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Black carbon decomposition under varying water regimes

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ABSTRACT

The stability of biomass-derived black carbon (BC) or biochar as a slow cycling pool in the global C cycle is an important property and is likely governed by environmental conditions. This study investigated the effects of water regimes (saturated, unsaturated and alternating saturated–unsaturated conditions) and differences in BC materials, produced by carbonizing corn residues and oak wood at two temperatures (350 °C and 600 °C) on BC degradation at 30 °C over 1 year in a full factorial experiment. Effects of water regime on C loss and potential cation exchange capacity (CECp at pH 7) significantly depended on biomass type. Corn BC was both mineralized (16% C loss for the first year) and was oxidized [1000 mmole(+) kg^{-1} C] significantly faster under unsaturated conditions than under other water regimes, whereas oak BC mineralized most rapidly (12%) under alternating saturated–unsaturated conditions with similar oxidation, irrespective of water regime. Over 1 year of saturated incubation, the O/C ratio values did not significantly ($P > 0.05$) increase even though BC was mineralized by 9% and CECp increased by 170 mmole(+) kg^{-1} C, in contrast to unsaturated and alternating saturated–unsaturated conditions. While mineralization and oxidation significantly decreased at higher charring temperature for corn, no difference was observed for oak ($P > 0.05$). Unsaturated and alternating conditions increased carboxylic and OH functional groups, while they decreased aliphatic groups. The pH increased by about one unit for corn BC, but decreased by 0.2 units for oak BC, indicating strong mineral dissolution of corn BC. Carbon loss strongly correlated with changes in O/C values of both corn BC and oak BC, indicating that oxidation of BC was most likely the major mechanism controlling its stability. However, under saturated conditions, additional mechanisms may govern BC degradation and require further investigation.

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1. Introduction

Black carbon (BC) is a general term used to describe products derived from incomplete combustion of vegetation and fossil fuels (Schmidt and Noack, 2000). It is a continuum of C forms rather than a particular compound. It can form through two different pathways of either recondensation of volatiles forming graphitized soot BC or of incomplete combustion leaving behind solid residues (Schmidt and Noack, 2000). This study focuses on the product derived from the latter process.

BC constitutes a considerable proportion of soil organic C (SOC), being as much as 30% in some Australian soils (Skjemstad et al., 1996), up to 35% in Terra Preta – Brazilian Oxisols (Glaser et al., 2000) and up to 45% in German Chernozemic soils (Schmidt et al., 1999, 2002). Since estimates of the annual global production of BC, 0.04–0.19 × 10^{15} g (Kuhlbusch, 1998), are much lower than global net primary production, 56 × 10^{15} g C (Zhao et al., 2005), BC must be much more stable relative to other soil organic matter forms. Accordingly, it is assumed to have a long mean residence time of possibly up to 10,000 years in soil (Swift, 2001). As a result, it may play a considerable role in sequestering C, and so merits

study in the light of recently reported global warming because of increasing carbon dioxide concentration in the atmosphere.

Even though BC appears to be relatively stable, it must eventually mineralize. Otherwise, global organic C stocks would be converted to BC on Earth's surface within 100,000 years (Goldberg, 1985). Glaser et al. (2002) concluded that BC was decomposable but its turnover was much slower than that of other soil organic substances. Slow BC decomposition in soils and sediments occurs through (i) microbial degradation (Shneour, 1966; Baldock and Smernik, 2002; Hamer et al., 2004) and (ii) abiotic oxidation (Cheng et al., 2006; Cohen-Ofri et al., 2007). O/C values (Brodowski et al., 2005; Liang et al., 2006) and carboxyl functional groups (Lehmann et al., 2005; Liang et al., 2006) were higher on the surfaces of BC particles than in their interior. Hamer et al. (2004) suggested that some microbes were able to use BC as sole C source. Moreover, Hofrichter et al. (1999) concluded that an enzyme, manganese peroxidase, released from ligninolytic basidiomycetes, a wood and leaf litter-decaying fungus, was able to decompose brown coal, indicating that BC could be degraded by microbes.

BC was found to persist in marine sediments for 13,900 years (Masiello and Druffel, 1998), while it was estimated to have mean residence times of only decades to one century in well aerated, tropical soil (Bird et al., 1999), suggesting that water regime may play an important role in BC degradation. Soil normally undergoes

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alternating drying and rewetting following seasonal weather changes or during cycles of rain events and dry spells, resulting in natural alternation of saturated and unsaturated conditions. The cycles of drying and rewetting have been reported to influence SOM decomposition (Soerensen, 1974), nutrient availability (Birch, 1958; Halverson et al., 2000; Nguyen and Marschner, 2005) and microbial activity (Gestel et al., 1993). Similarly, the alternation of saturated and unsaturated conditions may affect BC degradation to a greater extent than any single, constant phase. However, such effects have not been reported.

