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Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence

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Abstract

The aim of this work was to investigate changes in molecular form and surface charge of black carbon (BC) due to long-term natural oxidation and to examine how climatic and soil factors affect BC oxidation. Black C was collected from 11 historical charcoal blast furnace sites with a geographic distribution from Quebec, Canada, to Georgia, USA, and compared to BC that was newly produced (new BC) using rebuilt historical kilns. The results showed that the historical BC samples were substantially oxidized after 130 years in soils as compared to new BC or BC incubated for one year. The major alterations by natural oxidation of BC included: (1) changes in elemental composition with increases in oxygen (O) from 7.2% in new BC to 24.8% in historical BC and decreases in C from 90.8% to 70.5%; (2) formation of oxygen-containing functional groups, particularly carboxylic and phenolic functional groups, and (3) disappearance of surface positive charge and evolution of surface negative charge after 12 months of incubation. Although time of exposure significantly increased natural oxidation of BC, a significant positive relationship between mean annual temperature (MAT) and BC oxidation (O/C ratio with $r = 0.83$; $P < 0.01$) explained that BC oxidation was increased by 87 mmole kg C^{-1} per unit Celsius increase in MAT. This long-term oxidation was more pronounced on BC surfaces than for entire particles, and responded 7-fold stronger to increases in MAT. Our results also indicated that oxidation of BC was more important than adsorption of non-BC. Thus, natural oxidation of BC may play an important role in the effects of BC on soil biogeochemistry.

1. INTRODUCTION

Black carbon (BC) is the residue of incomplete combustion of biomass or fossil fuel. Black C is regarded as a chemically and biologically very stable C pool and can persist in nature for long periods of time (Goldberg, 1985; Schmidt and Noack, 2000; Knicker, 2007). Charring biomass into BC therefore has been proposed as a way to divert C from a rapid biological C cycle into a slow geological C cycle (Kuhlbusch and Crutzen, 1995) and prompts investigations into actively managing BC as a means to sequester atmospheric carbon dioxide in soils (Lehmann et al., 2006; Lehmann, 2007a,b).

However, the long-term persistence of BC does not mean that the properties of BC remain unchanged after its deposition. Puri (1961) and Cheng et al. (2006) have reported rapid oxidation of BC in short-term incubations, whereby BC properties were altered through the formation of oxygen-containing functional groups. Oxidation of BC in soils has important implications for BC transport (Hockaday et al., 2006), erosion (Rumpel et al., 2006), stability (Bird et al., 1999; Czimczik and Masiello, 2007), and cation retention (Liang et al., 2006). Up to now, however, systematic research about the natural oxidation of BC in soils remains scarce and little is known about such aspects as to how fast or to what extent BC is oxidized.

In addition, because BC is ubiquitous and found in a wide variety of environments (Goldberg, 1985), it is essen-

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tial to investigate the differences of natural oxidation of BC under different climatic and soil regimes. We know that oxidation and decomposition of organic matter and litter typically increase with temperature (Davidson and Janssens, 2006). However, our understanding of the factors that affect natural oxidation of BC across different climates is limited. Biotic (Hamer et al., 2004) and abiotic processes, such as greater temperature (Puri, 1961; Cheng et al., 2006) and moisture (Billinge and Evans, 1984), may facilitate BC oxidation, while aggregate protection of BC (Glaser et al., 2000; Brodowski et al., 2005) promoted in fine-textured soils may reduce BC oxidation. To what extent these processes affect oxidation of BC in soils across a range of different environments is not known.

Due to the high recalcitrance of BC, designing suitable laboratory or field experiments to investigate the long-term natural oxidation of BC is a challenge. In this study, we made use of BC samples from historical charcoal blast furnace sites in Quebec, Canada and the eastern U.S. These historical BC samples had similar deposition time, charring conditions and precursor wood. In addition, new BC made by the same method as the historical BC was collected to represent the “original” BC and was compared to the historical BC samples retrieved from soil. The wide geographic distribution of charcoal blast furnaces also made it possible to examine climatic and soil effects on historical BC samples. Our objective was to investigate changes in molecular form and surface charge of BC due to long-term natural oxidation along a climosequence. We hypothesized that long-term natural oxidation of BC leads to significant changes in both molecular form and surface charge and that the extent of BC oxidation is facilitated by greater temperature, moisture and biological activity but reduced by higher soil clay contents.

2. MATERIALS AND METHODS

2.1. Historical and new BC samples

Historical BC samples were collected from the remnants of historical charcoal blast furnaces. The BC found in soils near these furnace sites was only deposited during a relatively short period around the 1870s, as the rapid depletion of forest resources soon led to the replacement of charcoal furnaces by anthracite furnaces (Warren, 1973). The charcoal used for the blast furnaces was only produced from specific hardwoods. High specific gravity, crushing strength, and density were required, which was found in woods such as chestnut, hickory, oak, and sugar maple (Bining, 1938). In contrast to BC produced in forest fires, historical BC generated by colliers (charcoal workers) was of relatively uniform quality (Rolando, 1992).

In the 19th century, every eastern state in the U.S. (except for Delaware) had at least one furnace. In this study, eleven historical charcoal furnaces sites, spanning along a climosequence from Quebec (QC) to Georgia (GA), were selected. Some historical background and the climatic and soil characteristics of the selected furnace sites are shown in Table 1. Mean annual temperature (MAT), mean annual precipitation (MAP) and potential evapotranspiration

Table 1
Historical backgrounds and the climatic and soil characteristics of the selected historical charcoal blast furnaces in Canada and the U.S.

	Location	Vegetation type[b]	Abandoned year	MAT[c] (°C)	MAP[d] (mm)	PET[e] (mm)	Soil properties						
							C (g kg^{-1})	N (g kg^{-1})	pH (H_2O)	pH (KCl)	Silt (g kg^{-1})	Clay (g kg^{-1})	C_{min}[f] (g kg soil^{-1})
QC[a]	Trois-Riviera	G	1883	3.9	1030	470	404	6	4.9	3.7	260	230	1.07
NY	Port Henry	BL	1875	6.2	900	610	300	7	6.2	4.9	220	190	1.61
CT	Canaan	BL/G	1918	9.4	1190	635	364	4	7.2	6.4	170	220	0.71
PA-1	Huntingdon	BL	1874	9.4	940	635	303	6	7.2	6.6	210	280	1.46
PA-2	Huntingdon	C	1904	9.4	940	635	520	5	4.8	3.7	230	240	0.70
NJ	Oxford	BL	1884	10.0	1150	660	176	3	5.9	4.7	240	260	0.63
OH	Jackson	G/BL	1894	11.1	1070	755	212	2	6.1	5.0	180	340	0.23
MD	Snow Hill	C	1894	13.3	1030	710	165	2	4.5	2.8	210	80	0.47
KY	Cadiz	BL	1860	13.6	1290	850	250	4	6.5	5.4	170	500	0.87
TN	Dickson	BL	1850	14.4	1370	845	224	3	6.1	4.1	270	540	1.11
GA	Cartersville	BL	1864	15.7	1210	865	130	3	5.8	4.8	270	310	1.13

[a] Abbreviations of the province of Canada and the states of the U.S.
[b] Vegetation type: G, Grass; BL, broadleaf; C, conifer.
[c] MAT: mean annual temperature.
[d] MAP: mean annual precipitation.
[e] PET: potential evaportranspiration.
[f] C_{min}: potential cumulative mineralized C (g C—CO_2 per kg soil) for a 20-day incubation at 30 °C.

