



Ageing of black carbon along a temperature gradient

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ARTICLE INFO

Article history:

Received 13 November 2008

Received in revised form 12 January 2009

Accepted 13 January 2009

Available online 14 February 2009

Keywords:

Black carbon

Ageing

Surface charge

Surface functional groups

Adsorption

ABSTRACT

Black carbon (BC) is regarded as a chemically and biologically stable form of carbon and the changes of BC properties in nature are generally assumed to be minute. However, more and more observations have argued the inertness of BC. The objectives of this study were to characterize the changes of BC properties through ageing processes and to identify if these changes are associated with temperature. Our results showed that ageing of BC occurs over a temperature range from $-22\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$ within a short period of 12 months. The main changes of BC properties through ageing were found in elemental composition, surface chemistry, and adsorption properties, where the aged BCs were shown to have higher oxygen concentrations, surface acidity, and negative surface charge but lower C concentrations, pH, surface basicity, point of zero net charge, and also a lower adsorption capacity of hydroquinone, an allelopathic compound, than fresh BC. These ageing processes of BC were affected by temperature and changed over time, with higher temperature and longer incubation time enhancing BC ageing. Our results from a wide temperature range suggest that ageing of BC is likely to occur in any terrestrial regime and that the changes of BC properties through ageing should not be overlooked.

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1. Introduction

Black carbon (BC) is a residue of incomplete combustion of biomass and fossil fuel. Because of the thermal alteration of its structure, BC is regarded as a chemically and biologically stable form of carbon (C) and can persist in nature over long periods of time (Goldberg, 1985; Schmidt and Noack, 2000). Often, mineralization of BC is considered to be negligible. Archaeologists use the refractory properties of BC for dating deposits (Bird et al., 2002) and ecologists for evaluating past fire events (Korhola et al., 1996).

An increasing number of observations, however, have questioned the inertness of BC (Czimczik et al., 2003; Murage et al., 2007) and argued that BC properties could change, for example, by oxidation (Cheng et al., 2006, 2008a). These “ageing processes” of BC may have profound influences on its basic physicochemical properties, such as elemental composition (Cheng et al., 2006), hydrophilicity (Leon y Leon et al., 1992), and amphotericity (Lau et al., 1986). Thus, in addition to intrinsic differences due to its charring conditions or different precursors, it is likely that ageing of BC can additionally alter BC properties and then affect BC’s biogeochemical properties. The understandings of BC ageing and the associated changes in BC properties including adsorption of natural

compounds are still scarce and more detailed information is required.

The central issue in understanding BC ageing is to know how environmental factors affect the ageing processes. Temperature and time of exposure are likely to be major factors influencing BC ageing as shown by several studies (Puri, 1970; Cheng et al., 2006, 2008a). It is less clear, how BC aging responds to a wide gradient of temperature differences.

Therefore, our objectives were to (1) characterize the ageing of BC with respect to its elemental composition, surface chemistry, and adsorption properties, and (2) identify if these changes are associated with incubation temperature and time of exposure.

2. Materials and methods

2.1. BC sample

In this study, BC from traditional charcoal making was used to study the ageing processes of BC. The BC sample was collected from the Hopewell Furnace National Historical Site in Pennsylvania, where charcoal making was used as a demonstration for historical charcoal production. Wood logs of white oak and red oak were used as the BC precursors and were stacked in a cone-shape charcoal mound, around 2 m in height and 2.5 m in diameter, and carefully charred. The charcoal-making process took 5 d for charring and 7 d for cooling. We collected the BC sample approximately 1 month after charring. The collected BC pieces were ground to

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pass through a 2-mm size sieve and stored in a sealed glass jar, purged with N₂ to prevent further oxidation.

The method for making the present-day BC was the same as used by historical charcoal making during the 19th century. It was assumed that the present BC samples represented the time-zero BC in comparison to the historical BC samples collected from historical charcoal blast furnace sites. Results of the chemical differences between the present and historical BC samples have been reported by Cheng et al. (2008a).