In addition to environmental conditions, BC degradation may also be controlled by its quality, mainly as a result of charring temperature and the type of biomass. Based on BC characterization using infrared spectroscopy and thermogravimetry, Labbe et al. (2006) concluded that its properties were determined by both plant species and carbonization temperature. Hamer et al. (2004) reported that BC derived from corn stover and rye was mineralized more rapidly than that derived from wood, indicating the importance of plant material. In addition, increasing the charring temperature up to 350 °C decreased BC mineralization over 120 days of incubation (Baldock and Smernik, 2002). Whether different types of BC as a function of both charring temperature and biomass type respond differently to both saturated and unsaturated soil conditions has not been reported.

Therefore, the current study was conducted to address these knowledge gaps by investigating the response of different BC materials to varying water regimes. We hypothesized that (i) BC decomposition and oxidation would be slower under saturated than unsaturated and alternating saturated–unsaturated conditions, (ii) BC materials higher in mineral content (as a function of biomass type) and lower in aromaticity (as a function of charring temperature) would be less stable than materials lower in mineral content and higher in aromaticity.

2. Materials and methods

2.1. BC preparation

Corn stover residue (*Zea mays* L.) and oak shavings (*Quercus* spp.) were carbonized at two temperature levels, 350 and 600 °C, to produce 4 BC materials (corn-350 BC, corn-600 BC, oak-350 BC and oak-600 BC) using slow pyrolysis (Daisy Reactor, Best Energies, Inc., Cashton, WI, USA). Approximately 3 kg feedstock were manually placed into the main chamber, which was thoroughly purged with N_2 (with the mixer running). The pre-dried material (<10% moisture) was isothermically charred for 80–90 min, including rising temperature to the target with a few degrees per minute and holding at the final temperature for 15–20 min. After completion of pyrolysis, the furnace was turned off and the main chamber was allowed to cool before scooping the BC under N_2 purge to reduce rapid oxidation (leading to a more homogeneous product)

Table 2
Carbon loss and change in CECp, O/C ratio and pH over the first year ($N = 8$). Values followed by the same letter are not significantly different.

Biomass types	Charring temp. (°C)	Initial	Unsaturated	Saturated	Alternating
C loss (%)					
Corn residue	350	n/a	21.21[a]	10.90[bcd]	15.38[ab]
	600	n/a	11.21[bcd]	9.43[bcd]	10.37[bcd]
Oak wood	350	n/a	8.08[cd]	6.15[d]	13.86[bc]
	600	n/a	8.90[cd]	8.61[cd]	9.84[bcd]
O/C					
Corn residue	350	0.37	0.50[a]	0.38[b]	0.48[a,*]
	600	0.21	0.24[cd]	0.20[de]	0.23[cd]
Oak wood	350	0.26	0.35[b,*]	0.31[bc,*]	0.35[b]
	600	0.10	0.15[de,*]	0.13[e]	0.14[e,*]
CECp[a]					
Corn residue	350	610	1395[a,*]	856[c,*]	1046[b,*]
	600	215	616[d,*]	391[efg,*]	555[de,*]
Oak wood	350	131	251[fg,*]	253[fg,*]	418[ef,*]
	600	89	235[fg,*]	229[g,*]	241[fg,*]
pH[b]					
Corn residue	350	5.88	6.79[d,*]	7.06[c,*]	6.64[d,*]
	600	6.71	8.11[a,*]	7.80[b,*]	7.59[b,*]
Oak wood	350	4.84	4.54[e,*]	4.66[e,*]	4.62[e,*]
	600	4.91	4.69[e,*]	4.66[e,*]	4.75[e,*]

[a] CECp = potential cation exchange capacity in mmole (+) kg⁻¹ C.
[b] pH in 1:20 w:v water.
[*] Indicates significant ($P < 0.05$) differences from initial values; n/a not applicable – all C loss data are significantly different from zero.

and auto-ignition. We then slightly ground the BC to pass two consecutive 2 and 0.5 mm sieves and BC particles remaining on the 0.5 mm sieve were collected into separate plastic bags and stored in a desiccator for the incubation experiment. Initial BC properties are shown in Tables 1 and 2.

2.2. Water holding capacity

A mixture of 19 g pure white sand (Sigma Aldrich no. 274739, −50 +70 mesh; ignited at 500 °C for 24 h) and 1 g BC material were weighed on a funnel covered with Whatman no. 1 filter paper. The BC–sand mixture was mixed well and saturated with distilled water. After free draining until no additional water loss was recorded, the water content was determined by taking the difference in weight of the filter paper and BC–sand mixture before and after oven drying at 105 °C for 24 h. In addition, a Whatman filter paper-covered funnel without any sand and BC was also prepared as a control. Water content held by the filter paper was subtracted. The measured water holding capacity of the BC–sand mixtures

Table 1
Initial properties of BC materials.

