbon dioxide concentrations of 77 ppmv in the last century (Bala et al. 2005). BC may influence global C cycles and climate directly and indirectly. Direct effects involve adsorption of solar radiation by soot aerosols (Jacobson 2001). The indirect effects are the removal of carbon dioxide from rapid biosphere–atmosphere gas exchange through the formation of BC during fires. It remains largely unknown to what extent BC decomposition contributes to carbon dioxide emissions from soils and how recalcitrant this temporary C sink is (Koelmans et al. 2006; Preston and Schmidt 2006).

One of the distinguishing properties of BC is its high stability in the environment relative to other types of organic C substances. It can persist up to 13,900 years in deep-sea environments (Masiello and Druffel 1998) and was found to have a mean residence time of 10,000 years in soils (Swift 2001). In comparison, typical turnover times of soil organic matter were 6–20 years in surface horizons (Torn et al. 2005) and those of fine litter were 1.3 years in natural tropical forests (Weerakkody and Parkinson 2006). Consequently, BC gradually accumulates in soils, relative to other organic substances, and thus becomes a quantitatively important portion of soil organic matter.

However, we also know that BC must eventually decompose as global production and stocks do not match if BC is assumed inert (Schmidt 2004; Schmidt and Noack 2000). Information about turnover times of BC is scarce and most data are available from decomposition experiments over a limited number of years (Preston and Schmidt 2006). Measured decay rates varied significantly between 0.26% and 0.78% C losses over the first 60 days of incubation, largely due to different BC properties (Hamer et al. 2004), and remained below 2% C loss for 120 days of incubation (Baldock and Smernik 2002). Extrapolation from laboratory experiments to natural environments is hampered by inadequate simulation of long-term dynamics (Lehmann 2007) and lack of consideration of all factors affecting BC disappearance such as soil fauna and flora, wetting and drying cycles and leaching. One of the few field experiments reported a disappearance of 47% of biomass-derived BC from savanna fires during 50 years (Bird et al. 1999). Similar to laboratory experiments, however, such field observations are relatively short-term studies compared to the estimated turnover time of up to 10,000 years (Swift 2001; Masiello and Druffel 1998). While some information is available about temporal dynamics of BC stocks in unmanaged ecosystems (Preston and Schmidt 2006), very few studies report results from agricultural soil (Skjemstad et al. 2001). Therefore, observations of BC dynamics in cultivated soil over several decades to centuries are needed to begin to quantify BC loss processes.

During exposure in soil, BC not only gradually disappears as it mineralizes to CO_2, leaches or erodes as dissolved and particulate organic C, but BC particles are also chemically altered due to surface oxidation and interactions with non-BC (Liang et al. 2006). Brodowski et al. (2005) found that the O/C ratios were higher near the surface than the interior of BC particles in a German Chernozem, suggesting that oxidation of BC had occurred, starting from the surface of the particles. Such surface oxidation can occur over short periods of time and is able to significantly increase cation exchange capacity of BC particles and soils rich in BC within a few months (Cheng et al. 2006). Whether surface oxidation is further increased beyond a period of months or whether interior regions of BC particles are oxidized to the same degree as surfaces over decadal and centennial time scales is not known.

This study investigates changes in BC residence time and quality in cultivated soil over a period of 100 years. We hypothesize that an initial rapid disappearance of BC is followed by lower losses and that surfaces of BC are oxidized rapidly during the first few years, whereas oxidation of entire BC particles is significantly slower.

Materials and methods

Study sites

Details of the experimental sites that are part of a larger study were reported by Solomon et al. (2007) and Kimetu et al. (2008). The study sites used in the present work were located in South Nandi (00°04′30″ N, 34°58′34″ E), western Kenya, with altitudes ranging from 1,600 to 1,800 m above sea level, mean annual temperature of about 19°C and mean annual precipitation of about 2,000 mm. Soils were classified as Humic Nitosols (FAO/UNESCO) or Typic Palehumults (USDA), which were extremely deep dark reddish brown soils with friable clay and thick humic topsoils with 45–49% clay, 15–25% silt, and 26–40% sand (Kimetu et al. 2008).

Soil collection and preparation

Slash and burn had been used at the experimental site to convert the native forest to cultivated soils during the past hundred years. Forest trees were cut and burned on site during conversion. After conversion, the soil was plowed to 0.1–0.12 m depth for maize (*Zea mays* L.) cultivation without fertilizer application. Although most of the biomass C was transformed to carbon dioxide during the biomass burning and rapidly released into the atmosphere, a small amount of C was charred and remained in soil as BC after conversion (Forbes et al. 2006). Burning was not practiced on fields following the initial conversion. Therefore, ages of BC correspond to the time since conversion from forest to agriculture, making use of different conversion ages to construct a time series or chronosequence of BC ages (Solomon et al. 2007; Kimetu et al. 2008). A subset of the soil samples from the southern Nandi forest series (Solomon et al. 2007) was selected for this study to examine the long-term BC dynamics.

Soil sampling and preparation were described in detail by Solomon et al. (2007). In brief, 18 soil samples were collected in 2003 from 18 farmer's fields differing in their conversion ages ranging from 2 to 100 years prior to sample collection, in comparison to forest soil in southern Nandi, Kenya. We selected fields within a 12-km^2 area with similar climate, geology and soil type. Nine 200-cm^3 core sub-samples from the upper 0.1 m of soil were sampled in each field and then combined into one composite soil sample. The samples were then air-dried, sieved (<2 mm) and stored for analysis. The 18 soil samples were pooled into 8 composite samples based on their conversion ages (100, 80, 50, 30, 20, 5, 3, and 2 years before sampling) corresponding to 8 ages of BC, in comparison to a forest soil (Table 1).