(PET) for each site were obtained from long-term climate data of the closest recording station. Effective precipitation was defined as MAP minus PET (MAP – PET) and was used to represent soil moisture conditions (Clark and Royall, 1995). Samples of soils containing high levels of BC (BC-containing soils) were collected from the areas where furnace workers temporarily stored the charcoal before charging it into the furnace. Dark black soil color and even large BC fragments are conspicuous in these BC-containing soils. For each soil, at least five soil cores were collected.

Since we focused on the natural oxidation of BC itself and intended to minimize any artifact caused by adhering soil or organic matter, more than 40 large fragments of BC with a size over 4 mm, which were carefully picked from soil samples at a depth between 0.1 and 0.2 m, were pooled and used in this research. Isolated BC fragments were repeatedly rinsed with distilled water until the electric conductivity was close to the background of distilled water. The BC fragments were then oven-dried at 70 °C for 24 h for further analyses.

In addition to the historical BC samples, new BC samples produced in Pennsylvania at the Hopewell Furnace National Historic Site (New-BC_{HW}) and at the Greenwood Furnace State Park (New-BC_{GW}) were collected. Both of these new BC samples were made by the same traditional charcoal-making method, as done by charcoal workers in the 19th century. Charring conditions were carefully tended by the park rangers to obtain a high-quality metallurgical charcoal (Rolando, 1992). A mixture of white and red oak was charred at Hopewell (NEW-BC_{HW}), and only white oak wood was charred at Greenwood (NEW-BC_{GW}). The new BC samples are expected to have properties that were very close to the “original” status of the historical BC samples and were taken here to represent time-zero BC samples. The collected new BC samples were stored in glass jars purged with nitrogen gas to prevent further oxidation.

In order to provide the fundamental understanding of long-term natural oxidation of BC, new BC from the Hopewell Furnace (New-BC_{HW}) was subjected to short-term aging experiments and coating with humic acid (HA; Sigma–Aldrich, St. Louis, Missouri, USA) for simulating short-term BC exposure in soils. In the aging experiments, 4 mL deionized water was added to 10 g of new BC and incubated in the dark inside 500-mL glass jars at 30 °C and 70 °C for 12 months (denoted as BC30 and BC70) or at 70 °C for 6 months (denoted as $BC70_{6M}$, only for XPS analysis). Glass jars were opened for aeration, as well as verification and adjustment of the water contents, every week for the first two months and then every other week during the rest of the incubation. It was expected that a higher temperature would enhance the degree of oxidation compared to a lower temperature (Cheng et al., 2006). No inoculant was added, as the oxidation during the first few months was expected to be dominated by abiotic processes (Cheng et al., 2006). In the experiment of coating BC with HA, HA solution was prepared by dissolving 200 mg HA in 50 mL 0.1 N NaOH solution, and deionized water was added to make up the 200 mg L^{-1} HA solution. Forty milliliters of 200 mg L^{-1} HA solution were added to 2 g of BC and shaken for 3 days. Throughout shaking, the pH of the BC slurry was adjusted by 1 N HCl to a constant pH value of 6.8. After coating, the BC was washed with deionized water until the color of the filtrate was clear and reached a constant pH and then oven-dried at 70 °C for 24 h. The dissolved C of filtrates for both BC slurry and control HA solution was measured by a carbon analyzer (Model 1010 TOC Analyzer, OI Analytical, Texas) and the difference of dissolved C concentration was assumed to be the adsorption of HA. In this study, 2.52 mg HA were sorbed to 1 g of BC.

2.2. Analyses of BC fragments and soils

Total C and nitrogen (N) concentrations of BC fragments were measured by dry combustion using a Europa ANCA GSL sample combustion unit (PDZ Europa, Crewe, UK). Hydrogen (H) concentrations were measured after BC sample conversion to H_2 at 1400 °C over glassy C (Hekatech TCEA, Hekatech GmbH, Wegberg, Germany). Ash content was analyzed by the loss of weight via combusting the BC sample at 550 °C for 2 h. Oxygen (O) concentrations were determined by difference. Elemental composition of C, N, H, and O of BC samples were presented on a dry ash-free basis.

In addition to the BC fragments, the properties of BC-containing soils were measured as well. Total C and N concentrations of the BC-containing soils were measured by dry combustion. Soil texture was measured on adjacent soils which contained no visible BC particles using the hydrometer method. Potential soil biological activity was evaluated by measuring the cumulative soil C mineralization rate of the BC-containing soils over a 20-day incubation period. The incubation was carried out at the same temperature of 30 °C for all soils in the dark under 60% water holding capacity. The evolved CO_2 was trapped in 10 mL 0.1 N NaOH, which is placed in a small vessel inside the incubation jar, and measured by titration of the NaOH solution with standard 0.1 N HCl in excess of $BaCl_2$. The mineralized CO_2 was displayed per unit soil (g $C{-}CO_2$ kg $soil^{-1}$). Soil pH was measured in 1:2.5 (w/v) ratio with H_2O or 1 N KCl solution. In this study, pH values in BC fragments (1:20 w/v ratio) were close to the corresponding pH values in BC-containing soils.

2.3. X-ray photoelectron spectroscopy (XPS)

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). The 98-W, 107-μm diameter X-rays were rastered over a 1.4 by 0.2 mm rectangle on the sample. The XPS survey scan spectra in the 1000–0 eV binding energy range were recorded with a pass energy of 50 eV. High-energy resolution scan spectra of C1s were recorded in 0.2 eV steps with a pass energy of 20 eV. Low energy electrons and Ar ions were conducted for specimen neutralization in each measurement. In this study, XPS measurements were performed on both intact BC particles and ground BC samples representing the surface and entire particle, respectively (Cheng et al., 2006). Here, unwashed intact BC particles of 1–2 mm in size were used. The approximate amount of O bound to C (Oc) was obtained by subtraction of the contribution of inorganic O from total O contents, and was calculated using the following equation (Brodowski et al., 2005):

$$\begin{aligned}\mathrm{Oc} = \mathrm{O}\ (\text{total O}) - (\mathrm{Na} * 0.5 + \mathrm{Mg} * 1 + \mathrm{Al} * 1.5 \\ + \mathrm{Si} * 2 + \mathrm{K} * 0.5 + \mathrm{Ca} * 1 + \mathrm{Fe} * 1.176)\end{aligned} \quad (1)$$

For the narrow scan C1s spectra, the spectra were deconvoluted by a non-linear least squares curve fitting program (XPSPEAK Version 4.1 software) with a Gaussian-Lorentzian mix function and Shirley background subtraction. The C1s binding energy for C═C, C─C and C─H was assigned to 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). In this experiment, new BC and seven historical BC samples, including QC, NY, CT, OH, MD, TN, and GA, were measured.

2.4. Fourier transform infrared (FTIR)

The spectra of FTIR absorbance were recorded between 400 and 4000 cm^{-1} with a Matteson Model 5020 FTIR Spectrometer (Madison, Wisconsin, USA). Potassium bromide (KBr) pellets containing 0.3% of finely ground BC powder were prepared and scanned. One hundred scans from 400 to 4000 cm^{-1} were averaged with a resolution of 4 cm^{-1}.