2.2. Ageing experiment

Ageing of BC was conducted in an aerobic incubation experiment along a temperature gradient at –22 °C, 4 °C, 30 °C and 70 °C. Ten grams of BC were placed in a 500-mL glass jar, to which 4 mL of water were added to attain a moist environment, and then incubated in the dark. Glass jars were periodically opened for aerating and checking the water content every week during the first 2 months and then every other week during the rest of the incubation. After 6 or 12 months incubation time, the glass jars were removed and dried at 70 °C for 24 h. The incubation was conducted in duplicate and the results of chemical measurements were the average of duplicates.

In addition to the incubation, fresh BC coated with humic acid (Fresh BC-HA) and a historical BC sample, collected from Quebec (QC), Canada, were also obtained and used in the adsorption experiment in this study. More details on Fresh BC-HA and QC can be obtained from Cheng et al. (2008a).

2.3. Elemental and chemical analyses

Total C and nitrogen (N) concentrations were measured by dry combustion using a Europa ANCA GSL sample combustion unit (PDZ Europa, Crewe, UK). Hydrogen (H) concentrations were measured after conversion to H₂ at 1400 °C over glassy C (Hekatech TCEA, Hekatech GmbH, Wegberg, Germany). Ash content was analyzed by loss of weight via combusting the BC at 550 °C for 2 h. Oxygen (O) concentration was determined by difference. Elemental composition of C, N, H, and O of BC samples were presented on a dry ash-free basis.

The pH value of BC was measured in 1:20 w/v ratio in either H₂O or 1 N KCl solution. The pH value in 1 N KCl presents the potential pH, since high ionic KCl solution could release exchangeable protons of BC into solution.

Surface acidity of BC was measured by “base adsorption”, whereas surface basicity was measured by “acid adsorption” (Boehm, 1994). A 0.15 g subsample of BC was added to 15 mL of either 0.1 N NaOH or 0.1 N HCl solution and shaken with an end-over-end shaker for 30 h. The BC slurry was then filtered using a Whatman No. 42 filter paper. An aliquot of 5 mL of the NaOH filtrate was transferred to a 10-mL 0.1 N HCl solution that neutralized the unreacted base. The solution was back-titrated with 0.1 N NaOH against a phenolphthalein indicator. Surface basicity was measured similarly to the measurement of surface acidity and an aliquot of 5 mL of the HCl filtrate was directly titrated with 0.1 N NaOH. The base or acid uptake of BC was converted to the content of surface acidity or surface basicity (mmole g⁻¹), respectively.

2.4. Fourier transform infrared (FTIR) spectroscopy

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

2.5. X-ray photoelectron spectroscopy (XPS)

XPS measurements were conducted by using a Physical Electronics Quantum 2000 scanning ESCA Microprobe (Physical Electronics GmbH, Ismaning, Germany). The 98-W, 107- μ m diameter X-rays were rastered over a 1.4 by 0.2 mm rectangle on the sample. High-energy resolution scan spectra of C1s and O1s 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. Three BC samples, including fresh BC and the BC samples after incubation at 30 °C and 70 °C for 6 months, were measured. The C1s and O1s spectra were deconvoluted by a non-linear least squares curve fitting program (XPSPEAK Version 4.1 software) and the detailed procedures are described in Cheng et al. (2008a).

2.6. 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 bound by non-specific adsorption and surface positive charge was defined as the adsorption of anions (Cl⁻) and surface negative charge as the adsorption of cations (K⁺). Briefly, the method is comprised of 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, and (3) displacement of adsorbed K and Cl by 1 N ammonium nitrate (Cheng et al., 2008a). A quadratic model was used for fitting surface charge and pH. The point of zero net charge (PZNC) was obtained at the pH that had an equal amount of surface positive and negative charge. The surface charge of BC was presented on a C basis (mmole kg C⁻¹).