BC preparation

BC particles from these nine soil samples were separately hand-picked for FTIR and XPS analyses using super tweezers (N5, Dumont, Montignez, Switzerland) under a light microscope (303; SMZ-10, Nikon, Japan). BC particle sizes ranged from 5 to 90 µm. Two size classes of BC particles (<30 and >50 µm) were separated for FTIR scanning. In addition, a fresh BC sample, which was produced by natural combustion of the same native forest biomass, was also collected under field condition for

Table 1 Basic properties and information of the studied soils

Years since BC deposition	Carbon (%)	Nitrogen (%)	C/N	Bulk density (Mg m^{-3})
0	9.18	0.95	9.69	0.67
2	7.56	0.73	10.32	0.70
3	6.74	0.72	9.30	0.80
5	4.62	0.49	9.42	0.80
20	2.74	0.29	9.53	1.00
30	2.58	0.29	9.00	1.06
50	1.39	0.15	9.18	1.12
80	1.39	0.15	9.27	1.12
100	2.32	0.24	9.85	1.12

comparison. The fresh BC sample was measured by FTIR 4 weeks after production.

BC quantification

NMR analysis

BC concentrations of bulk soils were estimated from spectra of solid-state ^{13}C cross polarization-magic angle spinning nuclear magnetic resonance (^{13}C CP-MAS NMR) using the "molecular mixing model" developed by Nelson and Baldock (2005). In brief, this technique converts distributions of signal across chemical shift regions to distributions of biopolymers (carbohydrate, protein, lignin and aliphatic biopolymers) plus BC and pure carbonyl. In all cases a good fit was achieved, as demonstrated by a small "error" term of 1.1–4.3, as defined in Nelson and Baldock (2005).

Prior to NMR analysis, soil samples were treated with 2% HF acid, following the procedure proposed by Skjemstad et al. (1994). Solid-state ^{13}C CP NMR spectra were recorded at a frequency of 50.3 MHz on a Varian Unity 200 spectrometer (Varian Inc., Palo Alto, CA). Samples were packed in a 7-mm-diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5,000 ± 100 Hz in a Doty Scientific MAS probe.

Manual isolation

Approximately 5 g of each soil sample was weighed for hand-picking of BC particles using the same method described for BC preparation above. All soil BC particles, which were visualized under such light microscopy, were collected and then used for C analysis.

FTIR procedure

Fourier transformation infrared (FTIR) absorbance spectra were recorded on a Mattson Model 5020 FTIR Spectrometer (Madison, WI) at wave numbers from 400 to 4,000 cm^{-1}. KBr pellets were prepared containing 0.3 wt% of finely ground BC powder. One hundred scans were averaged with a resolution of 4 cm^{-1} by subtracting values obtained from pure KBr pellets. Carbon chemical functional groups were assigned to wave numbers from FTIR spectra following Solomon et al. (2007). Wave numbers were assigned as follows: 3,370 cm^{-1} to hydroxyl (O–H) groups of phenols with traces of amine (N–H), 2,920–2,853 cm^{-1} to aliphatic-C (CH_3 and CH_2), 1,700 cm^{-1} to carbonyl-C and ketonic-C (C=O), 1,642 cm^{-1} to aromatic-C (C=C) vibrations and to a smaller extent to C=O stretching in quinones and ketonic acids, 1,389 cm^{-1} to aliphatic deformation of CH_2 or CH_3 groups, and 1,036 cm^{-1} to C–O stretching vibrations of polysaccharides.

Each BC sample was analyzed in duplicate, and the results were averaged. Relative proportions (%) of C chemical species, such as O–H, C–H, C=O, C=C and C–O were obtained from corresponding spectrum intensities, which were measured by establishing individual base lines for each peak position. Using Omnic software, version 7.2 (Thermo Electron Corporation, 1992–2005) we located wavenumbers associated with detected peaks assigned to the C chemical species listed above after base line correction and normalization. Base lines were drawn as follows: 3,747–2,975 cm^{-1} for O–H, 2,991–2,769 cm^{-1} for C–H vibration at 2,920–2,853 cm^{-1}, 2,735–1,670 cm^{-1} for C=O, 1,733–500 cm^{-1} for C=O, 1,488–1,348 cm^{-1} for C–H vibration at 1,389 cm^{-1} and 1,315–946 cm^{-1} for C–O.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was used to characterize surfaces of BC particles in comparison to the properties of the interior of BC particles. Both intact BC particles for determining surface properties and finely ground powder for bulk properties of the same BC sample were analyzed by XPS. The maximum depth that XPS can probe is about 10 nm, allowing it to distinguish between surface and bulk properties using the analysis scheme described here. BC samples of both intact and ground powder were mounted onto Scotch brand double-sided tape and placed onto specifically designed samples holders for XPS analysis. Care was taken to mount a uniform and densely packed continuous layer of particles. The sample holder was then placed into the XPS vacuum introduction system and pumped to $<1 \times 10^{-6}$ Torr using a turbomolecular pumping system prior to introduction into the main ultra high vacuum system. The main vacuum system pressure is maintained at $<5 \times 10^{-9}$ Torr during analysis and pumped using a series of sputter ion pumps.

XPS measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe (Physical Electronics, Chanhassen, MN, USA, a division of ULVAC PHI). This system uses a focused monochromatic Al Kα X-ray (1486.7 eV) source and a spherical section analyzer. The instrument has a 16-element multichannel detector. The X-ray beam used was a 100 W, 100 μm diameter beam that was rastered over a 1.4 mm by 0.2 mm rectangle on the sample. The X-ray beam is incident normal to the sample and the photoelectron detector was at 45° off-normal. Wide scan data were collected using a pass energy of 117.4 eV. Narrow scan or high energy resolution spectra of C1s, O1s, Fe2p, Al2p and Si2p were collected using a pass energy of 46.95 eV.