In addition to the FTIR measurement of all BC samples, a series of pH adjustments of the QC and CT BC samples were also measured by FTIR. Basic and acidic QC and CT BC samples were obtained by adding 0.1 N HCl and KOH to the BC suspension (1:200 w/v ratio). The pH of the BC suspension was determined after shaking the suspension for 24 h and was applied to represent the adjusted pH of BC. Black C samples with pH adjustments were separated by centrifugation and dried at 70 °C for 24 h.

2.5. Surface charge characteristics

The surface charge of BC samples was assessed by the "index" or "indifferent" ion adsorption method (Uehara and Gillman, 1981; Chorover et al., 2006). A KCl electrolyte (0.01 N) was used in the present study, in which both K and Cl ions were assumed to be bound by non-specific adsorption. Briefly, the method comprised three main steps: (1) preparation of a KCl saturated BC paste, (2) adjustment of the pH of BC to a range of pH values under the same ionic strength, (3) displacement of adsorbed K and Cl by 1 N ammonium nitrate.

(1) BC saturation by KCl: Two grams BC were suspended in 20 mL of 1 N KCl in 30 mL centrifuge tubes for end-over-end shaking for 1 h. The suspension was then centrifuged at 48,000 RCF for 20 min. The supernatant was carefully aspirated and discarded. The remaining BC paste was repeatedly suspended in 0.2 N KCl and 0.01 N KCl for one and two times, respectively. After the last centrifugation step, the remaining BC paste was transferred to a petri dish, sealed with paraffin, and stored at 4 °C. The water content of the BC paste was measured by transferring a small portion of the BC paste to an aluminum dish and drying it at 105 °C for 24 h.

(2) pH adjustment: Around 0.15 g of the BC paste (on a dry weight basis) was transferred to 30 mL preweighed centrifuge tubes. Twenty milliliters 0.01 N KCl, adjusted by 0.1 N KOH or HCl across an adequate pH range under the same ionic strength, was added to a batch of the tubes. The tubes were shaken for 12 h and then centrifuged at 48,000 RCF for 20 min. The supernatant was carefully aspirated to a 30 mL bottle and the pH value was measured immediately. The concentrations of K and Cl in the supernatant were measured as well. The tubes with BC and entrained solution (0.01 N KCl) were weighed to calculate the mass of entrained K and Cl inside the centrifuge tubes.

(3) Displacement of adsorbed K and Cl by ammonium nitrate: Twenty milliliters 1 N ammonium nitrate were added to the centrifuge tubes which were shaken for 1 h to displace the adsorbed K and Cl ions. After centrifuging at 48,000 RCF for 20 min, the solution was aspirated into 60 mL bottles. The displacement by ammonium nitrate was repeated twice and the extracts pooled. The concentration of K and Cl extracted by 1 N ammonium nitrate solution was measured. Potassium ions were measured by atomic absorption spectrometry (Instrumentation Laboratory, Lexington, Massachusetts, USA) and Cl ions were measured by a chloridometer (Haake Buchler Instruments, Saddle Brook, New Jersey, USA).

The adsorption of K and Cl ions by BC was calculated using the following equation:

$$\mathrm{K\ or\ Cl} = n_{\mathrm{K}}\ (\mathrm{or}\ n_{\mathrm{Cl}}) - M_{\mathrm{entr}} m_{\mathrm{k}} (\mathrm{or}\ M_{\mathrm{entr}} m_{\mathrm{cl}}) \quad (2)$$

where n_{K} or n_{Cl} was the K and Cl determined in 1.0 N ammonium nitrate (in step 3). M_{entr} denotes the mass of entrained solution left in the centrifuge tube before ammonium nitrate replacement (in step 2), and m_{K} or m_{Cl} denotes the concentration of K or Cl ions in the supernatant (in step 2). Surface positive charge was defined as the adsorption of anions (Cl^{-}), and surface negative charge was the adsorption of cations (K^{+}).

In this study, surface charge of BC was represented on a C basis (mmole kg C^{-1}). A quadratic model was used for fitting surface charge and pH. Point of zero net charge (PZNC) was defined as the pH that had an equal amount of surface positive and negative charge. Anion exchange capacity (AEC) was defined as the amount of net surface positive charge at pH 3.5; effective cation exchange capacity (ECEC) was defined as the amount of surface negative charge at BC's pH (under H_2O or 1 N KCl suspension); and potential cation exchange capacity (PCEC) was defined as the amount of surface negative charge at pH 7.

2.6. Relationships between BC oxidation and the climatic and soil characteristics

Simple linear correlations between BC oxidation and the climatic and soil characteristics were conducted for examining if the properties of historical BC were related to climatic and soil characteristics. Stepwise multivariate regressions (SAS 9.1, Proc Reg, SAS Institute, Cary, NC) confirmed the observations of these individual correlations. The examined parameters of BC oxidation included elemental C and O concentrations, atomic O/C ratios, PCEC, and ECEC at pH_{H_2O} and pH_{KCl}. The examined climatic and soil characteristics included MAT, MAP, effective precipitation (MAP – PET), soil pH, clay content, soil C/N ratio, and soil mineralized C as a proxi for microbial activity. Since the data from the XPS and FTIR measurements were qualitative rather than quantitative, these results were not included in the correlation model. In a separate study, it was shown that the BC-containing soils under conifer vegetation had higher C storage than the soils under broadleaf or grass vegetation (Cheng, 2008). Therefore, correlations between BC oxidation and the climatic and soil characteristics were only conducted for the sites under broadleaf and grass vegetation.

3. RESULTS

3.1. Elemental composition and molecular structure

New BC contained high amounts of C (90.8%) and low amounts of O (7.2%) and H (1.7%) (Fig. 1a and Table EA1). With coating of HA (BC-HA), very small decreases in C and increases in O were found, while aging of BC by incubation for 12 months showed a slightly higher reduction in C concentrations and increases in O and H concentrations. Carbon concentrations were reduced to 88.2% and 85.8%, while O concentrations increased to 9.2% and 10.6% and H concentrations to 2.4% and 3.4% for BC incubated at 30 °C (BC30) and 70 °C (BC70), respectively. In contrast, all historical BC samples displayed substantially decreased amounts of C and increased amounts of O and H. The average C concentration of historical BC samples was 70.5%, and average O and H concentrations were 24.8% and 4.5%. Natural oxidation of BC concomitantly increased atomic O/C ratios, from 0.06 in new BC to 0.26 in historical BC, and H/C ratios, from 0.23 to 0.76 (Fig. 1b and Table EA1).

Except for BC-HA which demonstrated comparatively lower C and higher O, the elemental compositions obtained from XPS measurements had similar trends compared to the elemental analyses, in that new BC had higher C and lower O concentrations compared to historical BC (Table 2). High-resolution XPS C1s spectra further indicated that the increases of O were due to the formation of oxygen-containing functional groups. Our data also showed that higher oxygen-containing functional groups, as well as lower C and O contents, were found on BC surfaces compared to entire particles for the historical BC samples and the sum of all oxygen-containing functional groups of the historical BC samples were two times higher than that of surfaces and 60% higher than that of the entire particles of new BC.