2.7. Adsorption experiment

To gain insights in which way ageing processes affect the adsorption capability of BC, two adsorption experiments were conducted in aqueous solution using hydroquinone. Hydroquinone was used as an example that has shown allelopathic effects on plant growth and was examined in concentrations that were occurring naturally (Chou and Muller, 1972; Weidenhamer and Romeo, 2004). First, BC samples (0.1 g) and 20 mL of a solution containing one initial concentration of 50 mg L⁻¹ hydroquinone were placed in 25-mL glass vials. The suspensions were shaken at 27 °C for 24 h and then filtered through a Whatman No. 42 filter paper to remove the BC particles. The filter paper material was tested for hydroquinone adsorption and did not show any interference. An equilibration time of 24 h was found to be sufficient during preliminary experiments where no change in hydroquinone adsorption was detected beyond 12 h which is consistent with earlier work (Ayranci and Duman, 2005). The concentration of hydroquinone in the filtrate was analyzed by a UV-vis spectrophotometer at a wavelength of 285 nm, and corrected for any BC passing through the filter. Here, adsorption capability of all BC samples was compared in terms of the amount of hydroquinone adsorbed by BC (mg g⁻¹) at one initial concentration. Each experiment was conducted in duplicate under identical conditions and no pH adjustment was made.

Second, adsorption isotherms were determined for selected BC samples. The procedure was the same as described above, using batch solutions containing between 5 and 300 mg L⁻¹ hydroquinone. Adsorption isotherms were expressed as the amount of hydroquinone adsorbed by BC (mg g⁻¹) at the equilibrium concentration and fitted according to Langmuir and Freundlich equations. The expression of the Langmuir model was:

$$q_e = \frac{(q_{\max} b C_e)}{(1 + b C_e)}$$

where q_e is the amount of adsorbate adsorbed per unit mass of BC at equilibrium in mg g^{-1} , C_e is the concentration at equilibrium in mg L^{-1} , q_{\max} is the maximum adsorption at monolayer coverage in mg g^{-1} , b is the adsorption equilibrium constant. The empirical Freundlich equation is:

$$q_e = K_f C_e^{1/n}$$

where q_e is the amount of adsorbate adsorbed per unit mass of BC at equilibrium in mg g^{-1} , K_f and n are the Freundlich constant, and C_e is the concentration at equilibrium.

3. Results

3.1. Elemental and chemical analyses

The fresh BC showed a relatively high C concentration (908 mg g^{-1}) and low O concentration (68 mg g^{-1}) (Table 1). With the ageing of BC, a decrease in C concentration and an increase in O concentration were observed and the magnitude of these changes increased with incubation temperature and time. In contrast, the concentrations of N and H were low and did not display differences among BC samples, except the BC samples incubated at 70°C for which an increase in H content was observed.

The pH of fresh BC was 8.5 (Table 1). The pH values of the BC samples incubated at temperatures below 30°C decreased slightly, while the pH of the BC incubated at 70°C decreased substantially, from basic to acidic values. Both incubation temperature and incubation time decreased the pH values. The lower pH values in 1N KCl solution compared to in H_2O were the most distinct changes for the BC incubated at 70°C and were due to the release of exchangeable acidity in the KCl solution.

The change of surface acidity of BC through ageing was similar to the change in pH, increasing with incubation temperature and incubation time (Table 1). Surface basicity showed an inverse trend that decreased with incubation temperature and time, and this value even disappeared for the BC incubated for 12 months at 70°C . Overall, fresh BC and the BC samples incubated at temperatures below 30°C had higher surface basicity than surface acidity, while the BC incubated at 70°C showed the opposite.

3.2. Spectroscopic analyses

FTIR spectra showed a “flat” pattern for most BC samples and only a few poorly defined features could be identified (Fig. 1). An