Biomass type	Charring temp. (°C)	Elemental content (%)										C/N	O/C	H/C	Aromaticity[a]
		C	N	O	H	K	Ca	Fe	Si	Others	Sum				
Corn residue	350	67.5	0.93	25.1	4.74	1.04	0.27	0.05	0.02	0.51	100.2	73	0.37	0.07	77.6
	600	79.0	0.92	16.3	2.52	0.67	0.31	0.08	0.03	0.49	100.3	86	0.21	0.03	85.2
Oak wood	350	75.9	0.10	19.6	4.27	0.11	0.07	0.003	0.02	0.03	100.1	759	0.26	0.06	61.8
	600	88.4	0.12	9.0	2.13	0.22	0.09	0.13	0.01	0.07	100.2	737	0.10	0.02	68.4

[a] Quantified via X-ray diffraction (XRD) analysis.

was 44% for corn-350 BC, 42% for corn-600 BC, 40% for oak-350 BC and 34% for oak-600 BC.

2.3. Microbial and nutrient solution

We extracted microbial solution (2 l) from a surface soil sample (0–0.2 m) taken from a site of a historical charcoal blast furnace in Cartersville, Georgia, that was used by Cheng et al. (2008a). The soil sample had a high BC content, which was the remnant of wood charcoal, deposited to the soil between the 1830s and 1864 during the operation of a blast furnace for iron production. We expected the soil microbial community to be well adapted to the presence of BC after long term exposure to this BC-rich environment. As the soil sample had been stored at 5 °C after sampling, it was incubated at 30 °C for 2 weeks to activate the microbial community. The microbial extraction was carried out by adding 25 g soil to 2 l distilled water, shaking slightly for 30 min and filtering through a Whatman no. 1 filter paper. Nutrients were added to the solution to give 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 (Cheng et al., 2006).

2.4. Experimental design

A completely randomized full factorial experiment with eight replicates and three factors was set up. Four BC materials, produced by charring two biomass types at 350 and 600 °C, were incubated in the laboratory under saturated, unsaturated or alternating saturated–unsaturated conditions. About 19 g pure sand was weighed into 60 ml glass bottles, to which 1 g ground BC material was added. The bottles received 2 ml microbial nutrient solution and were incubated at 30 °C in a temperature controlled room. Carbon concentration in the 1:19 BC:sand mixtures was as follows: 3.38% for corn-350 BC and 3.98% for corn-600 BC, 3.82% for oak-350 BC and 4.45% for oak-600 BC.

At the beginning of the experiment, we initiated three different water regimes: (a) Constantly unsaturated conditions, here defined as 60% of water holding capacity; the mixture in the bottles was brought to 60% of water holding capacity with deionised water and kept constant during incubation. (b) Constantly saturated conditions, here defined as submerged in water: the mixture in the bottles was fully submerged in deionized water, and kept constant during incubation, the water level being ca. 20–30 mm higher than the level of the BC–sand mixture. (c) Alternating saturated–unsaturated conditions: the water regime in the mixture was subjected to periodic change from saturated to unsaturated conditions. We started with the saturated phase by adding distilled water to the bottles to about 150% of water holding capacity, which led to submerged conditions. The saturated phase continued for about 7–9 days and water in the bottles was then allowed to rapidly evaporate, leading to the unsaturated phase. After 2 weeks, when water contents decreased to ca. 30–40% of water holding capacity, we began a new cycle by re-submerging the mixture and adjusting to 150% water holding capacity. These cycles were repeated continuously for 1 year.

For improving the accuracy of the water maintenance, we placed eight bottles of the same water treatment in a plastic tray, which was partially covered with Al foil. Distilled water was added to the trays. We covered the trays containing incubations under alternating saturated–unsaturated conditions to accelerate water evaporation to reach unsaturated conditions within 7–9 days. We created five small holes in the covered Al foil of the saturated and unsaturated treatments for appropriate air exchange. Water status in the plastic trays and of the mixture in bottles was monitored weekly by weighing and adding an appropriate amount of distilled water.

By the end of the 1 year incubation, the trays were uncovered for air-drying in a 30 °C-controlled room. The BC–sand mixture was remixed well and dried in an oven at 60 °C for 2 days before sampling. About 5 g of mixture in each bottle were taken for BC particle isolation using super tweezers (N5, Dumont, Montignez, Switzerland). Another 5 g of the mixture were sampled and ball milled for total elemental analysis. The last 10 g were used for pH and CECp measurements.

2.5. Total elemental analysis

Mineral content was measured by grinding 2 g of BC material followed by HNO_3 digestion in a closed microwave system for 12 h. The digest was used for total elemental determination using inductively coupled plasma (ICP) spectrometry (ICP-AES, Spectro CIROS, CCD, Germany). Total C and N were measured using continuous flow isotope ratio mass spectrometry (IRMS; 20–20 Mass Spectrometer, Sercon, Crewe, UK) after sample combustion to CO_2 and N_2 at 1000 °C in an on line elemental analyzer (PDZEuropa ANCA-GSL, Crewe, UK). The gases were separated on a Carbosieve G column (Supelco, Bellefonte, PA, USA) before IRMS measurement. Total N and C were calculated from the integrated total beam energy of the sample in the mass spectrometer compared to a calibration curve derived from standard samples of known C and N content. Total H was measured using continuous flow TCEA (thermal conversion elemental analysis) using a Hekatech furnace (1400 °C) by reaction with glassy carbon in a molybdenum foil-lined ceramic reaction tube to yield H_2. Hydrogen was calculated from the integrated total beam energy of the sample in the mass spectrometer compared to a calibration curve derived from standard samples of known H content.