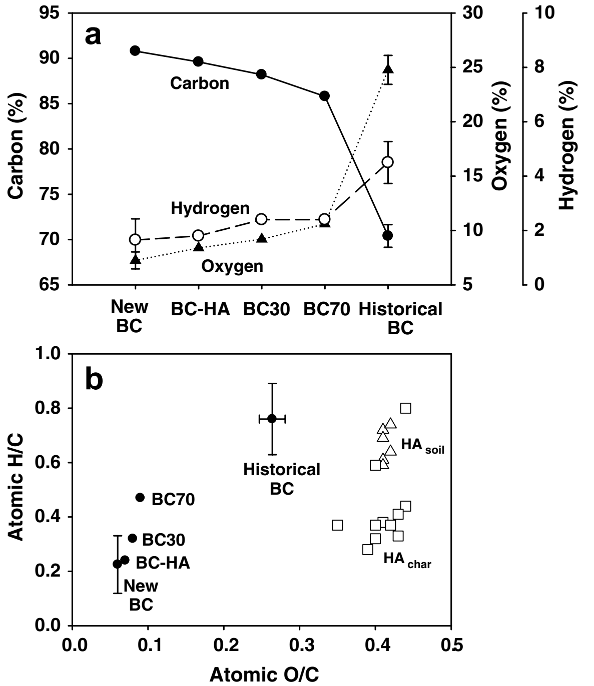

Fig. 1. (a) Elemental composition of carbon, oxygen and hydrogen; (b) atomic O/C versus H/C ratios (van Krevelen Diagram) of new ($n = 2$) and historical BC samples ($n = 11$). BC-HA represents the coating of new BC with HA. BC30 and BC70 denote aging of new BC under 30 and 70 °C for 12 months. HA$_{soil}$ (open triangles, Haumaier and Zech, 1995) and HA$_{char}$ (open squares, Trompowsky et al., 2006) represent the humic acid extracted from BC-rich soils and charcoal. Error bars represent 1 standard deviation.

The FTIR spectra of new BC, as well as BC-HA and BC30, showed a “flat” pattern and no bands were observed (Fig. 2). With progressive oxidation, the bands of functional groups evolved. The spectrum of BC70 showed discernable bands at wavenumbers of 1700 cm^{-1} and 1600 cm^{-1}. All historical BC displayed well resolved FTIR spectra (Fig. 2), with major bands at wavenumbers of 3400, 1700, 1600, 1585, 1380, and 1260 cm^{-1}. The band at 3400 cm^{-1} was assigned to OH bonds, 1700 cm^{-1} to carboxylic acid groups, 1600 cm^{-1} to molecular vibration of ring stretching in C═C, 1585 and 1380 cm^{-1}to carboxylate, and 1260 cm^{-1} to phenolic acid functional (C—O) and COOH groups (Starsinic et al., 1983; Guo and Bustin, 1998; Jia and Thomas, 2000).

Detailed FTIR measurements of QC and CT BC under different pH adjustments indicated that most bands of historical BC samples were pH dependent (Fig. 3). The band intensities at 1700 and 1260 cm^{-1} decreased with increasing pH; whereas the band intensities at 1585 and 1380 cm^{-1}increased with increasing pH. With the rise of pH values, the aromatic C═C band intensity at 1600 cm^{-1} was obscured by the increasing intensity of carboxylate bands at 1585 cm^{-1}. These results ascertained our band assignments.

Table 2
XPS widescan of the atomic compositions of carbon and oxygen and the deconvolution of C1s narrow scan spectra of new and historical BC samples

	Surface analyses								Bulk analyses							
	C (%)	Oc[a](%)	Oc/C	C1s composition (%)[b]					C (%)	Oc (%)	Oc/C	C1s composition (%)[b]				
				C=C	Sum[c]	C–O	C=O	COO				C=C	Sum[c]	C–O	C=O	COO
New BC																
New-BC$_{HW}$	91.3	8.7	0.10	77.5	22.3	15.4	3.6	3.3	ND	ND	ND	ND	ND	ND	ND	ND
New-BC$_{GW}$	90.2	9.6	0.11	77.2	22.9	14.5	4.5	3.9	ND	ND	ND	ND	ND	ND	ND	ND
BC-HA	84.0	14.5	0.17	71.0	28.9	19.3	4.6	5.0	ND	ND	ND	ND	ND	ND	ND	ND
BC70$_{6M}$[d]	86.5	13.0	0.15	71.2	28.8	19.9	4.1	4.8	ND	ND	ND	ND	ND	ND	ND	ND
Historical BC																
QC	61.1	30.5	0.50	50.5	49.5	25.9	17.0	6.6	77.3	21.1	0.27	67.8	32.2	16.1	8.8	7.3
NY	59.1	29.5	0.50	46.4	53.6	27.5	21.2	4.9	70.8	25.9	0.37	58.1	41.9	23.1	12.2	6.6
CT	ND	ND	ND	ND	ND	ND	ND	ND	69.7	25.8	0.37	61.4	38.6	17.6	12.2	8.8
OH	33.0	26.9	0.82	55.5	44.5	20.8	18.7	5.0	68.8	26.6	0.39	67.6	32.2	15.0	11.0	6.2
MD	51.3	27.4	0.54	49.3	50.7	28.1	16.4	6.2	75.0	23.5	0.31	65.2	34.8	17.1	10.1	7.6
TN	278	25.9	0.92	49.8	50.1	26.8	19.3	4.0	72.2	24.2	0.34	69.2	30.8	12.9	9.5	8.4
GA	30.6	34.0	1.11	46.5	53.6	29.1	20.5	4.0	67.7	28.2	0.42	62.2	37.9	17.9	11.5	8.5

ND, not determined.

[a] Oc: oxygen bound to carbon.

[b] 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 O–C=O.

[c] Sum of oxygen-containing functional groups.

[d] Incubation of new BC at 70 °C for 6 months.