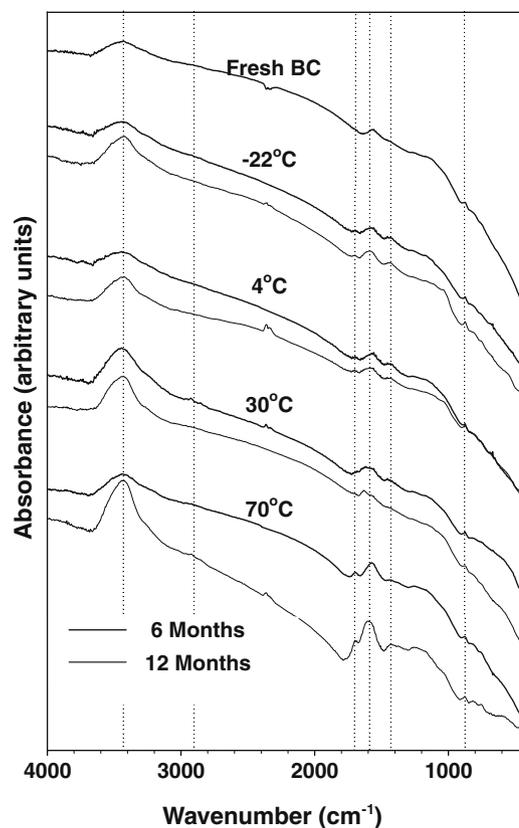


Fig. 1. Fourier transform infrared (FT-IR) spectra of fresh BC and BC after incubation along a temperature gradient from -22°C to 70°C for 6 and 12 months.

increase of spectra intensity and development of new surface functional groups was identified for the BC samples incubated at 70°C , where the bands centered at 1700 cm^{-1} were assigned to carboxylic (COOH) groups, 1600 cm^{-1} and 1420 cm^{-1} were assigned to the bands of ring stretching in C=C, and 1260 cm^{-1} indicated the appearance of phenolic (C—O) and COOH groups (Cheng et al., 2008a).

Similar to FTIR spectra, XPS spectra also suggested the development of new surface functional groups for the aged BC (Fig. 2). Shifts of C1s spectra to higher binding energy for the aged BC samples indicated the formation of oxygen-containing functional groups, and shifts of O1s spectra displayed increases from O—C single bonds (533.1 eV) to O=C double bonds (531.3 eV). Among the

Table 1

Elemental composition and chemical characteristics of fresh BC and BC after incubation along a temperature gradient from -22°C to 70°C for 6 and 12 months.

	C ^a (mg g^{-1})	H ^a (mg g^{-1})	O ^a (mg g^{-1})	N ^a (mg g^{-1})	Ash ^b (mg g^{-1})	pH (H_2O)	pH (KCl)	Surface basicity (mmol g^{-1})	Surface acidity (mmol g^{-1})	PZNC ^c	Hydroquinone adsorption (mg g^{-1})
Fresh BC	908	22	68	2	19	8.5	8.4	0.41	0.13	7.4	9.61
6M -22°C	904	28	66	2	19	8.4	8.3	0.42	0.15	6.3	8.50
6M 4°C	901	25	72	2	21	8.5	8.4	0.39	0.15	5.8	9.06
6M 30°C	884	22	92	2	20	8.4	8.3	0.31	0.27	4.4	8.71
6M 70°C	871	29	98	2	16	7.9	6.0	0.17	0.59	3.9	4.93
12M -22°C	898	24	76	2	23	8.5	8.3	0.35	0.15	5.7	8.60
12M 4°C	897	22	79	2	22	8.6	8.4	0.27	0.25	5.4	9.16
12M 30°C	882	24	92	2	22	8.4	8.1	0.27	0.41	4.0	8.46
12M 70°C	858	34	106	2	19	6.3	4.1	0.10	0.88	2.7	2.65
Fresh BC-HA ^d	886	18	84	2	22	6.0	6.3			6.8	9.08
QC ^e	721	42	236	1	12	4.8	2.9			2.0	4.28

^a Dry ash-free basis.

^b Dry basis.

^c PZNC: point of zero net charge.

^d Fresh BC coated with humic acid (Cheng et al., 2008a).

^e Historical BC collected from Quebec, Canada (Cheng et al., 2008a).

