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Stability of black carbon in soils across a climatic gradient

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[1] The recalcitrant properties of black carbon (BC) grant it to be a significant pool of stable organic C (OC) in soils. Up to now, however, the longevity of BC under different climates is still unclear. In this study, we used BC samples from historical charcoal blast furnace sites to examine the stability of BC across a climatic gradient of mean annual temperatures (MAT) from 3.9 to 17.2°C. The results showed that OC concentration and OC storage in the BC-containing soils at a soil depth of 0–0.2 m were 9.0 and 4.7 times higher than those in adjacent soils, respectively. Organic C in the BC-containing soils was more stable, with a significantly lower amount of the labile OC fraction (4.4 mg g^{-1} OC versus 27.5 mg g^{-1} OC) and longer half-life of the recalcitrant OC fraction (59 years versus 9 years) than the adjacent soils determined by incubation experiments. The stability of BC was primarily due to its inherently recalcitrant chemical composition as suggested by short-term incubation and solid state ^{13}C nuclear magnetic resonance spectra of isolated BC particles. A significant negative relationship between OC storage and MAT further indicated that OC storage was decreased with warmer climate. However, the lack of a relationship between MAT and BC mineralization suggested that the stability of the remaining BC was similar between sites with very different MAT. Despite the fact that warming or cooling result in immediate consequences for BC stocks, it may have little impact on the stability of remaining BC over the period studied.

1. Introduction

[2] Soil organic carbon (OC) represents the largest C reservoir of the biosphere-atmosphere system and even small changes of the soil OC pools can substantially influence the global C balance and therefore global climate [*IPCC*, 2007]. Recent evidence suggests that black C (BC) from biomass burning constitutes a significant pool of OC in soils [*Schmidt and Noack*, 2000; *Masiello*, 2004; *Preston and Schmidt*, 2006]. Although the estimated global rate of BC production (50–270 Tg yr^{-1} [*Forbes et al.*, 2006]; 50–600 Tg yr^{-1} [*Crutzen and Andreae*, 1990; *Kuhlbusch and Crutzen*, 1996]) is small compared to total C flows in the biosphere [*IPCC*, 2007], total BC stocks in soils are large because it is so recalcitrant to decomposition [*Schmidt and Noack*, 2000]. This chemical recalcitrance to microbial decay has also prompted investigations into actively managing BC as a means to sequester atmospheric carbon dioxide in soils [*Lehmann et al.*, 2006; *Lehmann*, 2007a, 2007b].

[3] However, the notion of the longevity of BC is not unchallenged by experimental evidence. On the one hand, BC typically shows the oldest radiocarbon ages that are older than the most stable non-BC fractions in soil [*Pessenda et al.*, 2001; *Krull et al.*, 2006] and certain dark earths in the Amazon Basin (so-called 'terra preta' or Amazonian Dark Earths) provide direct evidence of how BC can be preserved in soils for hundreds and thousands of years [*Glaser et al.*, 2001]. On the other hand, some short residence times of BC have been found. *Bird et al.* [1999] reported that BC can be significantly degraded in the order of decades. *Murage et al.* [2007] showed that the mean residence time of the free light fraction containing BC lies between 21.0 and 23.4 years. Therefore, more detailed information about the stability of BC in soils is required.

[4] Apart from random variability between sites, BC stability may respond to variations in environmental properties. Climate is one of the main drivers of OC decay and greater temperature significantly increases decomposition [*Jenkinson and Ayanaba*, 1977]. There is no reason to suspect that this will be different for BC. On the contrary, decomposition of chemically more stable OC compounds is suspected to react to warming to a greater extent [*Davidson and Janssens*, 2006]. *Glaser and Amelung* [2003] found a strong relationship between both mean annual precipitation (MAP) and temperature (MAT) and the proportion of BC across a climate transect in North America. Since climate variables also affected the production and disappearance of

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BC other than heterotrophic respiration [*Czimczik and Masiello*, 2007], the decomposition of BC could not be quantified separately [*Glaser and Amelung*, 2003].

[5] In this study, our objective was to investigate the long-term stability of BC as a function of temperature and moisture. We made use of the accumulation of BC from historic charcoal blast furnace sites to examine the stability of BC across a climate gradient in the eastern United States and Canada. We hypothesized that greater temperature and moisture decrease BC stability.