Ash and sand material in percent of the mixture were quantified by combusting 50 mg ground BC–sand mixture at 630 °C in a furnace for 24 h. Oxygen concentration was determined by difference from contents of C, N, H and the ash–sand mixture. This method was used by Baldock and Smernik (2002) in a 120 day experiment using a similar BC–sand incubation, although O concentration quantified with this method may contain small amounts of sulfur, which were not accounted for.

The pH in water was measured at a ratio of 1:20 (w/v water). Distilled water (20 ml) was added to 1 g of the BC–sand mixture. After 1 h with occasional stirring, pH values were read twice using a pH meter. Potential cation exchange capacity (CECp) was determined by saturating 3.0 g BC–sand mixture with 30 ml of 1 N NH_4Ac at pH 7 twice for 1 h. To the mixture, after NH_4Ac extraction using an extractor, were added 40 ml of 2 N KCl to replace the absorbed NH_4^+ cations. The extracted NH_4^+ was quantified using a continuous flow analyzer (Technicon Auto Analyzer, Chauncey, CT, USA) and calculated as CECp.

2.6. BC particle characterization

BC particles from eight replicates were pooled into two composite samples for characterization of the molecular functional group chemistry using Fourier transform infrared (FTIR) spectroscopy. BC samples were first pH standardized with a pH 7 solution by saturating BC materials with distilled water overnight. We standardized the pH of the BC materials to avoid effects of dissociation of chemical functional groups on spectral properties determined from FTIR (Cheng et al., 2008a). Details of the FTIR technique were described by Cheng et al. (2006). In brief, spectra were recorded with a Mattson Model 5020 FTIR Spectrometer (Madison, WI) over 500–4000 cm^{-1}. KBr pellets, containing 0.3 wt% of finely ground BC powder were prepared and scanned (100×). Chemical functional groups were proportionally quantified using FTIR spectra and

Omnic 7.2 (Thermo Electron Corporation, 1992–2005). Details of quantification were described by Nguyen et al. (2008).

2.7. Aromaticity

X-ray diffraction analysis (XRD) was performed with a Theta–Theta Diffractometer (Scintag, Inc., Cupertino, CA, USA). The generator was set at 45 kV and 40 mA. The slits for the tubes were set at #1 and #3 and, for the detector at #0.3 and # 0.5. Scans were run over a 2-θ range from 1.5° to 100° with step size of 0.03 and preset time of 1.2 s/step. The spectra were processed using DMSNT software and areas covering a 5°–35° range (2θ) were deconvoluted into (0 0 2) and γ bands. Areas covered by the (0 0 2) band and the γ band were determined using the same software and the aromaticity was calculate on the basis of a ratio of $\frac{A_{(002)}}{A_{(002)} + A_\gamma}$ (Lu et al., 2000); where $A_{(002)}$ and A_γ are the areas of the (0 0 2) and γ bands, respectively.

2.8. BC loss

The BC loss over a 1 year period of incubation was estimated by taking the difference in C concentration (%), determined from elemental C analysis after incubation and at the beginning of experiment.

2.9. Statistical analysis

Analysis of variance was applied using a completely randomized, factorial design with eight replicates and three experimental factors, after verifying homogeneity and normal distribution. Least significant difference (LSD) and Student test were used to classify treatments that significantly differed in means from each other. All statistical analysis was carried out with JMP 6.0 and Sigma plot 9.0.

3. Results

3.1. BC mineralization

Averaged for all BC types, C loss under both unsaturated and alternating conditions was significantly ($P < 0.05$) higher than under saturated conditions (Table 2). In comparison, C loss from corn BC was higher than that from oak BC and C loss from BC produced at 350 °C was greater than that at 600 °C. However, C loss of BC produced from the two biomass types depended on water regime (significant interaction between biomass type and water condition at $P < 0.05$, Table 2 and Electronic Annex Table 1), but did not differ with production temperature. For corn BC, unsaturated conditions resulted in the highest C loss rate (16% for the first year) while for oak BC the alternating saturated–unsaturated conditions led to the highest C loss (12% for the first year). The lowest C loss (7–8%) was recorded under saturated conditions for both oak and corn BC. In addition, C loss from BC produced from the two biomass types also depended significantly on charring temperature (significant interaction at $P < 0.05$). The production temperature significantly affected mineralization of corn BC, but it had no effect on mineralization of oak BC (Table 2).