Quantification of elemental proportions and C species from XPS spectra

XPS spectra were deconvoluted to separately identify C-bonded O species and different C forms. Deconvolution was accomplished with the non-linear least squares curve fitting program XPSPEAK Version 4.1. The procedure was described in detail by Cheng et al. (2006). C1s binding energy levels were assigned as follows: at 284.6 eV to C–C, C=C, and C–H bonds, at 286.2 eV to C–O, at 287.6 eV to C=O, and at 289.1 eV to COO. Oxygen bonded to C (Oc) was computed using the sum of all organic O species. Elemental contents are given as relative proportions of all five investigated elements (C, O, Si, Al, and Fe) and contents of C species were reported as relative proportions of all four deconvoluted C species.

Statistical analyses

Dynamics of BC stocks, C species obtained by FTIR and elemental proportion recorded by XPS as a function of time (years) after BC deposition, were calculated using a first order kinetic model with three parameters $f = Y_0 + ae^{-bt}$ and $f = Y_0 + a\left(1 - e^{-bt}\right)$, where f is the BC content at time t (year), Y_o is the BC content at time zero, a is a constant and b is a reaction rate constant, applied for decay and rise observations, respectively. Linear regression was conducted to test the correlation coefficients between BC stocks and elemental contents. Statistical analyses were done with Sigma Plot 8.0 and Microsoft Excel.

Results

Dynamics of BC stocks over 100 years of cultivation

BC entered these soils both from fires predating land conversion and from the burning that occurred when land was converted to agriculture. Irrespective of the origin of the BC, BC concentrations per unit soil mass decreased rapidly to 30% of their initial contents during the first 30 years as estimated by NMR, while by manual quantification, BC stocks decreased to 16% of their initial contents during the first 5 years (Fig. 1a, b). Corresponding BC stock losses per unit area were 60% and 89% of their initial stocks for NMR and manual quantification, respectively (Fig. 1e, f). The stocks were calculated based on BC contents and bulk density in the top 0.1 m layer. Beyond 30 years, BC stocks leveled off close to a steady state. BC losses after 100 years totaled about 6,000 kg C ha^{-1} to a depth of 0.1 m determined by NMR quantification. Macro BC particles, whose sizes, as defined here, were greater than 50 μm, were not observed beyond 30 years. The proportion of BC as a fraction of SOC showed a weak ($P > 0.05$) trend to increase over time since deposition (Fig. 1c, d).

BC properties by XPS investigation

Carbon and oxygen contents of isolated BC particles

Carbon contents, recorded for BC surfaces and for entire particles, decreased from 44.6% to 18.8% and from 51.1% to 34.2%, respectively, during the first 40 years since conversion (Fig. 2). In contrast, total O contents rapidly increased from 45.2% to 61.5% on BC surfaces and from 40.9% to 50.6% in entire particles during the same period of time. Surface properties of both C and O changed more rapidly than those of bulk properties. Beyond 40 years following conversion, C and O proportions of bulk properties continued to change, while those of surface properties leveled off at around 18.8% for C and 61.5% for O after the initially rapid change in the first 40 years.

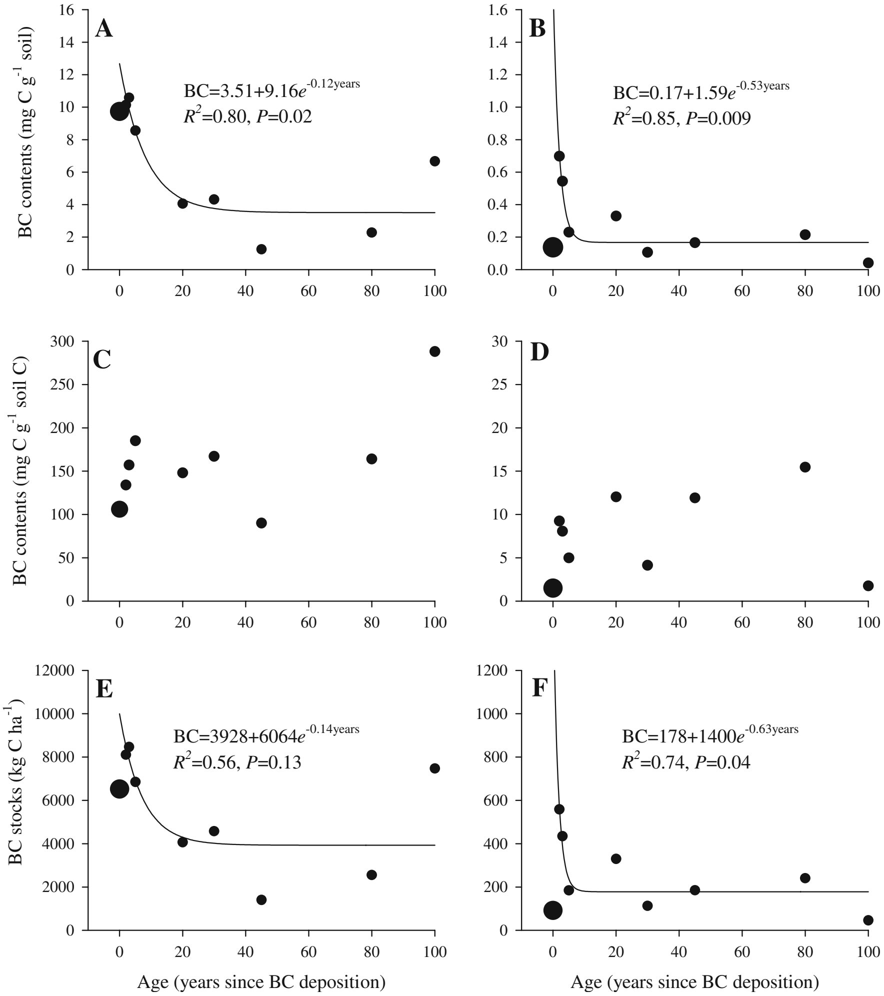

Fig. 1 Long-term dynamics of BC contents and stocks determined by NMR (**a**, **c**, **e**) and by manual (**b**, **d**, **f**) quantification over 100 years. The large circles denote BC contents of forest soil. First order kinetics were fitted, based on BC contents and stocks derived from eight cultivated soil samples. BC stocks were calculated for a soil depth of 0.1 m