2. Materials and Methods

2.1. Charcoal Blast Furnaces

[6] BC samples were collected from the remnants of historic charcoal blast furnaces. 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]. Here, BC used for the blast furnaces was only produced from some specific hardwoods and therefore captured biomass-derived BC of a charcoal type [*Schmidt and Noack*, 2000; *Masiello*, 2004]. A high specific gravity, crushing strength, and greater density were required, found in woods such as chestnut, hickory, oak, and sugar maple [*Bining*, 1938]. Compared with BC found in forest fires, the BC from historic charcoal production was generated under relatively uniform charring conditions, which were carefully tended by colliers (charcoal workmen) [*Rolando*, 1992], and is similar to BC that is produced by modern pyrolysis, such as biochar [*Lehmann et al.*, 2006; *Lehmann*, 2007a]. On the other hand, thus produced BC captures only a fraction of the BC forms produced by natural fires which may contain a wide range of different chemical forms of biomass-derived BC from soot to charcoal to weakly charred material [*Schmidt and Noack*, 2000; *Masiello*, 2004].

[7] In the 19th century, each eastern state in the U.S. (except for Delaware) had at least one furnace. In this study, soils from 16 furnace sites, spanning a wide geographic distribution from Quebec (QC) to Alabama (AL), were collected. Historical and climatic background of the furnace sites is shown in Table 1. MAT, MAP and potential evapotranspiration (PET) for each site were obtained from historical average data (1971–2000) of the closest recording station. Effective precipitation was defined as MAP minus PET and was used to represent average moisture conditions [*Clark and Royall*, 1995]. Sites were initially selected for their variation in MAT. MAP as well as PET were not only both strongly correlated with MAT, as expected, but also with each other (see Table S1, available as auxiliary material).[1] However, effective precipitation of the sites was not significantly related to MAT, enabling us to test the effects of temperature and moisture separately.

[8] 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. After thoroughly mapping the storage areas by hand augering, the samples were taken

from soil profiles at depths of 0–0.1 m (surface soil) and 0.1–0.2 m (subsurface soil). Samples of adjacent soils, which did not contain visible charcoal, were taken to represent the background of soils with low or no BC. Throughout our field soil sampling, archeological maps were consulted to identify storage areas in comparison to sites that were unaffected by charcoal making. For each site, between 5 and about 15 soil cores were collected from both BC-containing and adjacent soils, depending on the size of the storage areas which averaged about 20 by 20 m. Dark black soil color and even large BC fragments are conspicuous in the BC-containing soils.

[9] Soil samples were air-dried and ground to pass through a 2-mm sieve. Carbon concentrations were analyzed as total OC determined by dry combustion (Europa ANCA GSL sample combustion unit, PDZ Europa, Crewe, UK) after removing inorganic C with 0.1N HCl. Bulk density was determined by the core method. OC storage (kg m^{-2}) for the soils was the product of OC concentration, bulk density, and the thickness of the soil horizon. OC storage in this study only represented the soil depth from 0 to 0.2 m. The soil pH was measured in a 1:2.5 soil:solution (w/v) 0.01N CaCl$_2$ suspension.

2.2. Incubation Experiments

[10] We performed incubation experiments to evaluate the OC stability of BC. Incubation experiments were set up at 30°C under 60% of water holding capacity (WHC). This is an optimum condition for many microbial processes and was used for maximizing mineralization rates. Seven furnace sites, including Maine (ME), New York (NY), Pennsylvania – 1 (PA-1), Ohio (OH), Tennessee (TN), Georgia (GA), and Alabama (AL), were selected and the incubation experiments were separately conducted for the subsurface soils and BC particles.

[11] Twenty grams of BC-containing soils and 30 g of adjacent soils were placed into incubation jars (500 mL Mason jar). Distilled water was added to the jars to bring the moisture content to 60% of WHC for each soil. The incubation experiments were initiated immediately after wetting. The evolved CO$_2$ was trapped in 10 mL 0.1N NaOH, which was placed in a small vessel inside the incubation jars. After 3 d, then weekly to 1 month and biweekly after 1 month, NaOH vessels were removed and replaced with a new vessel. The trapped CO$_2$ was precipitated by an excess of 1N BaCl$_2$ solution and back titrated with standard 0.1N HCl to determine evolved CO$_2$. Total incubation time was 177 d.