3.2. Oxidation, potential cation exchange capacity (CECp) and pH

During incubation, O/C values of all four BC materials increased significantly ($P < 0.05$), unless incubated under continuous saturated conditions (Table 2). Only the main effects of water regime, biomass type and charring temperature on O/C value were significant (Table 2), whereas none of the interactions were significant ($P > 0.05$). Unsaturated and alternating conditions resulted in O/C values of 0.31 and of 0.30, respectively, significantly higher than values under saturated conditions of 0.26 (Table 2).

After 1 year, water regime, biomass type and production temperature all significantly ($P < 0.05$) influenced both CECp and pH (Table 2). Similar to C loss dynamics, changes in CECp and pH for corn BC were significantly affected by charring temperature, whereas the charring temperature did not affect changes for oak BC. As also seen for C loss, unsaturated conditions increased CECp the most for corn BC, whereas for oak BC this was the case with alternating saturated–unsaturated conditions.

The pH values for corn BC were initially 1–1.8 pH units greater than those for oak BC (Table 2). During incubation, the pH of corn BC increased by 0.95 (at 350 °C) and 1.12 (at 600 °C), whereas the pH of oak BC decreased by 0.24–0.21 (at both 350 and 600 °C) pH (Table 2 and Electronic Annex).

In general, C loss was significantly related to O/C ratio and its increment (ΔO/C) for both corn and oak BC (Table 3). The increase in CECp (ΔCECp) was also well related with O/C, ΔO/C and pH for only corn BC. Changes in pH (ΔpH) were not correlated with any other parameters for both corn and oak BC (Table 3).

3.3. Changes in functional group chemistry

Only small differences between corn BC and oak BC were found with respect to the relative proportions of functional groups of OH ($3192–3411$ cm^{-1}), C=O (1700 cm^{-1}), C=C ($1595–1630$ cm^{-1}) and aliphatic groups at $2856–2922$ cm^{-1} and at $1430–1440$ cm^{-1} (Table 4 and Fig. 1). Increasing charring temperature decreased, however, the proportions of C=O and aliphatic groups, while it increased the proportions of OH groups for both corn and oak BC. After 1 year's incubation, both corn and oak BC under unsaturated and alternating saturated–unsaturated conditions contained a higher proportion of OH groups and a lower proportion of aliphatic forms than those under saturated conditions. C=O groups in corn BC also increased to a greater extent under unsaturated and alter-

Table 3
Correlation coefficients between observations of BC properties ($n = 48$).

Index	Corn BC							Oak BC						
	C loss	O/C	CEC	pH	ΔO/C	ΔCEC	ΔpH	C loss	O/C	CEC	pH	ΔO/C	ΔCEC	ΔpH
C loss	1.00							1.00						
O/C	0.54*	1.00						0.40*	1.00					
CEC	0.54*	0.60*	1.00					0.09ns	0.19ns	1.00				
pH	−0.40*	−0.64*	−0.67*	1.00				−0.10ns	−0.27ns	−0.07ns	1.00			
ΔO/C	0.48*	0.86*	0.31*	−0.28ns	1.00			0.64*	0.79*	0.02ns	−0.13ns	1.00		
ΔCEC	0.49*	0.33*	0.88*	−0.36*	0.23ns	1.00		0.09ns	0.06ns	0.99*	−0.02ns	−0.03ns	1.00	
ΔpH	−0.26ns	−0.23ns	−0.30ns	0.75*	−0.15ns	−0.25ns	1.00	−0.06ns	−0.09ns	0.03ns	0.97*	−0.04ns	0.04ns	1.00

* and ns indicate significant ($P < 0.05$) or not significant ($P > 0.05$) relationship, respectively. Δ: change during incubation (obtained by subtraction of initial values from final values).

Table 4
Relative proportion of chemical functional groups quantified from FTIR spectroscopy (measurement of pooled samples from $N = 8$).

Biomass type	Charring temp. (°C)	Original	Unsaturated	Saturated	Alternating
Aromatic (C=C)					
Corn	350	35.7	36.9	38.2	38.2
residue	600	37.1	36.0	37.7	33.9
Oak wood	350	35.3	36.8	37.1	35.6
	600	29.9	31.8	31.5	29.4
Carboxyl (C=O)					
Corn	350	20.4	21.7	21.3	22.4
residue	600	9.1	10.0	8.9	10.3
Oak wood	350	19.6	20.9	21.4	22.7
	600	8.6	10.3	9.6	9.7
Hydroxyl (O—H)					
Corn	350	32.8	32.4	29.7	30.2
residue	600	47.3	49.6	48.1	52.0
Oak wood	350	35.7	33.5	31.4	32.7
	600	54.9	53.7	53.5	56.5
Aliphatic ($CH_2 + CH_3$)					
Corn	350	11.2	9.0	10.8	9.1
residue	600	6.6	4.3	5.4	3.8
Oak wood	350	9.4	8.8	10.2	9.0
	600	6.5	4.2	5.5	4.5

nating conditions than under saturated condition, whereas oak BC showed inconsistent trends between water regimes.