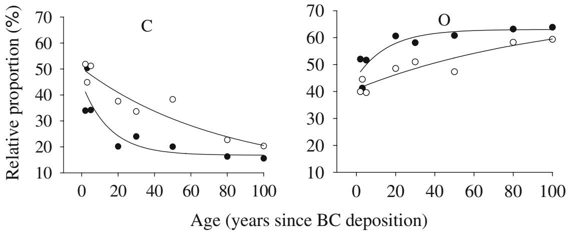

Fig. 2 Quantitative dynamics of O (including mineral and organic O) and C of BC surfaces and entire BC particles by XPS over 100 years in cultivated soil. Solid black circles are the observations of surfaces of BC particles, while open circles are observations of bulk properties of BC particles

Consequently, the largest difference between bulk and surface properties with respect to C and O contents was observed in the period of 20–40 years following conversion. In comparison, the elemental contents collected 3 years after BC deposition were similar between surface and bulk properties. After 100 years, the C contents of the entire BC particles (22%) approached the C contents of BC surfaces (19%). Correspondingly, the O contents were still slightly higher on BC surfaces (63%) than in the entire particle (58%) after 100 years. To mathematically quantify changes in elemental contents of BC, a first order kinetic model was applied to the XPS data (Table 2). The rate of change (*b*) for O and C contents on BC surfaces was 6 times higher than the rate for the entire particles.

Surfaces of BC contained more oxidized functional groups than entire particles, most of which were C–O and C=O groups (Fig. 3). Carboxyl C on BC surfaces (COO) increased rapidly within the first 5 years, in contrast to entire BC particles (Fig. 3). Total oxidized functional groups increased over time on BC surfaces, but remained constant for entire BC

Table 2 Model parameters of quantified elements on BC surfaces and in entire BC particles as a function of time (years) since deposition

Elements	Properties of	b	a	Y_0	R^2	P
C	Surface	0.0657	27.8	16.8	0.79	0.020
	Bulk	0.0129	41.9	9.2	0.90	0.003
O	Surface	0.0622	17.8	45.2	0.79	0.02
	Bulk	0.0100	29.3	40.9	0.88	0.005
Al	Surface	0.1279	4.2	3.7	0.73	0.04
	Bulk	0.0489	3.5	3.3	0.82	0.01
Si	Surface	0.0636	4.9	5.5	0.79	0.02
	Bulk	0.0254	5.4	4.2	0.93	0.001
Fe	Surface	0.0095	2.6	0.7	0.87	0.006
	Bulk	0.0029	8.9	0.9	0.95	0.0006

A first order kinetic model was fitted. A decay curve of $f = Y_0 + ae^{-bt}$ was applied for C and a rise curve of $f = Y_0 + a(1 - e^{-bt})$ was applied for O, Al, Si and Fe

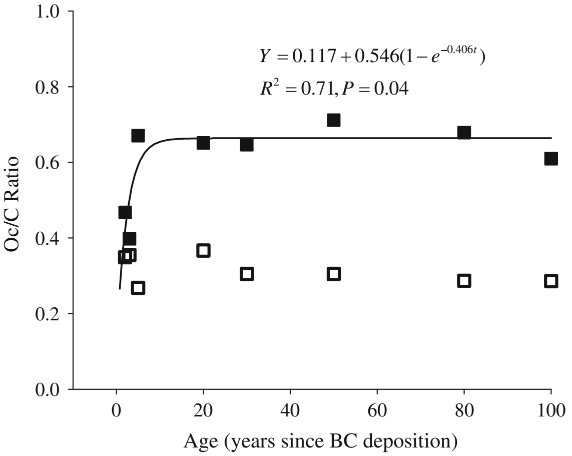

Fig. 4 Oc/C ratios of surface and entire BC particles based on deconvolution results (only O bound to C, denoted by Oc). Solid black squares were the observations of BC surfaces and open squares those of entire BC particles

particles. Similar trends were observed when calculating O/C ratios for O bound to C using the deconvolution results (Fig. 4). These Oc/C ratios of BC surfaces increased rapidly in the first 5 years since deposition and were higher than those recorded for entire particles, which showed no change in their Oc/C ratios over time (Fig. 4).

Aluminum, iron and silicon of isolated BC particles

The dynamics of Al and Si on BC surfaces and entire particles over 100 years were similar to that of O, and increased with time. The increases were more rapid on surfaces than in the entire particles. Thirty years following deposition, Al contents were about 7.8% for surfaces and 6% for the entire particles, while Si contents were 9.7% for surfaces and 7.1% for the entire particles (Fig. 5). Beyond 30 years, Al and Si contents of the entire particle continued to increase, while those of BC surfaces leveled off. Elemental contents of Al and Si of the entire particles approached those of BC surfaces after 100 years, yet remained slightly lower. Fe contents were generally low (below 3%) compared to the other investigated elements (Fig. 5). Fe contents in both bulk and surface properties slightly and constantly increased over the entire period of 100 years.