[12] BC particles with a size between 1 mm and 2 mm were carefully hand picked from BC-containing soils. Incubation of these BC particles predominantly provided information for the stability of BC itself but the particles most likely still contained some adsorbed non-BC [*Lehmann et al.*, 2005]. BC particles were thoroughly mixed with sand in a ratio of 0.8 g of BC to 20 g sand and then placed into the same size incubation jars as described above for the soils. Distilled water, microbial inoculum, and micronutrient solution were added to the jars to maintain biological activity. Microbial inoculum was obtained from extracts of the BC-containing soils from GA, which had the highest biological activity. Two milliliters of inoculum, obtained from a 1:50 w/v soil and water ratio filtrate after

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Table 1. Climatic and Site Characteristics of the Selected Historical Charcoal Blast Furnaces

	Location	Furnace Name	Abandoned Year	Vegetation Type[a]	MAT,[b] °C	MAP,[c] mm	PET,[d] mm	MAP-PET, mm	Sand	Silt	Clay	pH[e] BC	pH[e] Adj.
									g kg^{-1}				
QC[f]	Trois-Rivieres	Forges du Saint-Maurice	1883	G	3.9	1030	470	560	510	260	230	4.1	4.8
ME	Dover-Foxcroft	Katahdin iron work	1890	C	4.4	1100	550	550	880	30	90	3.8	5.2
NY	Port Henry	Fletcherville Furnace	1875	BL	6.2	900	610	290	590	220	190	4.8	4.2
CT	Canaan	Beckley Furnace	1918	BL/G	9.4	1190	635	555	610	170	220	6.6	7.0
PA-1	Huntingdon	Etna Furnace	1874	BL	9.4	940	635	305	510	210	280	5.3	7.1
PA-2	Huntingdon	Greenwood Furnace	1904	C	9.4	940	635	305	530	230	240	3.4	3.0
PA-3	Huntingdon	Monroe Furnace	1882	BL	9.4	940	635	305	540	210	250	6.4	7.0
NJ	Oxford	Oxford Furnace	1884	BL	10.0	1150	660	490	500	240	260	5.9	6.1
OH	Jackson	Buckeye Furnace	1894	G/BL	11.1	1070	755	315	480	180	340	5.2	4.0
KY-1	Greenup	Buffalo Furnace	1875	BL	11.3	1070	755	315	440	190	370	6.7	5.4
MD	Snow Hill	Nassawango Furnace	1850	C	13.3	1030	710	320	710	210	80	4.2	3.3
KY-2	Cadiz	Centers Furnace	1860	BL	13.6	1290	850	440	330	170	500	6.5	3.9
TN	Dickson	Laurel Furnace	1850	BL	14.4	1370	845	525	190	270	540	5.3	5.1
NC	Iron town	Iron town	1880s	BL	15.4	1180	895	285	760	80	160	6.2	7.0
GA	Cartersville	Coopers Furnace	1864	BL	15.7	1210	865	345	420	270	310	4.4	6.5
AL	McCalla	Tannehill Furnace	1865	BL	17.2	1500	895	605	540	110	350	5.0	4.8

[a]Vegetation type: G, grass; BL, broadleaf; C: conifer.
[b]MAT: mean annual temperature.
[c]MAP: mean annual precipitation.
[d]PET: annual potential evapotranspiration.
[e]pH: 1:2.5 (w/v) ratio in 0.01N $CaCl_2$ solution for surface soils of BC-containing and adjacent soils.
[f]Abbreviations of the province in Canada and the states in the U.S.

soil was incubated under 60% WHC at 30°C for 7 d, was added. The micronutrient solution was 4mM NH_3NO_3, 4mM $CaCl_2$, 2mM KH_2PO_4, 1mM K_2SO_4, 1mM $MgSO_4$, 25μM $MnSO_4$, 2μM $ZnSO_4$, 0.5μM $CuSO_4$, and 0.5μM Na_2MoO_4 of which 2 mL was added to each jar. The sand was obtained from Sigma-Aldrich Inc. (St. Louis, MO, USA) in the size of 50–70 mesh. The sand provided a support matrix to maintain an adequate moisture content and aeration during the incubation experiments for the BC particles. Prior to mixing with BC, the sand was heated to 500°C for 24 h in a muffle furnace to remove any organic materials. Total incubation time for the BC particles was 50 d.