4. Discussion

4.1. Effect of water regime

The more pronounced effects of unsaturated than saturated conditions on C loss, O/C ratio and CECp can be explained by the availability of oxygen for both abiotic and biotic oxidation and decomposition, which is well known for soil organic matter (Soerensen, 1974; Morris et al., 2004). However, alternating saturated–unsaturated conditions typically result in greater mineralization of

soil organic matter than constantly unsaturated conditions (Birch, 1958; Cabrera, 1993; Gestel et al., 1993; Wu and Brookes, 2005). The reason for the often greater mineralization during drying and rewetting lies in destruction of soil structure by breaking down soil aggregates (Chepkwony et al., 2001; Denef et al., 2001), in greater soil nutrient availability (Gestel et al., 1993; Nguyen and Marschner, 2005), in higher microbial activity (Birch, 1958; Gordon et al., 2008) or in the turnover of microbial matter (Gestel et al., 1991). Yet, aggregate protection of BC may not have occurred in this study, because BC was incubated in a sand medium and aggregates did not form. In addition, low amounts of labile C sources may have restricted microbial activity in general. Further studies are warranted that include clay minerals of varying mineralogy as well as labile C addition.

BC–C loss of between 6% and 21% during the first year was rapid compared to estimated mean residence times for both naturally-produced and anthropogenic BC in the soil environment, which were estimated to exceed 1000 years (Skjemstad et al., 1998; Swift, 2001; Schmidt et al., 2002; Cheng et al., 2008b; Lehmann et al., 2008). The rapid decomposition of BC in our study could result from a numbers of reasons:

(1) High and consistent incubation temperature was applied throughout, facilitating BC oxidation and thereby decomposition. BC may show unusually great increases in mineralization rate as a result of increasing incubation temperature as a result of its high chemical stability (Davidson and Janssens, 2006). Cheng et al. (2008b) calculated an increase in mineralization of BC produced from hardwood by a factor of 3.4 with every 10 °C temperature increase (the so-called Q_{10}), which is at the upper end of Q_{10} values found for uncharred litter.
(2) Mixing BC with sand created an oxygen-rich environment, promoting rapid oxidation of BC.
(3) BC-protecting mechanisms were unavailable. In soil, BC particles are either physically encapsulated into micro-aggregates (Brodowski et al., 2006), or may form interactions with mineral surfaces (Glaser et al., 2000) or may adsorb non-BC organic matter (Liang et al., 2006), thereby reducing decomposition. It is likely that this effect is the most important reason for the observed difference.
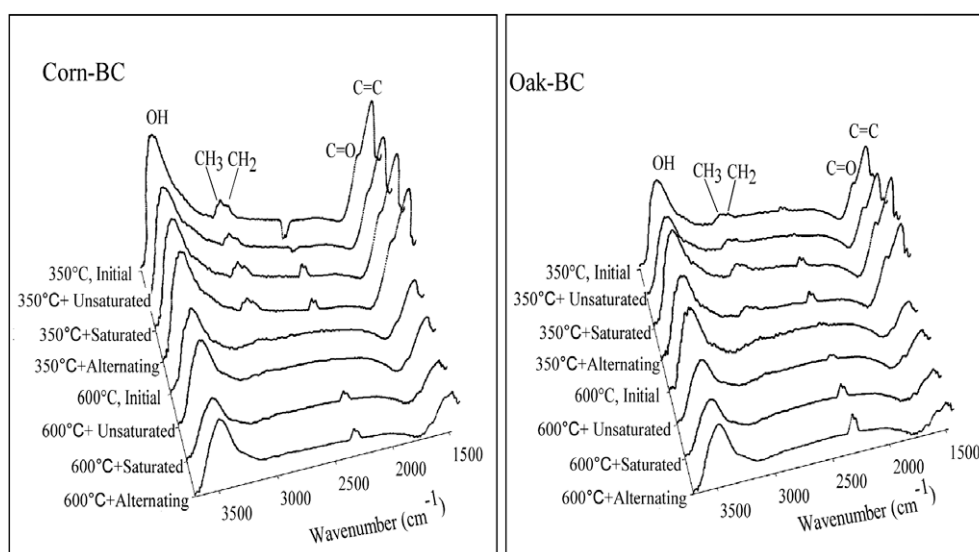

Fig. 1. FTIR spectra of corn and oak BC materials before and after 1 year's incubation as influenced by water regime and production temperature. FTIR spectroscopy was applied to pH-standardized BC particles collected from eight replicates.