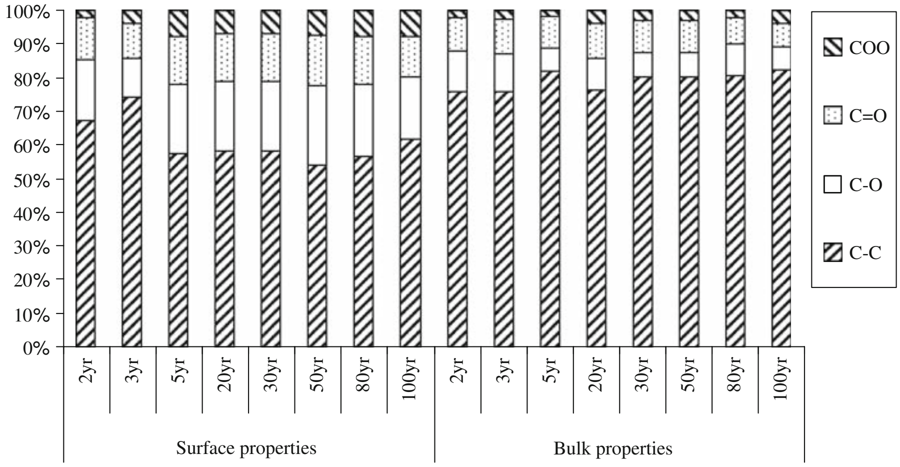

Fig. 3 Carbon chemical species from XPS spectra of BC surfaces and entire BC particles, quantified by deconvolution of XPS spectra

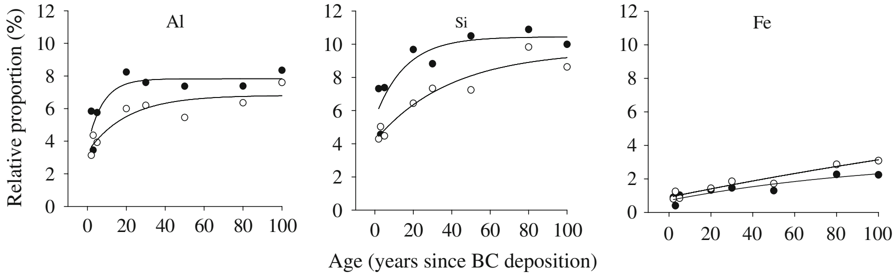

Fig. 5 Dynamics of Al, Fe and Si on BC surfaces (filled circles) and in entire BC particles (open circles) over 100 years

Similar to C and O, the rate of change (*b*) for BC surfaces was also higher for Al, Si and Fe than the rate for the entire particles, albeit only by a factor of three (Table 2). This result again indicated that changes in elemental contents of surface properties were faster than those of the entire particles.

Carbon chemical speciation of isolated BC particles by FTIR analysis

The relative proportions of aromatic groups (C=C) detected at 1,642 cm^{-1}, aliphatic C–H at 1,389 and 2,920 cm^{-1} and hydroxyl group (O–H) at 3,370 cm^{-1} decreased, while C–O at 1,036 cm^{-1} and carbonyl groups (C=O) at 1,700 cm^{-1} rose over 100 years (Fig. 6). Of the six C chemical species, the relative proportion of aliphatic C–H at 1,389 cm^{-1} decreased the most from 24.3% to 5.8% during the first 5 years and remained at this proportion, while aliphatic C–H groups vibrating at 2,920 cm^{-1} decreased more slowly to a very low content of 1.1% after 20 years. O–H of phenols decreased to 35.5% while C–O group of polysaccharides increased rapidly to 40.4% during the first 10 years. Carbonyl changed at a slower rate towards a steady state from 1.3% to 3.7% and aromatic groups from 20.7% to 12.0% during the first 90 years after BC deposition. Chemical C species changed at a similar rate irrespective of the size of the BC particles, whether small (<30 μm) or large (50–2,000 μm) (Fig. 6).

Discussion

BC production

Based on NMR quantification, and the first order kinetic model (Fig. 1e), BC stocks at deposition were estimated to be approximately 10,000 kg C ha^{-1}, compared to 6,500 kg C ha^{-1} at the forest site. The difference of 3,500 kg C ha^{-1} of BC can be interpreted as BC residues derived from incomplete combustion of aboveground forest biomass during forest conversion. Aboveground C stocks in similar East African highland forests were reported to be about 330 ± 65 Mg C ha^{-1} (Glenday 2006). Consequently, an estimated 0.9–1.3% of the initial forest C was converted to BC and deposited to soil. This is in good agreement with other studies. Preston and Schmidt (2006) reported a BC production of 1–3% of biomass C by combustion. Forbes et al. (2006) documented average proportions of 0.7–2.9% of the initial biomass C that remained after fires in tropical forests, and Schmidt and Noack (2000) proposed a maximum conversion rate of 1.8 ± 0.2% when burning efficiently.

BC losses from cultivated topsoil over 100 years

BC contents were found to lie in the range of 1–11 mg C g^{-1} soil or 10–29% of total organic C by NMR and from 0.1 to 0.7 mg C g^{-1} soil or 0.15–1.54% of total organic C by manual quantification (Fig. 1a–d). These results were comparable to other studies. In agricultural soils in the US, Skjemstad et al. (2002) showed soil BC contents ranging from 1.8 to 13.6 mg C g^{-1} soil or 10–35% of total organic C using the UV-NMR method which captures a similar range of BC forms as the NMR method used here. In Siberian Scots pine forests, Czimczik et al. (2003) found mean BC concentrations of 4.0 and 13.5 mg g^{-1} soil for unburned and burned sites, respectively, using a molecular marker method for BC quantification. Manual quantification commonly underestimates BC contents (Forbes et al. 2006), because small particles cannot be identified and removed under a light microscope. Consequently, in this study manual quantification resulted in