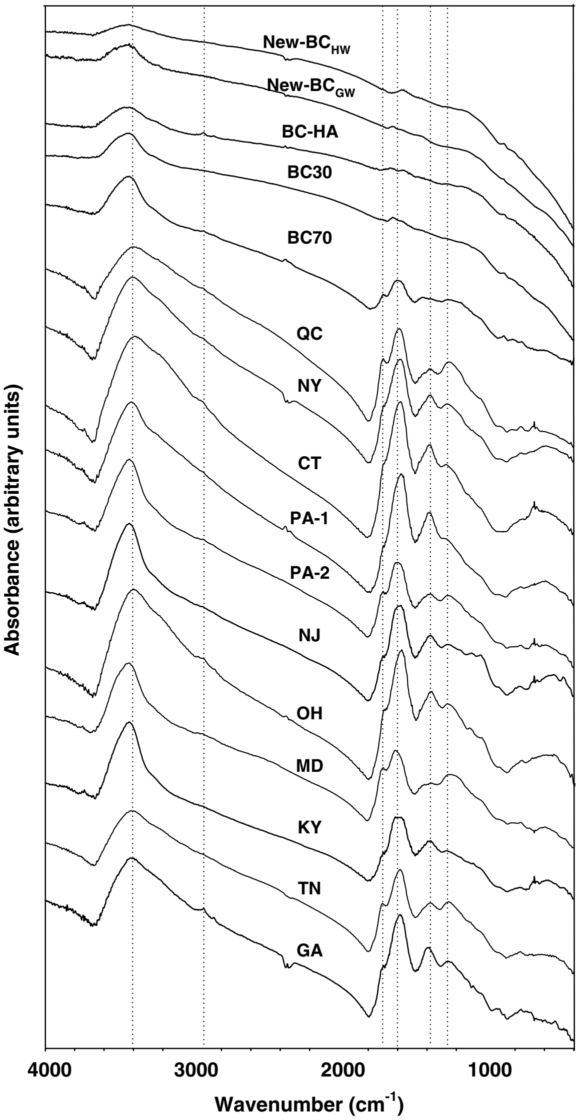

Fig. 2. FTIR spectra of new and historical BC samples. Flat spectra of new BC samples indicate absence of functional groups. With increasing oxidation of new BC, the band intensities are enhanced (BC70) and finally approach the well resolved spectra of historical BC. The band at 3400 cm^{-1} is assigned to OH bonds, 1700 cm^{-1} to carboxylic acid groups, 1600 cm^{-1} to molecular vibration of ring stretching in C=C, 1585 and 1380 cm^{-1}to carboxylate, and 1260 cm^{-1} to phenolic acid functional (C–O) and COOH groups.

3.2. Surface charge characteristics

The charge of most BC samples was strongly dependent on pH (Fig. 4). New BC had high amounts of surface positive charge (+71 mmole kg C^{-1} at pH 3.5), but very low amounts of surface negative charge (Table 3 and SI Table 2). With coating of HA (BC-HA), a slight decrease of positive charge and increase of surface negative charge were found, whereas aging of BC by a 12-month incubation caused greater alteration of surface charge than the coating of HA. Progressive oxidation of BC led to higher amounts

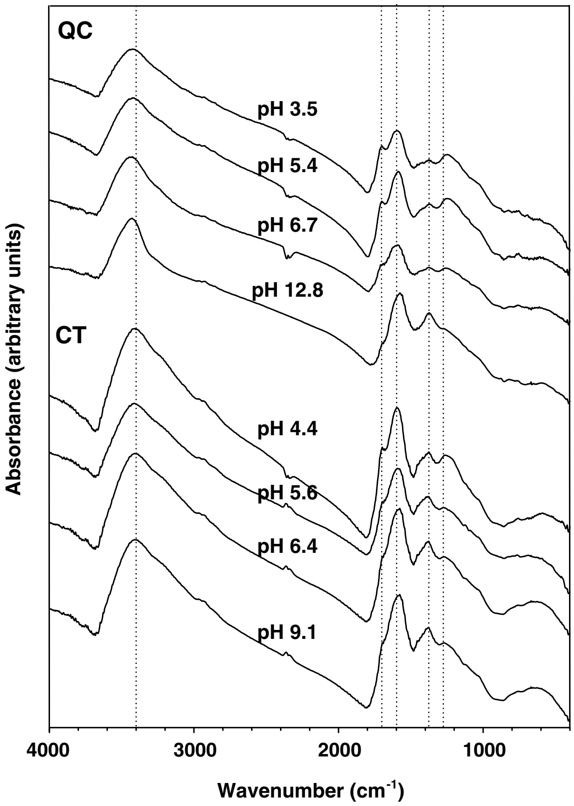

Fig. 3. FTIR spectra of the QC and CT BC samples at different pH values. Most bands are pH dependent and the band intensities at 1700 cm^{-1}(carboxylic groups) and 1260 cm^{-1} (carboxylic and phenolic groups) decrease with increasing pH, while the bands intensities at 1585 cm^{-1} (carboxylate) and 1380 cm^{-1} (carboxylate) increase with increasing pH.

of surface negative charge but lower amounts of surface positive charge, in which surface negative charge at pH 7.0 in BC70 was 201 mmole kg C^{-1} and BC30 was 71 mmole kg C^{-1} and surface positive charge in BC70 even diminished to zero. In contrast to new BC, all historical BC showed substantial amounts of surface negative charge and had an average surface negative charge of 1644 mmole kg C^{-1} at pH 7.0. At the same time, no positive charge existed in historical BC, which was similar to the results for BC70.

The PZNC of new BC was at pH 7.0 (Table 3). The PZNC of BC-HA slightly shifted to pH 6.8, while the PZNC dropped to pH 3.4 and 2.7 during aging of BC at 30 and 70 °C for 12 months, respectively. Similar to the aged BC, all historical BC samples showed acidic PZNC values of around pH 3.

3.3. Correlation between BC oxidation and climatic and soil characteristics

Of all climatic and soil characteristics examined, MAT was the best predictor for BC oxidation (Table 4, and Fig. EA1). Based on simple linear regression, MAT significantly explained 84% of the variability of C concentrations ($r = -0.92$; $P < 0.01$), 52% of the variability of O concentrations ($r = 0.72$; $P < 0.01$), 60% of the variability of atomic O/C ratios ($r = 0.78$; $P < 0.01$), and 69% of the variability of PCEC ($r = 0.83$; $P < 0.01$) (Fig. 5a). Thus, lower C concentrations and higher O concentrations, O/C ratios, and PCEC values were found for the BC samples from warmer areas. Effective CEC was significantly and positively correlated with soil pH, which explained 70% of the variability ($r = 0.85$ in average; $P < 0.01$), while no other correlation was found between pH and BC oxidation parameters. In addition, no other climatic or soil characteristic, such as MAP, effective precipitation (MAP-PET), C/N, clay content, or potential C mineralization, showed a significant correlation with BC oxidation.

MAT was better correlated with the Oc/C ratios of BC surfaces ($r = 0.97$; $P < 0.01$) than with the Oc/C ratios of entire BC particles ($r = 0.67$; $P > 0.05$; Fig. 5b). The Oc/C ratios of surfaces responded 7-fold stronger to increases in MAT than entire particles.

4. DISCUSSION

4.1. Natural oxidation of BC

Our data clearly indicate that historical BC samples, representing a wide variety of geographic environments, are substantially oxidized after 130 years of exposure to soil. The van Krevelen diagram demonstrates the fundamental pathway of natural oxidation of BC (Fig. 1b), and indicates that the processes of natural oxidation of increasing both atomic H/C and O/C ratios display an opposite trend from pyrolytic processes (Shindo, 1991; Baldock and Smernik, 2002). It is also interesting to note that the O/C ratios of humic acids extracted from charcoal (Trompowsky et al., 2006) and BC-containing soil (Haumaier and Zech, 1995) were significantly greater, while H/C ratios of soils were similar and H/C ratios of charcoal were lower than those of historical BC (Fig. 1b). Extracted humic acids from charcoal had an average H/C ratio of 0.5 and O/C ratio of 0.4 (Trompowsky et al., 2006), and BC-rich soils had an average H/C ratio of 0.67 and O/C ratio of 0.41 (Haumaier and Zech, 1995). Therefore, extractable HA from BC appeared to be more oxidized than the particulate BC studied here.