(4) A significant amount of an easily decomposable fraction of BC used in this study as well as surfaces of BC may have reacted quickly and been completely mineralized to CO_2 soon after the incubation started. A preferential mineralization of a labile BC fraction is confirmed by the observed reduction in alkyl C (dealkylation) after incubation (Fig. 1). Rapid surface oxidation and disappearance of comparatively labile aliphatic C forms during 4 months incubation at 30 °C were found by Cheng et al. (2006) for hardwood BC. In addition, BC produced using slow pyrolysis under an N_2 atmosphere is likely different in chemical and structural properties from BC produced naturally partly under conditions of abundant oxygen. This may contribute to differences in stability of BC between the current and other studies.

However, absolute C loss rates in this study were even higher than those from other incubation studies using sand media. In a 60 day incubation Hamer et al. (2004) reported a C loss rate of 0.3% 60 day^{-1} for oak BC and 0.8% 60 day^{-1} for maize BC. The incubation temperature (20 °C) in their study was significantly lower than that (30 °C) in our study, which may explain the difference in C loss rate, in addition to the difference in length of incubation time. Similar explanations may hold for comparison with data from Baldock and Smernik (2002), who reported a C mineralization rate below 2% for sapwood BC formed at 200–300 °C in a 120 day incubation at 25 °C.

4.2. BC quality

The effect of water regime on mineralization rate largely depended on BC source material, with greater effects observed for the more labile types of BC, produced from corn and at lower temperature. These differences in C loss and oxidation under varying water regime may be attributed to different BC physical and chemical properties. Physically, corn BC was soft, friable and easily broken down; in contrast, oak BC was hard and more resistant to pressure. In general, a lower plant density corresponds to a lower BC density (Byrne and Nagle, 1997) reflecting the structures of the original plant tissue in BC materials formed at low production temperature (Brodowski et al., 2005; Kim and Hanna, 2006). Consequently, corn residue, which has a low density, formed low-density BC material, while the hardwood of oak created high-density BC material in this study.

Chemically, higher charring temperature increasingly changed O-alkyl C to aryl and O-aryl furan-like structures (Baldock and Smernik, 2002; Masiello, 2004) reflecting increased condensation of C structures (Nishimiya et al., 1998). Consequently we observed higher aromaticity, lower H/C and O/C ratios in BC produced at 600 °C than at 350 °C (Table 1). Similar increases in C associated with decreases in H and O contents have been described for many different biomass types over the temperature range examined here (Czimczik et al., 2002; Antal and Grønli, 2003; Mochidzuki et al., 2003; Braadbaart et al., 2004; Trompowsky et al., 2005). With respect to the differences between feedstock, a higher decomposition rate of corn BC that shows lower C/N values and aryl C contents but higher O/C values is consistent with findings by Hamer et al. (2004) and Antal and Grønli (2003).

The lack of a correlation between oxidation or C loss and pH changes (Table 3) may be the result of two different processes. Oxidation indeed increases carboxyl C groups, with significant acidity as seen from the FTIR results and the O/C values. The same conclusions were drawn by Cheng et al. (2006) for incubation of BC produced from hardwood. At the same time, however, dissolution of mineral matter originating from high ash-containing biomass increases the pH, as seen for corn BC, which contained 1.5% alkaline metals such as Na, K, Mg and Ca in comparison to 0.3% in oak. The

release of these alkaline metals may compensate for acidification by oxidation, resulting in a net increase in pH with corn BC, whereas small contents of the alkaline metals in oak BC were insufficient to compensate for oxidation, resulting in a net pH decrease as shown in Table 2.

4.3. Decomposition processes

Although relatively stable compared to uncharred organic matter (Baldock and Smernik, 2002), BC was mineralized in this study, with significant differences depending on moisture conditions and BC properties. Reported BC decomposition likely followed two major processes (i) microbial degradation (Hamer et al., 2004) and (ii) abiotic oxidation (Cheng et al., 2006; Cohen-Ofri et al., 2007). Oxidation may play an important role in controlling BC stability in this study, as we observed significant correlation coefficients between O/C ratio and C loss rate (Table 3). Likewise, Cohen-Ofri et al. (2007) concluded that oxidation processes were the major mechanism degrading fossilized charcoal.

The C loss under saturated conditions was significant even though the BC was submerged for the duration of the experiment. Either the dissolved oxygen content in the water was sufficient for microorganisms to oxidize the BC, or other sources of oxygen were present for both biotic and abiotic oxidation. For example, Endo et al. (1996) concluded that oxidation with MnO_2 converted benzyl alcohols to the corresponding aldehydes. Moreover, Lequart et al. (1998) reported a decrease in lignin content collected from wheat straw when incubated with Na oxalate and MnO_2-buffering solution for 20 h at room temperature. They concluded that interaction between MnO_2 and oxalate directly oxidized lignin phenolic moieties. In our study, Mn was detected in corn BC, but not in oak BC. Mn species may interact with oxalate from the inoculum or BC decomposition products, serving as an abiotic catalytic reagent in BC oxidation and degradation. In addition, NO_3^- and Mn^{2+} added with the nutrient solution as well as minerals in the BC can serve as electron acceptors, facilitating BC oxidation under oxygen-limited conditions. Under saturated conditions, O/C ratio was significantly correlated with CECp ($r^2 = 0.48$, $P < 0.05$) but not significantly with C loss ($r^2 = 0.05$, $P > 0.05$), whereas under unsaturated conditions O/C ratio significantly correlated with both CECp ($r^2 = 0.58$, $P < 005$) and C loss ($r^2 = 0.59$, $P < 005$). This indicates that, under oxygen-limited conditions, oxidation may significantly decompose BC and thereby enhance CECp, but may not be strong enough to mineralize BC to carbon dioxide to account for significant C loss. Additional mechanisms, such as those using NO_3^- or Mn^{2+} as electron acceptors, may have been responsible for BC mineralization. Such mechanisms require further investigation.