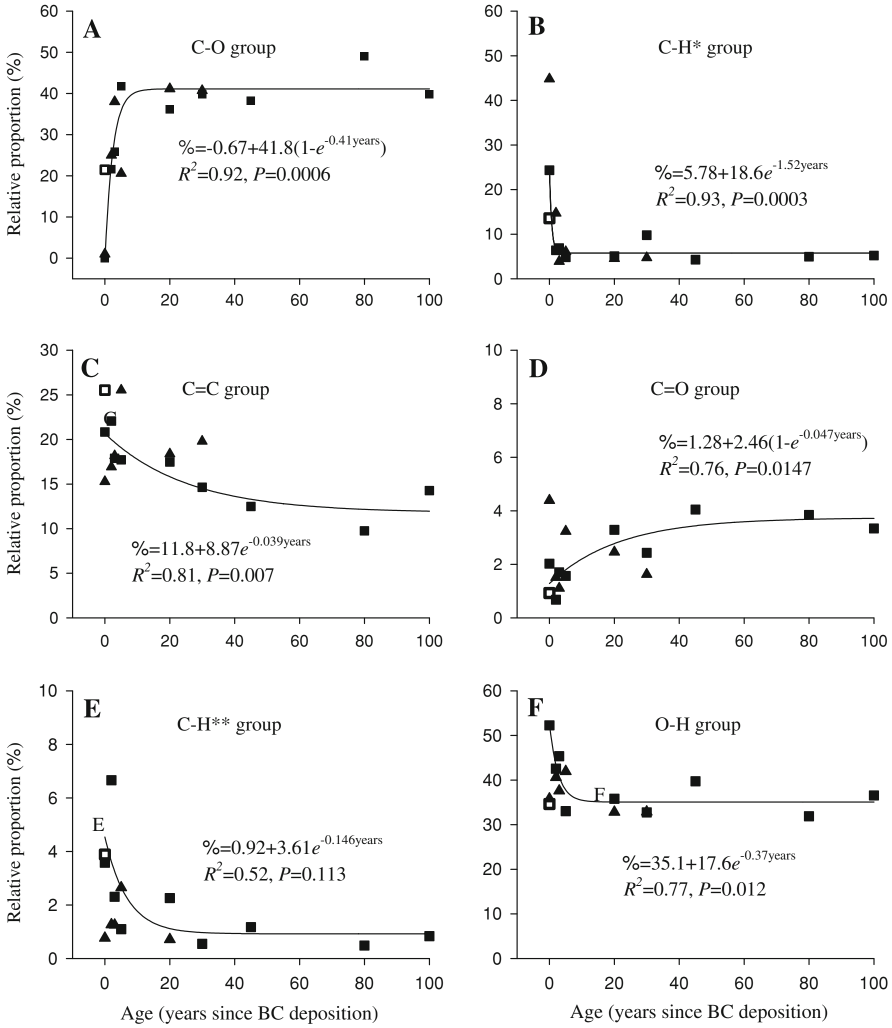

Fig. 6 Dynamics of C functional groups characterized by FTIR of micro-particle (solid squares) and macro-particle BC (solid triangles). The curves were fitted, based only on spectrum intensities of micro-particle BC samples from eight cultivated soil samples and the fresh BC sample. The open square denotes the observation of forest soil BC. (*) aliphatic C–H vibrating at 1,389 cm^{-1}. (**) C–H of asymmetric and symmetric CH_3 and CH_2 groups vibrating at 2,910 cm^{-1}

93–95% lower estimates of BC contents than NMR quantification.

Soil BC contents and stocks decreased rapidly in the first 30 years following conversion and leveled off afterwards (Fig. 1a, b, e, and f). Such a dynamic was also reported by Gavin et al. (2003), who showed an exponential decrease in BC mass with increasing time since the last forest fire. In our study, the dynamics of BC contents could be separated into two phases of different disappearance rates. The first phase of 30 years is characterized by a rapid loss of BC by 70% from the topsoil. The second phase of the last 70 years had a slower loss rate, where BC contents decreased very slowly to gradually approach the steady state at 3.5 mg C g^{-1} soil or 3,900 kg C ha^{-1} determined by NMR quantification.

The losses observed in this study can be explained by both a decomposition of BC to CO_2 as well as by a physical export below the sampled soil horizon or laterally by erosion. Erosion losses are presumed to be low in the present experiment, since flat landscape positions were selected to minimize lateral soil export. Long-term losses by erosion or vertical transport were low since BC stocks did not decrease beyond 20 years. Shortly after the fire event, however, a certain proportion of BC was likely lost by transport from the topsoil due to low interaction with the mineral matter. Enrichment of BC in subsurface horizons of anthropogenic soils have been reported by Glaser et al. (2000) and Schmidt et al. (1999), although it is not clear whether this was a result of bioturbation, illuviation or direct BC deposition to the subsurface horizon. Dai et al. (2005) concluded that the proportion of BC to total SOM increases with soil depth. They proposed a mechanism of mass movement of BC with clay and silt and accumulation in deeper soil horizons. Relocation of BC to deeper horizons was also one of the reasons that Czimczik et al. (2003) proposed to explain the low topsoil contents of BC in their study and export of BC from watersheds in dissolved form has been found at multiple locations (Hockaday et al. 2007; Guggenberger et al. 2008).

The combination of decomposition and lateral as well as vertical export below a depth of 0.1 m during the first years after BC deposition explains the short mean residence time of 8.3 years, calculated from the inverse of the rate of disappearance (Fig. 1a). This mean residence time is much shorter than estimates from ^{14}C ages of 2,400 to 13,900 years in ocean sediments (Masiello and Druffel 1998), 5,000 years in soils (Skjemstad et al. 1998), half life of 6,623 years in a coastal temperate rain forest of western Vancouver (calculated by Preston and Schmidt 2006 from Gavin et al. 2003), and of decades to centuries of BC from grass fires in well-aerated tropical savanna soil in Zimbabwe (Bird et al. 1999).