2.3. Mineralization Model

[13] For the BC-containing and the adjacent soils, a double exponential model with two mineralization rate constants of labile and recalcitrant pools was used to describe the OC mineralization kinetics.

$$OCcum(t) = OC_0(1 - \exp(-kt)) + (TOC - OC_0)$$
$$\cdot (1 - \exp(-ht)) \quad (1)$$

where OCcum (t) is the cumulative mineralized OC at time t; OC_0 is the fraction of organic labile OC fraction (mg g^{-1} soil OC); TOC is total OC; k and h are the first-order kinetic decomposition rate constants for the labile and recalcitrant OC fractions (day^{-1}), respectively.

[14] For the BC particles, a one-compartment first-order exponential model was used to fit OC mineralization kinetics.

$$OCcum(t) = OC_0(1 - \exp(-kt)) \quad (2)$$

where OCcum(t) is the cumulative mineralized OC at time t; OC_0 represents the amount of "potential" mineralizable OC (mg g^{-1} BC C); k is the decomposition rate constant for potential C mineralization (day^{-1}). OC_0 is the readily mineralizable OC pool with the decomposition rate k.

[15] We calculated the time for 50% of the each pool to mineralize ($t_{1/2}$, half-life) in the exponential models as:

$$t_{1/2} = (1/k \text{ or } h) \ln 2 \quad (3)$$

2.4. Solid-State Nuclear Magnetic Resonance Spectroscopy

[16] Solid-state ^{13}C nuclear magnetic resonance (NMR) measurements were done on ground BC particles. We conducted the measurement at the Wiley Environmental Molecular Sciences Laboratory (EMSL) by using an Infinity CMX 300-MHz spectrometer (Varian Inc., Palo Alto, CA, USA). Variable amplitude cross-polarization (vacp) magic angle spinning (MAS) experiments were run using a 7.5 mm MAS HX Chemagnetics probe. The sleeves of the pencil design rotors were made from zirconia and used Kel-F drive tips and low carbon background spacers. Between 100 and 200 mg BC powder was packed into the capsule. The experiments were run using a speed of 7 kHz, the contact time was 0.5 ms and the delay time was 3 s. Carbon chemical shifts were externally referenced to the methyl resonance of hexamethybenzene at 17.36 ppm. Approximately 8000 transients were recorded for each sample.

2.5. Data Analysis

[17] For the incubation experiments, we used SAS 9.1 (SAS Institute, Cary, NC, USA) PROC NLIN for fitting the nonlinear regression model. Differences in soil OC storage and incubation kinetic parameters between BC-containing and adjacent soils were analyzed using a paired t test.

3. Results

3.1. Organic Carbon Concentration and Storage

[18] High OC concentrations were found in all BC-containing soils compared to adjacent soils. The OC concentrations of BC-containing soils ranged from 66 to 518 g kg^{-1} in the surface and from 53 to 572 g kg^{-1} in

Table 2. Organic Carbon Concentrations and Carbon Stocks of BC-Containing and Adjacent Surface (0−0.1 m) and Subsurface (0.1−0.2 m) Soils