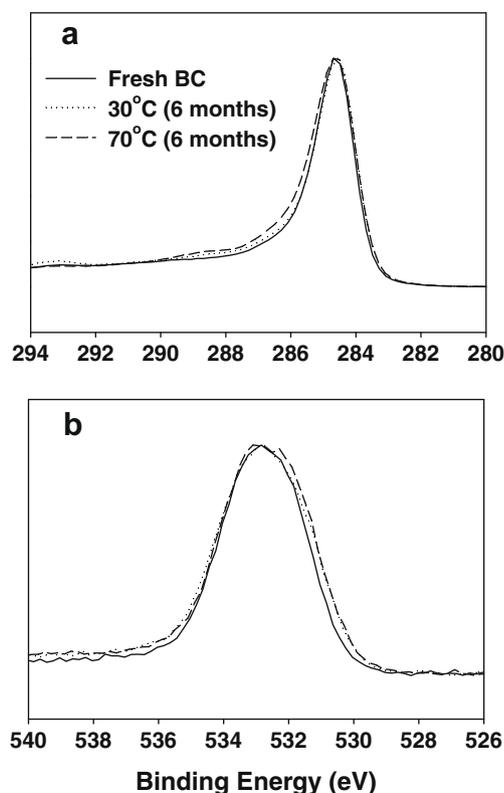


Fig. 2. X-ray photoelectron spectroscopy (XPS) spectra of C1s (a) and O1s (b) for fresh BC and BC after incubation at 30 °C and 70 °C for 6 months.

XPS spectra, the BC sample incubated at 70 °C had the highest portion of C in COO groups and O in O=C bonds (Table S1).

3.3. Surface charge characteristics

Both surface positive and negative charges for the BC samples displayed significant pH dependency, whereby surface positive charge decreased with increasing pH and surface negative charge increased with increasing pH (Fig. 3 and Figure S1). The fresh BC showed the highest surface positive charge and the lowest surface negative charge. Decreases of surface positive charge and increases of surface negative charge were found for the aged BC samples and these changes correlated well with both incubation temperature and incubation time. Thus, the BC sample incubated at 70 °C for 12 months displayed the highest surface negative charge of 200 mmole kg C⁻¹ at pH 7 and the lowest, or even negligible, surface positive charge. A strong effect of incubation temperature and incubation time on the PZNC was also observed (Table 1). The PZNC steadily decreased with higher incubation temperature and longer incubation time, from pH at 7.5 in fresh BC to pH at 2.7 in BC after incubation at 70 °C for 12 months.

3.4. Adsorption experiments

The fresh BC showed the highest adsorption capacity for hydroquinone (Table 1). Similar to other examined properties, only slight decreases were found for the BC samples incubated at temperatures below 30 °C, while a considerable reduction in adsorption capacity was observed for the BC incubated at 70 °C: from 9.61 mg g⁻¹ in the fresh BC to 2.65 mg g⁻¹. Historical BC (QC) also displayed a low adsorption capacity at 4.28 mg g⁻¹.

Adsorption isotherms for the aged BC samples further showed the reduction of monolayer adsorption capacity (q_{\max}) and the free

energy of adsorption (b) (Fig. 4 and Table S2). The fresh BC coated with HA did not show a reduction of adsorption at low equilibrium concentration (<15 mg L⁻¹), while a reduction was observed at high equilibrium concentration. It was also observed that for highly aged BC samples, such as the BC incubated at 70 °C for 12 months and QC, the best fitting model tended to shift from the Langmuir model to the Freundlich model.

4. Discussion

Our results clearly show that ageing of BC occurs over a wide temperature range from -22 °C to 70 °C within a short time of 12 months. Major changes of BC properties through ageing can be classified into three important aspects: (i) elemental composition, (ii) surface chemistry, and (iii) adsorption characteristics.

(i) *Elemental composition.* Ageing of BC leads to increased O and decreased C concentrations. Puri (1970) and Cheng et al. (2006) indicated these changes in elemental composition were due to the chemisorption of oxygen onto BC surfaces through the formation of surface functional groups. N and H concentrations are relatively unchanged after the ageing process studied here, except for an increase of H concentrations for the highly aged BC samples which may be due to the formation of carboxylic and phenolic functional groups. Beyond the short-term laboratory ageing, further changes of increasing O and decreasing C concentrations are likely, as the historical BC displayed a considerable increase in O concentrations and decrease in C concentrations (Cheng et al., 2008a).