In addition to a physical redistribution within the landscape, the initial phase of rapid BC losses may be the result of rapid mineralization of an easily degradable portion of BC material, which could be decomposed by biotic and abiotic mechanisms. Biotic mechanisms primarily include the activity of heterotrophic soil microorganisms (Hamer et al. 2004), and plant root activities, while abiotic mechanism such as chemical oxidative reactions may also be involved (Middelburg et al. 1999).

Despite the possibility of a rapid mineralization of the labile fraction of BC, decomposition of BC appeared to be slower than decomposition of other C. Another study performed on the same samples described here (Solomon et al. 2007) showed a rapid depletion of 46–73% SOC within the first 4 years following conversion. In the current study, we observed a 33% slower change in total BC contents (with a rate of 0.12 year^{-1}, Fig. 1a) than a change in total C remaining (with a rate of 0.16 year^{-1}; from Solomon et al. (2007)). Therefore, BC was conserved to a greater extent than other C in the studied soils. Enrichment of BC as a fraction of total organic C with increasing time of continuous cultivation was also found by Skjemstad et al. (2001) in Australia. Similarly, the proportion of BC increased with increasing oxidation over time in marine sediments (Middelburg et al. 1999).

Following the first phase of around 30 years, most of the remaining BC material may have undergone two processes apart from physical export: (a) the labile portion of the BC continuum may have decomposed (Hamer et al. 2004), leaving a BC material behind that is more recalcitrant to decomposition (Bird et al. 1999); and (b) BC material was likely incorporated into the soil matrix, and thus was physically protected within aggregates (Brodowski et al. 2006) or even by interactions with mineral surfaces. Furthermore, the initially large BC particles may have broken down into small particles by physical pressure derived from agricultural operations, such as plowing, or by earthworm activity, which ingest BC and defecate casts containing small BC fragments (Ponge et al. 2006). The physical breakdown is confirmed by the ratio of BC contents determined by NMR and manual quantification. According to the first order kinetic model, BC stocks determined by NMR were about 7 times higher than those obtained by manual quantification shortly after BC deposition, but were 23 times higher than those obtained by manual quantification after 30 years. This means during the first 30 years, a large amount of BC particles was broken down into particles <5 μm, which could not be identified under the light microscope. In fact we did not recognize any BC particles >50 μm under the light microscope in soil samples after more than 30 years. The small, broken BC particles, which were more likely to be encapsulated by adsorption to soil components (Krull et al. 2003), further facilitated physical protection of BC materials. This argument is also supported by the fact that elemental Al, Si and Fe were increasingly found on BC surfaces over the course of 100 years (Fig. 5). As a result, less BC material would be available for decomposition, and thus much slower BC losses were observed beyond the first 30 years. The protection by physical and chemical stabilization was apparently sufficient to minimize either decomposition or physical export by erosion and vertical transport below 0.1 m or both beyond 30 years.

Changes in BC oxidation

The much more rapid oxidation of surfaces exemplified by greater Oc/C ratios of the BC surfaces than of the interior of BC particles (Fig. 4) is in agreement with other studies. Brodowski et al. (2005) also observed an increasing O/C ratio from interior to exterior by SEM-EDX. Cheng et al. (2006) concluded from an incubation experiment that oxidation started at surfaces of BC particles. They further stated that the interior of BC particles would be gradually oxidized with long BC exposure in soil. However, our data show that even after 100 years, the Oc/C ratios of the entire BC particle did not increase (Fig. 4). Oc/C ratios of BC surfaces increased rapidly during the first 5 years and then leveled off at a high level of O, while that of bulk properties was lower and stable during 100 years since BC deposition (Figs. 3, 4). Oxidation increased apparently following an exponential behavior and started from surfaces of particles.

The Oc/C ratios determined by deconvolution of XPS spectra of BC surfaces in our study ranging from 0.4 to 0.7 are higher than the threshold of 0.33 that was proposed to distinguish BC from non-BC by Brodowski et al. (2005), while those of entire BC particles, ranging from 0.27 to 0.37 are comparable to such a ratio. Discounting surface oxidation and adsorption of non-BC, our results suggest an Oc/C ratio of 0.3 for fire-derived and aged BC obtained from soils including only O bonded to C (from deconvolution of XPS data), which agrees well with results from 11 sites in the Eastern U.S. (Cheng et al. 2008).

Molecular changes of BC

Changes in BC properties were also observed in the functional group composition of C–O, C–H, C=C, C=O and O–H (Fig. 6). Within the first 20 years, aliphatic C–H groups rapidly decreased to a very low proportion, below 1% for C–H vibrating at around 2,920 cm^{-1} and below 6% for C–H vibrating at 1,389 cm^{-1}. Cheng et al. (2006) also observed a significant decrease in intensity of aliphatic groups vibrating around 2,900 cm^{-1} after 4 months of incubation of BC at 30 and 70°C. Cody and Alexander (2005) explained their observations of a selective loss of aliphatic groups to chemical oxidation reactions, which transformed aliphatic groups to either CO groups or soluble organic acids and CO_2. They also pointed out that environmental oxidative potential could be enhanced by the abundance of iron in solution. This argument seems relevant to the present study which showed an increasing abundance of Fe on BC particles.

After 90 years, carbonyl groups (C=O) increased by a factor of 2.8 (from 1.3 to about 3.6%), with a much slower rate of change relative to aliphatic C–H groups. Presumably, this resulted from partial conversion of C–H and/or C=C to C=O, while some BC was completely converted to CO_2 by oxidation. A predominant band at 1,036 cm^{-1}, assigned to C–O groups which are mainly derived from polysaccharides of plant litter adsorbed on BC particles, was also observed. Within the first 10 years since conversion the proportion of C–O groups increased dramatically from zero in fresh BC material to almost 41% (Fig. 6a). Cheng et al. (2006) also observed a distinct band at 1,035 cm^{-1}, which they attributed to the sorption of organic matter from added manure. The abrupt increase in C–O groups in our study could therefore be a result of sorption of organic matter to BC. Cornelissen et al. (2005) concluded that carbonaceous geosorbents, including BC, could adsorb as much as 10–100 times more organic substances than could amorphous organic matter. The third predominant band, assigned to aromatic groups, was observed with a relative proportion of 12% after 90 years. The only slowly decreasing proportion of C=C groups, by 8% over 90 years, was an indication of their high stability and low penetration of oxidation into the BC particles.