In addition, minerals may have also directly influenced BC stability. Significant amounts of minerals in corn BC may possibly cause defects in aromatic structures, reducing cross links between layers to reduce the stability of an overall structure that is dominated by C links. Minerals may also have indirectly affected BC mineralization through microbial activity. Microbial biomass is not only enhanced by N but also by nutrients such as K (Xiao et al., 2007). As a result, greater mineral content in corn BC may have led to greater microbial activity and consequent biotic oxidation of BC.

Oxidation again depended on BC quality and the greater recalcitrance of oak BC than corn BC resulted in lower surface oxidation and CEC. A number of studies reported BC oxidation and consequent increase in negative surface charge (CECp). Glaser et al. (2002) assumed that formation of carboxylic groups by oxidation on the edges of the aromatic backbone of BC was responsible for increasing CEC. As a result, the high CEC of Amazonian Dark Earths was attributed to BC oxidation (Glaser et al., 2003; Liang et al., 2006). Oxidation was demonstrated to start from surfaces of BC

particles and to penetrate to a limited extent into BC particles over long periods of time (Lehmann et al., 2005; Cheng et al., 2006; Nguyen et al., 2008). Consequently, changes were more pronounced for CECp than for oxidized functional groups determined from FTIR, because CECp was quantified on the basis of NH_4^+ exchange, which captures only surface negative charge, in contrast to FTIR analysis of finely ground BC powder, characterizing entire BC particles. Surface oxidation of BC may therefore explain the comparatively rapid BC losses to a greater extent than oxidation of the bulk BC. This observation agrees with results showing oxidized functional groups being limited to BC surfaces even after several hundreds (Nguyen et al., 2008) to thousands of years (Lehmann et al., 2005).

4.4. Environmental implications

The difference in C loss between moisture conditions was likely related to availability of oxygen. As a result, one may expect BC materials to be present in smaller amounts in aerated soils but in high amounts in wetlands. However, a number of reasons contribute to such differences, involving BC production and transport in addition to mineralization (Czimzcik and Masiello, 2007). The differences between saturated and unsaturated conditions found in our study do not fully explain estimated differences between mean residence times in soils of hundreds to thousands of years (Skjemstad et al., 1998; Bird et al., 1999; Swift, 2001; Cheng et al., 2008b; Lehmann et al., 2008) and presence in ocean sediments for more than 13,000 years as reported by Masiello and Druffel (1998). This may be a result of extremely oxygen-limiting conditions in deep sea sediments compared to terrestrial environments, because of differential effects of the labile fraction of BC or of still high oxygen availability even in the saturated incubation vessels.

In this study, BC changes and mineralization were studied under controlled conditions using a sand medium that was inoculated with a microbial culture to investigate the relative effects of different water regimes. BC in the soil environment is likely influenced by a number of additional factors, including presence of other organic matter that could lead to co-metabolism (Hamer et al., 2004), soil minerals (with varying mineralogy) or soil tillage (Nguyen et al., 2008), which may result in differential responses of BC materials. In addition, a well-defined BC produced under N_2 was added at the beginning and environmental conditions such as temperature were kept constant during the study, which is not the case in the environment. These experimental conditions are limitations when translating the findings to mineralization rates that would likely be observed in natural or managed landscapes. However, the study provides several guiding principles for investigation of the effect of water regime on BC stability in the environment that are difficult to isolate under natural conditions.

5. Conclusions

BC mineralization and changes in BC properties such as acidity and negative surface charge significantly depended on water regime and initial properties of BC materials. Notably, the effects of water regime greatly differed depending on the initial properties. The more labile BC types, such as those produced from corn or at lower temperature were subject to greater change in quantity and quality by different water regimes than more stable BC forms. This may indicate that changes for more stable BC can be more easily predicted than for less stable BC. Changes over time also depended on initial BC properties, to the extent that increases in pH values in corn BC contrasted with decreases in oak BC. Oxidation processes were shown to be a major mechanism responsible for BC change and mineralization. However, mechanisms controlling BC decomposition under submerged conditions require addi-

tional research. The findings suggest future studies that should include different minerals, organic matter and changing water regimes under natural conditions.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.orggeochem.2009.05.004.

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