(ii) *Surface chemistry.* The FTIR and XPS spectra show the development of surface functional groups, especially carboxylic and phenolic structures, through BC ageing. Accordingly, surface acidity, pH values, surface negative charge (cation exchange capacity) and PZNC display similar trends, where surface acidity and surface negative charge are increased and values of pH and PZNC are reduced for aged BC. In contrast to surface acidity, surface basicity decreases with the ageing processes. Leon y Leon et al. (1992) proposed that the decrease of surface basicity was due to the incorporation of oxygen which caused a dislocation of π electrons in the periphery of the basal planes. It is interesting to notice the disappearance of surface basicity for the highly aged BC, such as the BC incubated at 70 °C for 12 months. Long-term natural oxidation of BC shows similar but quantitatively more pronounced changes than the BC incubated at 70 °C for 12 months, with even greater surface acidity and negligible surface positive charge (Cheng et al., 2008a).

(iii) *Adsorption characteristics.* For the aged BC, a decrease in adsorption capacity for hydroquinone is evident and can be explained by the increase of charge repulsion between adsorbates and BC surface. It is also interesting to see that the fitting models for these highly aged BC samples may indicate a shift from a Langmuir model to a Freundlich model, suggesting changes of surface complexity from homogeneous to heterogeneous surface characteristics (Cornelissen and Gustafsson, 2004), which deserve further investigation. An additional decrease is observed from the coating of BC surfaces with HA. For the BC coated with HA, the adsorption affinity at low equilibrium concentration seems to be not reduced compared to that of the fresh BC samples, which may be due to the adsorption of hydroquinone at interior pores that are not coated by the HA (Pignatello et al., 2006), whereas the reduction of maximum adsorption capacity may be due to the effects of HA on surface chemistry. It can be anticipated that both BC ageing and adsorption of other organic matter influence adsorption characteristics of BC as shown in this study.

Our results show that temperature is a critical factor in enhancing BC ageing. This greater BC ageing with higher temperature is