Since BC surfaces were highly oxidized as determined by XPS, one could have expected small BC particles to be more oxidized than large particles as determined by FTIR. However, both small and large BC particles had similar molecular chemical properties. This may be explained by a very thin layer of oxidized C on BC surfaces that is sufficiently masked by bulk analyses as obtained by FTIR and do therefore not reflect differences between those sizes of BC particles investigated here. A preferential leaching loss of less oxidized BC as shown by Leifeld et al. (2007) for soot in comparison to larger char particles is unlikely able to explain the observed increase in oxidation, as only char was sampled here with particle sizes that are much larger than condensation products from combustion.

Interactions of BC with soil mineral matter

Si and Al quickly associated with BC surfaces (Fig. 5) in the first 30 years, followed by slow rates, with which Al and Si contents approached a steady state. Unlike Al and Si, Fe contents were similar both on BC surfaces and in entire particles, and increased only slightly over time. These dynamics of interaction between mineral elements and BC could be interpreted as evidence for BC encapsulation, and thus physical protection by soil mineral adsorption. Similarly, Brodowski et al. (2006) found a large proportion of BC protected within aggregates. This indicates that soil mineral adsorption may play an important role in slowing down BC losses both by decomposition as well as by physical export in the second phase after 30 years as argued above.

BC surface oxidation and sorption

There were at least two processes causing the BC dynamics in the soils described here: oxidation and non-BC sorption. These two mechanisms developed proportionally and rapidly in the first few years since BC deposition. The increases in elemental O and carbonyl groups (Figs. 2, 6) with time are indicators of oxidation of BC, the rate of which decreased over time. The Oc/C ratios of BC surfaces were found to be higher than those of entire BC particles (Fig. 4), confirming our hypothesis that BC particles were oxidized, beginning from the outside of particles. This is in agreement with other authors (Brodowski et al. 2005; Lehmann et al. 2005; Cheng et al. 2006). Kawamoto et al. (2005) observed an increase in O/C ratios of BC after treatment with ozone occurring on the edges of hexagonal C layers. Liang et al. (2006) showed a dramatic increase in O/C ratios from interior (0.01–0.02) to surfaces (0.09–0.19) of BC particles using a microprobe, indicating a higher level of oxidation on the surface than in the interior of BC particles.

Oxidation may either mineralize BC to CO_2 or change the BC into other organic C forms containing more O. In either case, we found a significant negative correlation, −0.78 and −0.79 ($P < 0.001$), between surface Oc/C ratios and both BC stocks or C of BC surfaces, respectively, suggesting that oxidative degradation was likely one of the most important processes controlling BC stock dynamics. We also found that absolute correlation coefficients between BC stocks and elemental contents were higher for BC surfaces than for entire particles, indicating that dynamics of BC stocks were related to oxidation dynamics on surfaces of BC particles. As a result of increasing oxidation, charge density of BC particles likely increased, resulting in more polar non-BC substances to be adsorbed to surfaces of BC particles (Liang et al. 2006; Cheng et al. 2006). Consequently, elemental contents of O on BC surfaces and thus surface oxidation likely derived from both oxidized BC materials and non-BC adsorbed organic materials. Compared to the ratio found here for entire particles of 0.27–0.37 and to the one suggested by Brodowski et al. (2005) of 0.33 for BC, the higher O/C ratios, from 0.4 to 0.7, observed for BC surfaces after 5 years since deposition in our study, also suggest adsorption of non-BC organic materials or oxidation of BC to non-BC. It cannot be fully excluded that preferential leaching or erosion of certain types of BC created the observed dynamics, but is unlikely given the nature of the change. For example, the increasing surface oxidation of BC isolated from the topsoil is unlikely a result of preferential export of unoxidized BC, since mobile BC found in pore water and streams is typically not the least oxidized fraction (Hockaday et al. 2007; Guggenberger et al. 2008).

Adsorption of non-BC materials on BC surfaces could be an important process reducing the oxygen-exposed surface area of BC particles and consequently oxidation potential. The increasing sorption of non-BC organic and inorganic substances on BC materials was suggested by the occurrence of C–O groups indicative of polysaccharides (Fig. 6a) and by the relative proportion of Al, Si and Fe (Fig. 5), which rapidly increased during the first few years since BC deposition. Consequently, the increasing adsorption of non-BC materials on surfaces of BC in our study may accelerate physical protection of BC in soil and thus increases protection of BC against oxidation and then decomposition.

Conclusions

BC stocks decreased rapidly within the first 30 years after deposition and leveled off afterwards. The change in BC stocks likely involved a number of processes, including decomposition, erosion and transport below the depth of observation. Oxidation may degrade BC material, but adsorption of organic and inorganic materials may increase protection of BC against decomposition by reducing air-exposed surface area of BC particles and oxidative degradation. Changes in BC properties over time were found to be highly correlated with BC quantity, indicating that changes in BC quantity and quality occurred concurrently. Oxidation and non-BC adsorption were identified to control BC dynamics over the hundred years of observation. However, the molecular processes by which non-BC or minerals interacted with BC surfaces remained unclear. Also other soil processes such as an encapsulation of BC by soil particles through aggregation may have contributed to the long-term stability of BC. In addition, physical export played a role but was not quantified separately and warrants further research.

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