The differences between surface and bulk properties by XPS measurements highlight the fact that higher oxidative states were found on the surface region of BC particles relative to the interior (Brodowski et al., 2005; Lehmann et al., 2005; Liang et al., 2006). For the field BC samples, however, it is still difficult to unambiguously distinguish whether surface oxygen functional groups were due to adsorption of non-BC or the oxidation of BC itself. In our study, the significant relationship between MAT and surface atomic O/C ratios may suggest a significant contribution from surface oxidation of BC itself rather than adsorption of non-BC (Fig. 5b). The lower increase in oxidation and PCEC by coating with HA than short-term incubation points in the same direction. On the long term, the exposure of BC in soils still resulted in considerable penetration of BC oxidation into the interior compared to new BC samples.

The flat FTIR spectrum of new BC implies that the functional groups were completely eliminated during the charring processes (Nishimiva et al., 1998). With the oxidation of new BC, the band intensities were enhanced through the introduction of dipole moments from forming functional groups (Starsinic et al., 1983; Morterra et al., 1984) and finally approached a well resolved spectrum, as shown by historical BC. The distribution of bands for the different

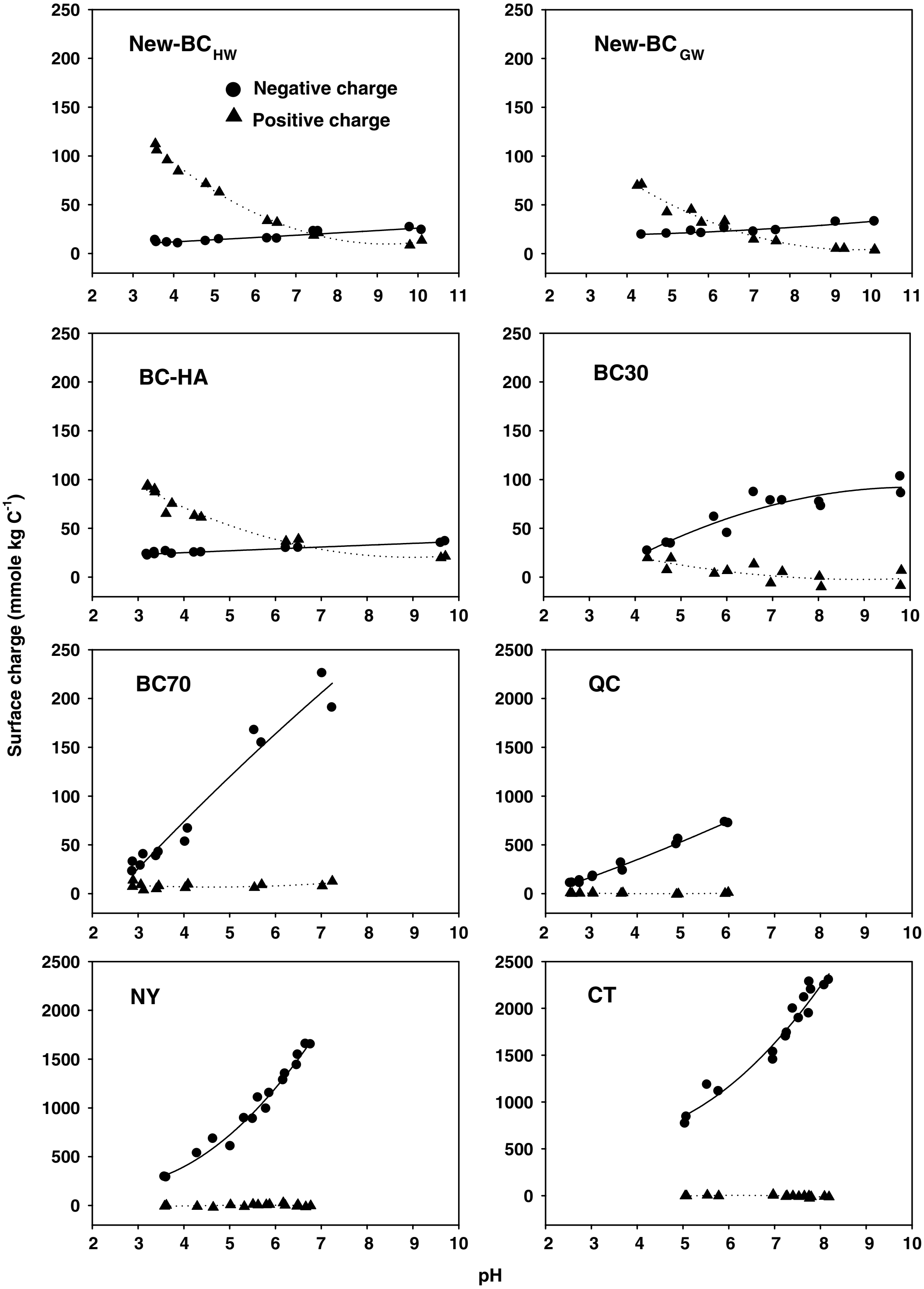

Fig. 4. The values of surface positive charge (triangles) and surface negative charge (circles) versus pH of new and historical BC samples. Quadratic regressions for surface positive charge and surface negative charge are shown with dotted and solid lines, respectively. Point of zero net charge (PZNC) is the pH of the intercept point between negative and positive charge curves. With progressive oxidation, positive charge decreases, negative charge increases, and PZNC shifts from pH 7 in new BC to pH 3 in historical BC. Note the different scale of the y axes between new and historical BC samples.