| | BC-Containing Soils | | | | | Adjacent Soils | | | | |
| | OC Concentration, g kg^{-1} | | OC Stock, kg m^{-2} | | | OC Concentration, g kg^{-1} | | OC Stock, kg m^{-2} | | |
	Surface	Subsurface	Surface	Subsurface	Total	Surface	Subsurface	Surface	Subsurface	Total
QC[a]	372	404	18.2	19.8	38.0	41	32	3.9	3.5	7.4
ME	89	572	5.4	20.8	26.2	109	30	8.3	3.9	12.2
NY	261	300	14.6	16.8	31.4	82	59	8.0	6.4	14.4
CT	294	310	11.5	11.9	23.4	81	41	6.0	3.5	9.5
PA-1	365	360	12.0	16.3	28.3	64	66	6.1	8.4	14.5
PA-2	518	520	17.6	17.7	35.4	149	30	3.1	3.2	6.3
PA-3	311	310	14.0	18.4	32.5	91	94	7.2	9.8	17.0
NJ	120	176	7.7	11.2	18.9	39	30	3.2	2.7	5.9
OH	186	213	14.1	16.6	30.7	21	15	2.2	1.8	4.0
KY-1	163	156	9.7	10.5	20.1	29	8	2.9	0.8	3.7
MD	118	300	10.0	25.5	35.5	16	10	1.5	1.3	2.8
KY-2	211	250	9.3	14.6	23.9	25	17	1.8	2.3	4.1
TN	286	225	13.5	10.6	24.1	32	13	2.8	1.3	4.1
NC	101	53	6.8	4.4	11.2	9	10	1.1	0.9	2.0
GA	186	130	11.1	10.0	21.1	31	29	2.1	3.0	5.1
AL	66	114	5.9	7.6	13.5	26	8	2.8	1.1	3.9
Average	228	275	11.3	14.5	25.9	53	31	3.9	3.4	7.3
Ratio[b]	5.7	12.3	3.8	6.4	4.7					

[a]Abbreviations of the province in Canada and the states in the U.S.
[b]Average ratio of concentrations and stocks of BC-containing soils and adjacent soils.

the subsurface (Table 2). For the adjacent soils, OC concentrations ranged from 9 to 149 g kg^{-1} in the surface and from 8 to 94 g kg^{-1} in the subsurface. Average OC concentrations of the BC-containing soils were 5.7 and 12.3 times higher than the adjacent soils for surface and subsurface, respectively.

[19] The BC-containing soils also showed higher amounts of OC storage compared to the adjacent soils. In BC-containing soils, OC storage in the upper 0−0.2 m soil ranged from 11 to 38 kg m^{-2} with an average OC storage of 25.9 kg m^{-2} (Table 2). The average OC storage in the BC-containing soils was 4.7 times higher than in the adjacent soils. Smaller differences in OC storage than in OC concentration were due to the lower bulk density in the BC-containing soils than in the adjacent soils.

[20] MAT, MAP, and PET were found to be significantly and negatively correlated with total OC storage for both BC-containing and adjacent soils, whereas MAP-PET was not significantly correlated (Table 3). A weaker positive relationship was also observed between pH and total OC storage in the BC-containing soils. However, this significance disappeared once the sites under conifer vegetation

were excluded. No relationship existed between soil texture and OC contents for either BC-containing soils or adjacent soils.

3.2. Soil Carbon Mineralization

[21] Throughout the 177 d of incubation, BC-containing soils had slightly higher cumulative mineralized OC (expressed per gram of soil) than adjacent soils (except for the GA site) (Table 4). However, the fraction of mineralized OC (expressed per gram of initial OC) was much lower in the BC-containing soils than in the adjacent soils. Only from 3.9 to 23.3 mg g^{-1} soil OC had been mineralized in the BC-containing soils, while from 30.3 to 184.8 mg g^{-1} soil OC were mineralized in the adjacent soils (Table 4).

[22] The mineralization kinetics for both BC-containing soils and adjacent soils were well captured by the double exponential model, with a P value below 0.0001 (Figure 1 and Table 4). The parameters of the regression model showed that less than 10 mg g^{-1} soil OC was assigned to the labile OC pool in the BC-containing soils, while a higher portion of labile soil OC, from 10 to 64 mg g^{-1} soil

Table 3. Relationships Between Organic Carbon Concentration and Carbon Storage at Soil Depth 0−0.2 m and the Environmental Factors for the BC-Containing Soils and the Adjacent Soils[a]

| | BC-Containing Soils | | Adjacent Soils | |
	OC Concentration	OC Storage	OC Concentration	OC Storage
MAT	−0.68**	−0.62**	−0.63**	−0.65**
MAP	−0.58*	−0.69**	−0.57**	−0.57**
PET	−0.73**	−0.70**	−0.64**	−0.64**
MAP-PET	−0.02	−0.21	−0.13	−0.10
Clay	−0.17	−0.25	−0.31	−0.31
pH	−0.46* (−0.19)[b]	−0.50* (−0.35)[b]	−0.23	−0.02

[a]Significant at P < 0.05 (*) and P < 0.01 (**) probability level, respectively.
[b]Values in parentheses exclude the conifer vegetation sites ME, PA-2, and MD.