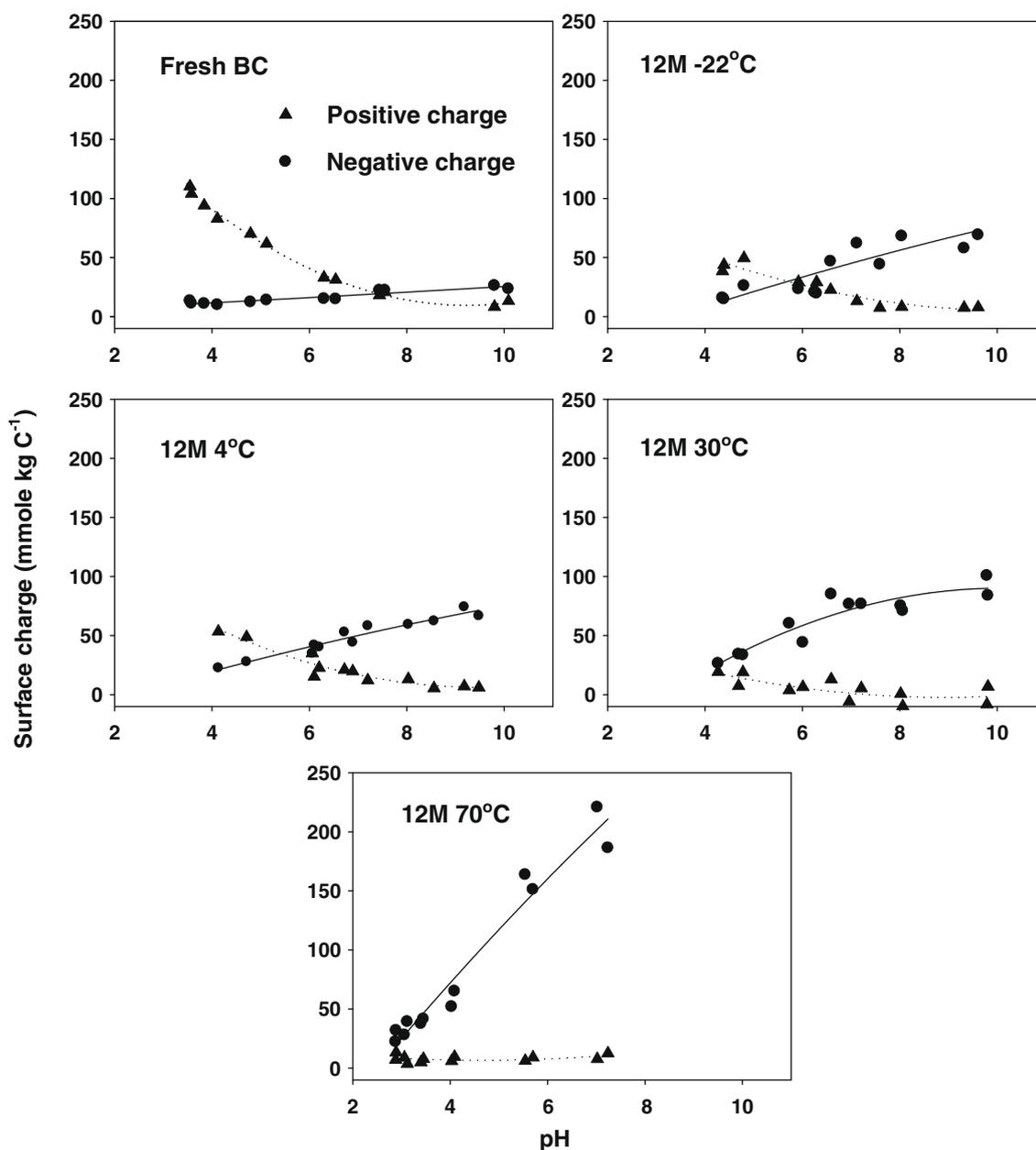


Fig. 3. Surface positive charge (triangles) and surface negative charge (circles) of fresh BC and BC after incubation along a temperature gradient from -22 °C to 70 °C for 12 months.

likely due to the endothermic reaction of the chemisorption between oxygen and BC surfaces (Rideal and Wright, 1925; Puri, 1970; Cheng et al., 2006). As discussed above, the BC incubated at 70 °C showed the greatest change compared to the fresh BC, whereas the BC incubated at temperatures lower than 30 °C only displayed slight changes compared to fresh BC. The temperature dependency of BC ageing seems to be non-linear and can be tentatively depicted in the Arrhenius plots on the data of surface basicity and acidity after incubation for 6 and 12 months, respectively (Figure S2). Similar results of temperature dependency following the Arrhenius equation were also reported by Allardice (1966) for short-time oxygen adsorption on BC surfaces. However, the chemical properties as shown in this study were a product of several complicated reactions, not of a single chemical reaction, and the Arrhenius equation may therefore be an oversimplification for describing the properties of BC during ageing at different temperatures. The long-term naturally oxidized BC samples

also display a temperature dependency, showing a linear increase between surface charge and mean annual temperature (Cheng et al., 2008a).

It is worth noting that detectable ageing occurred even at the lowest temperature (-22 °C), albeit at a relatively slow rate. Similar studies of oxidation of carbonaceous materials at low temperature were also reported by Zarifyanz et al. (1967) who showed irreversible adsorption between graphite dust and oxygen at a temperature below -40 °C and by Bansal et al. (1970) who indicated that chemisorption of oxygen on carbon black could occur at a temperature of as low as -78 °C.

Not only the temperature but also the time of exposure affects the degree and quality of ageing. It is plausible that a certain time is required for the penetration of oxidation into interior regions of BC particles and for the development of functional groups, such as phenolic and carboxylic functional groups (Cheng et al., 2006). For the present study, ageing of BC beyond the examined time of 12