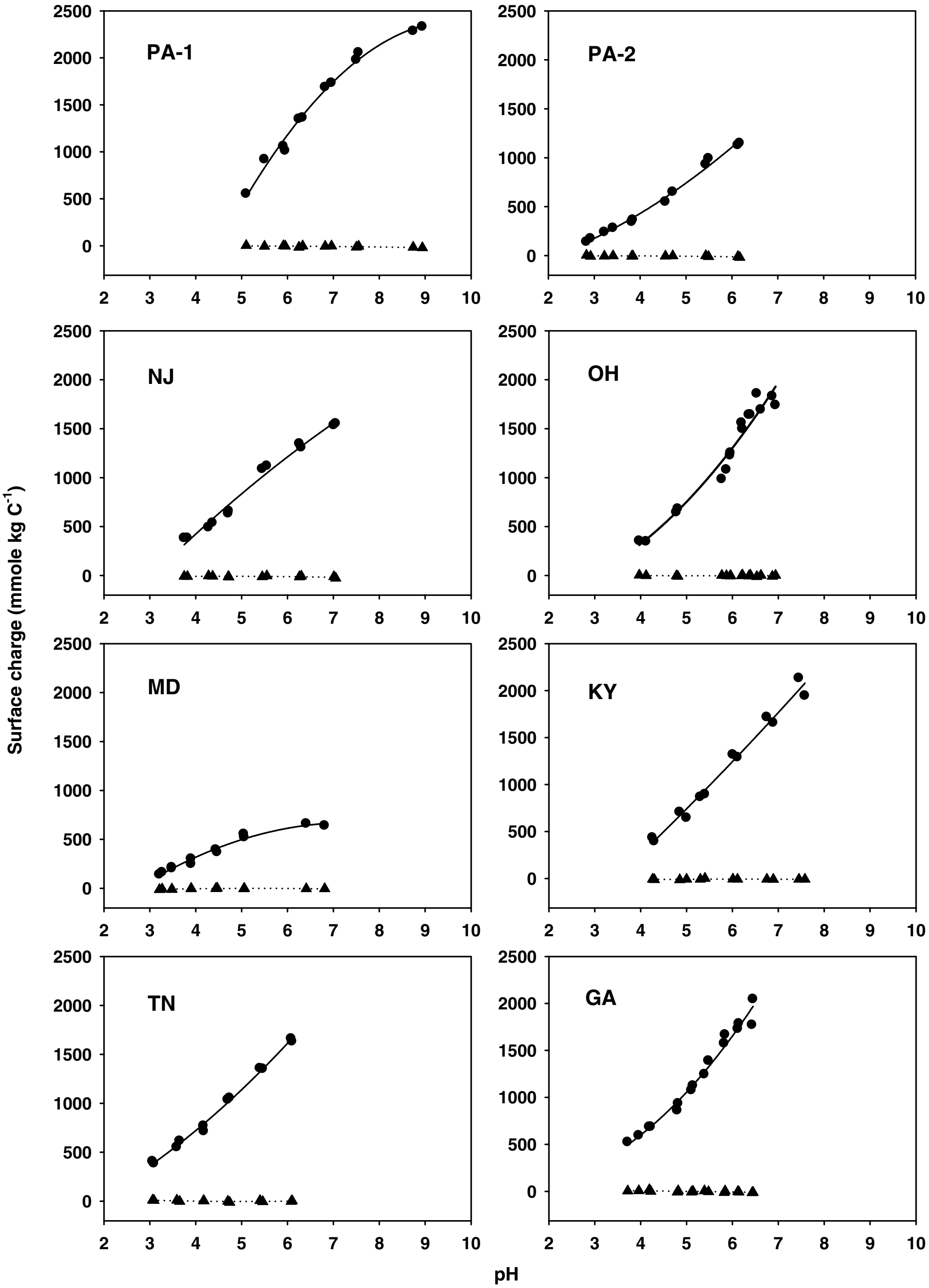

Fig. 4 (*continued*)

historical BC samples and therefore the main functional groups were similar, even though the BC samples were collected from different locations. Our results from XPS and FTIR directly indicate that the increase of O was not merely an adsorption of O to BC surfaces but a formation of oxygen-containing functional groups through natural oxidation of BC (Puri, 1970; Boehm, 1994). FTIR spectra suggest that carboxylic and phenolic functional groups were the dominant functional groups in the historical BC samples.

Formation of functional groups provides sites for surface negative charge. With progressive oxidation, surface negative charge of BC concurrently increased. Unlike new BC which contained AEC, both BC incubated at 70 °C and historical BC always exhibited CEC at any pH values above pH 3. Although aging of new BC at 70 °C for 12

Table 3
Point of zero net charge (PZNC), surface positive charge (AEC), effective cation exchange capacity (ECEC), potential cation exchange capacity (PCEC) of new BC and historical BC samples

	PZNC	AEC $pH_{3.5}$ (mmole kg^{-1} C)	PCEC $pH_{7.0}$ (mmole kg^{-1} C)	ECEC pH_{H_2O} (mmole kg^{-1} C)	ECEC pH_{KCl} (mmole kg^{-1} C)
New BC	7.1 (0.5)[a]	+84[b] (20.7)	+1.7 (9.7)	9.5 (3.1)	9.2 (3.6)
BC-HA	6.8	+58	2	+10	+6
BC30	3.4	+18	71	85	83
BC70	2.7	Nil	201	173	77
Historical BC	2.8 (0.6)[a]	Nil	1644 (504)	1125 (424)	668 (410)

[a] Standard deviation ($n = 2$ for new BC; $n = 11$ for historical BC).

[b] +: net positive surface charge at the assigned pH value.

Table 4
Correlation coefficients between BC properties and the corresponding climatic and soil characteristics ($n = 9$)[a]

	C	O	Atomic O/C	PCEC[b] $pH_{7.0}$	ECEC[c] pH_{H_2O}	ECEC[c] pH_{KCl}
MAT	-0.92^{f}	0.72^{f}	0.78^{f}	0.83^{f}	0.50	0.29
MAP	−0.52	0.41	0.44	0.37	0.00	−0.05
MAP-PET	0.37	−0.27	−0.29	−0.50	−0.54	−0.31
Soil pH_{H_2O}	0.09	−0.22	−0.33	0.11	0.87^{f}	0.89^{f}
Soil pH_{KCl}	−0.02	−0.35	−0.23	0.21	0.73^{f}	0.91^{f}
Soil C/N	0.13	−0.34	−0.30	−0.04	0.08	0.10
Silt	−0.29	0.63^{e}	0.57	0.09	−0.47	−0.58
Clay	−0.58	0.54	0.55	0.43	−0.04	−0.03
C_{min}[d]	0.01	0.17	0.14	0.04	−0.06	0.02

[a] PA-2 and MD sites were not included in the model due to different vegetation types.

[b] PCEC: potential cation exchange capacity.

[c] ECEC: effective cation exchange capacity.

[d] C_{min}: potential cumulative mineralized C (g C—CO_2 per kg soil) for a 20-day incubation at 30 °C.

[e,f] Significant correlation at *P*-value 0.05 and 0.01, respectively.

months yielded a significant amount of CEC, the values were still much lower than by long-term natural oxidation as shown for the historical BC samples, which contained one order of magnitude greater CEC.

Concomitant to the increase of surface negative charge, surface positive charge decreased with progressive oxidation of BC and eventually disappeared. Similar results of decreasing surface positive charge through oxidation were also reported by Weller and Young (1948) and Papirer et al. (1987). Since the incorporation of O can localize π electrons and reduce the capability of anion adsorption (Leon y Leon et al., 1992), the decline of positive charge and the shift of PZNC to lower pH occurred rapidly and was even faster than the massive buildup of surface charge. In our study, for example, AEC and PZNC of BC incubated at 30 °C rapidly dropped from 84 mmole kg C^{-1} for New-BC_{HW} to 18 mmole kg C^{-1} and from pH 7.1 to pH 3.4, respectively; while PCEC only increased from +1.7 to 71 mmole kg C^{-1}. These values were much lower than the high CEC values when fresh BC was incubated at 70 °C or the CEC values of historical BC samples.

4.2. Adsorption of non-BC materials

With the coating of new BC by HA, surface negative charge slightly increased and surface positive charge and PZNC slightly decreased. Similar results have also been reported by Rivera-Utrilla et al. (2001). However, our data showed that the extent of change of BC properties by coating with HA were significantly lower than those by the oxidation of BC itself, especially compared to oxidized BC samples, such as BC70. From a long-term perspective, oxidation of BC itself was therefore more likely to influence BC properties rather than the adsorption of non-BC materials.

4.3. Effects of climatic and soil characteristics on BC oxidation

To our knowledge, this study is the first to compare the temperature dependence of long-term BC oxidation in soils across a wide geographic range. Although the long duration of time is an important cause for the high level of natural oxidation of BC, BC oxidation is significantly related to increasing MAT. Our data even suggest that temperature had a greater effect on BC oxidation than the time of exposure to soil. Enhanced BC oxidation (Puri, 1961; Cheng et al., 2006) and irreversible chemisorption of oxygen by char (Allardice, 1966) at higher temperatures have been reported in laboratory experiments and coincide well with our results on the natural oxidation of BC in soils. Our study further indicates that higher MAT increased the surface negative charge by 87 mmole kg C^{-1} for each degree Cel-

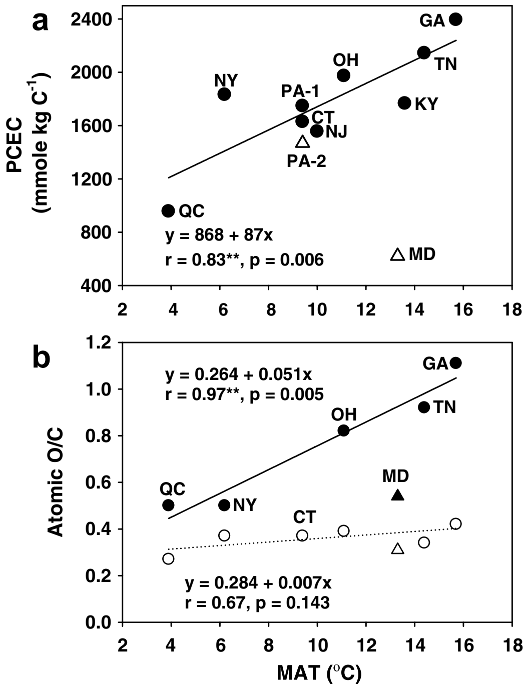

Fig. 5. (a) The relationship between mean annual temperature (MAT) and potential cation exchange capacity (PCEC) ($n = 9$); (b) the relationship between MAT and atomic O/C ratios measured by X-ray photoelectron spectroscopy (XPS) ($n = 6$), for surface (filled circles) and bulk data (open circles) of the historical BC samples. Triangles in both (a) and (b) denote sites under conifer vegetation (PA-2 and MD), which were excluded from the regression.

sius (Fig. 5a) and CEC ranges from 956 mmole kg C^{-1} in Quebec to 2354 mmole kg C^{-1} in Georgia. This very large negative charge is related to an oxidation of surfaces of BC which increases with greater temperature but has much lower effects on entire BC particles (Fig. 5b).

In contrast to the general understanding of weathering of mineral matter in soil which results in greater surface positive charge and higher PZNC with greater MAT as exemplified in tropical soils (Marcano-Martinez and McBride, 1989; Chorover and Sposito, 1995), higher MAT enhanced surface negative charge and oxidation lowered PZNC of BC. Since considerable amounts of CEC can be generated by BC, the presence of BC can even exceed the AEC in tropical soils. Consequently, high CEC was reported in tropical BC-containing soils, despite the fact that these soils contained highly weathered minerals (Liang et al., 2006).

The ECEC of the historical BC samples was positively correlated with pH values. These observations reinforce the findings that BC contains pH-dependent variable charge and that the in-situ ionization of BC directly depends on soil pH values. In archaeological research, Cohen-Ofri et al. (2006) found that self-humification of BC can be accelerated in soils with basic environments. However, it was not observed that pH influenced molecular structure and potential surface charge of BC, since there was no relationship between pH and the parameters of BC oxidation in our data set. The furnace sites of PA-2 and MD under conifer vegetation excluded from our calculation may require further investigation for their low oxidation and low pH values in order to understand the possible direct and indirect effects of pH and vegetation types on BC oxidation.

Although occlusion of small BC particles (<250 μm) inside aggregates or interactions with mineral surfaces were suspected to reduce BC oxidation (Glaser et al., 2000; Brodowski et al., 2005), no correlation was found between soil texture and BC oxidation in this study. This disparity may be due in part to the large size of BC fragments used in this study, which may reduce the interactions between BC and minerals. However, it is more likely that the wide range of MAT studied in this experiment masked the effects of soil texture on BC oxidation, and that a targeted research design is required to study soil texture effects. In addition, there was no correlation between soil organic matter quality or potential biological activity, such as soil C/N ratios and potential C mineralization, and BC oxidation. This finding may indicate that microbiological activity was not controlled to a different extent by substrate quality between BC-containing soils at different MAT. Differences in oxidation can then be explained by MAT and may not be limited by substrate quality.

4.4. Environmental significance

In natural ecosystems, evolution of negative charge may be an important ecological change of BC after forest or savanna fires. Annual BC production is estimated to be 50–270 Tg yr^{-1}, with a major source coming from vegetation fires (Kuhlbusch and Crutzen, 1995; Forbes et al., 2006). Unlike the BC samples used in this study that were produced at high temperature (>500 °C) (Hollingdale et al., 1999), BC from vegetation fire is generally produced at lower temperature (below 450 °C) (Chandler et al., 1983). Puri (1961) proposed that oxidation rates increase for BC produced at lower charring temperatures. It can be anticipated that most naturally produced BC should undergo more rapid oxidation than the BC samples used in this study.

Through natural oxidation in soil, the purposeful application of BC (often called biochar in this context) may evolve into a management tool to increase nutrient retention (Lehmann, 2007a,b). Production temperatures of about 450–600 °C reached in modern pyrolysis facilities for bioenergy and concurrent biochar production are similar to the ones reported for traditional kilns, and the information obtained from the present experiment provides guiding principles for the behaviour of biochar when applied to soil (Lehmann, 2007a,b). Lehmann et al. (2003) showed that BC-containing soils decreased the leaching of applied ammonium and that leaching of Ca was lower despite greater plant availability of Ca. High CEC is also an important reason for the high soil fertility in Amazon Dark Earths (Terra preta), where BC was deposited in pre-Columbian periods (Glaser et al., 2001). However, the relatively low oxidation and PCEC of incubated BC in comparison to 130-year old BC (this study) as well as the BC of Dark Earths with ages of up to several thousand years (Liang et al., 2006) still bears the question what the minimum time and temperature conditions are that generate high CEC on BC.

BC persists in soils for long periods of time, typically showing radiocarbon ages that are older than the most stable non-BC fractions in soils (Pessenda et al., 2001; Krull et al., 2006), and have been dated to originate from fire hundreds to thousands of years ago (Preston and Schmidt, 2006). Thus, BC found in soil is expected to be highly oxidized after such long-term exposure to natural oxidation processes. Oxidation of BC through both short- and long-term natural oxidation may therefore play an important role in the global BC cycles and in the effects of BC on soil biogeochemistry.

5. CONCLUSION

This paper reports substantial oxidation of BC in soils over a 130 year period, greatly exceeding oxidation by short-term laboratory incubation or by adsorption of organic matter. The principle oxidation processes of BC included: (1) increase of O and H and decrease of C, (2) formation of O-containing functional groups, and (3) decrease of surface positive charge and evolution of surface negative charge. While oxidation of BC significantly increased over time, it was also significantly modified by temperature, increasing with higher MAT. However, the dynamics of the development of oxidation and exchange sites and temperature sensitivity over time periods of decades still remain unclear. Future research should also address in what way soil clay content, clay mineralogy and pH influences the dynamics and temperature sensitivity of BC oxidation.

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APPENDIX A. SUPPLEMENTARY DATA

Elemental composition and pH values of BC samples (Table EA1), surface charge values of BC (Table EA2) and the linear regression of BC properties and environmental factors (Fig. EA1) are presented as online supporting material. This material is available free of charge via the Internet at http://www.sciencedirect.com/science/journal/00167037. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2008.01.010.

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