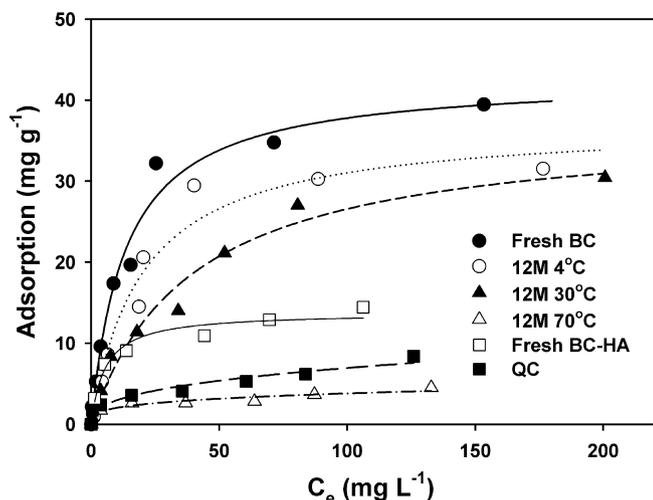


Fig. 4. Adsorption isotherms of hydroquinone to fresh BC, BC after incubation at 4 °C, 30 °C, and 70 °C for 12 months, fresh BC coated with HA (Fresh BC-HA), and a historical BC (QC).

months is expected, as historical BC samples after 130 years of exposure in soils showed much greater oxidation (Cheng et al., 2008a).

BC collected in the present study was obtained from a kiln and produced for metallurgical purposes. From the high C content (90%) and the flat FTIR spectra, it can be estimated that the BC was produced at the temperature higher than 600 °C (Nishimiva et al., 1998; Schenkel et al., 1998). Unlike this man-made BC, BC produced from forest fires or during land clearing burning for agriculture is likely to have a higher ageing rate. Firstly, a large proportion of BC from fires is produced at lower temperatures (200–600 °C; Chandler et al., 1983) than the BC studied here and the rate of ageing may therefore be faster (Puri, 1961). Secondly, biotic oxidation in natural soils also enhances the ageing of BC (Fakoussa and Hofrichter, 1999). Thirdly, BC in the environment may also be oxidized by the presence of ozone (Decesari et al., 2002).

In nature, ageing of BC plays an important role in affecting its biogeochemical properties and global BC cycles. For instance, the changes in BC properties through ageing could then significantly influence BC's transport (Hockaday et al., 2007), erosion (Rumpel et al., 2006), stability (Masiello, 2004; Cheng et al., 2008b), or cation retention (Liang et al., 2006). Our results from a wide range of temperatures, from –22 °C to 70 °C, suggest that ageing of BC is likely to occur in any terrestrial regime, which is relevant due to the ubiquitous nature of BC (Goldberg, 1985). Hence, ageing of BC should not be overlooked. Using fresh or newly produced BC as a surrogate for the study of naturally occurring BC may be inadequate.

5. Conclusions

The results clearly indicate that ageing of BC occurs over a wide temperature range from –22 °C to 70 °C within 12 months. It is also suggested that oxidation is kinetically restricted and duration is a major factor affecting ageing processes. In addition to changes in elemental composition such as increasing O and decreasing C concentrations, ageing processes can lead to the development of acidic surface functional groups resulting in lower pH, higher surface acidity, higher negative surface charge, less surface basicity, and lower PZNC. These changes in surface chemistry further alter its adsorption characteristics, resulting in a lower adsorption capacity for substances such as hydroquinone. The results from the examined wide temperature range indicate that ageing of BC

can occur in any terrestrial regime and that changes of BC properties through ageing should not be overlooked.

Acknowledgements

We thank the Hopewell Furnace National Historical Site in Pennsylvania and the Forges du Saint-Maurice National Historic Site in Quebec for permitting us to take the BC samples. We also thank Steven Ambrose, Feil Norman, Pierre Drouin, Daniel Toutant, and Chang-Ya Chen for their help with the field work. The XPS experiments were performed at the Environmental Molecular Sciences Laboratory, a national scientific user facility, located at Pacific Northwest National Laboratory, WA. We are indebted to Dr. Mark Engelhard from PNNL for help with the XPS measurements. We are very grateful for financial support from the Ministry of Education in Taiwan, the Henry Wu Scholarship, and the Keckhefer Adirondack Fellowship of Cornell University to C.H.C.

Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.01.045.

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