Table 4. Carbon Mineralization and the Kinetic Parameters for the Double-Exponential Model of BC-Containing and Adjacent Soils After 177 Days Incubation at 30°C

		Mineralized OC, mg g^{-1} soil	Fraction of Mineralized OC, mg g^{-1} soil OC	OC$_0$, mg g^{-1} soil OC	k, day^{-1}	t$_{(1/2)}$, days	h($*10^{-4}$), day^{-1}	t$_{(1/2)}$, years	P-Value
ME	BC soil	2.85	5.01	0.88	0.002	347	0.27	70	<0.0001
	Adjacent soil	1.30	38.33	17.20	0.087	8	1.30	15	<0.0001
NY	BC soil	4.29	14.32	5.65	0.091	8	0.53	36	<0.0001
	Adjacent soil	2.30	30.28	10.60	0.111	6	1.14	17	<0.0001
PA-1	BC soil	3.66	10.17	3.52	0.115	6	0.40	47	<0.0001
	Adjacent soil	3.42	54.20	21.90	0.128	5	2.02	9	<0.0001
OH	BC soil	0.63	3.92	1.34	0.138	5	0.15	127	<0.0001
	Adjacent soil	0.61	41.24	14.04	0.130	5	1.66	11	<0.0001
TN	BC soil	3.51	15.76	4.40	0.116	6	0.68	28	<0.0001
	Adjacent soil	2.40	184.83	39.40	0.240	3	9.79	2	<0.0001
GA	BC soil	3.04	23.33	10.61	0.063	11	0.77	25	<0.0001
	Adjacent soil	4.02	139.44	64.14	0.076	9	5.02	4	<0.0001
AL	BC soil	1.16	8.36	4.30	0.044	16	0.24	79	<0.0001
	Adjacent soil	0.64	82.10	25.50	0.144	5	3.64	5	<0.0001
Average	BC soil	2.73	11.55	4.39	0.093[a]	9[a]	0.43	59	
	Adjacent soil	2.10	81.49	27.54	0.131	6	3.51	9	
Difference[b]		0.145	0.015*	0.009**	0.106	0.108	0.034*	0.010**	

[a]ME site was excluded.
[b]P-value of difference between BC-containing soils and adjacent soils at P < 0.05 (*) and P < 0.01 (**) probability level, respectively.

OC, was assigned to this pool in the adjacent soils. These labile OC pools had a short half-life, from 5 to 16 d, and no significant difference was found between BC-containing soils and adjacent soils, except for the ME soils. In contrast, the recalcitrant OC pools were higher in the BC-containing soils than in the adjacent soils. A significantly (P < 0.01) longer half-life (average of 59 years) was found in the BC-containing soils than in the adjacent soils (average of 9 years).

[23] For the isolated BC particles, only very little OC, less than 4 mg per gram of initial OC (or 0.4%), was mineralized during the incubation period of 50 d (Figure 2 and Table 5). These BC particles displayed from 22 to 78% lower mineralized OC as a proportion of their total OC content (mg per g of initial OC) compared to their corresponding total soils during the same incubation period of 50 d. The kinetics of C mineralization was fitted to a first-order exponential model. The potential mineralized OC (labile OC pools) comprised less than 4 mg g^{-1} BC C and had a mean half-life of around 19 d.

[24] The relationships between incubation parameters and environmental factors in BC-containing soils and BC particles are shown in Table 6. Neither the mineralization rates nor the pool sizes of any of the soils or the BC particles were significantly related to MAT, MAP, PET, or MAP-PET. In addition, no significant relationship was found between clay content or pH value and incubation parameters.

3.3. Molecular Composition of BC: NMR Spectra

[25] The NMR spectra of isolated BC particles displayed highly condensed aromatic C, with a single dominant peak at 130 ppm (Figure 3). In addition to aromatic C, the shoulders of the asymmetric peak showed the existence of phenolic C at 152–155 ppm and carbonyl and carboxylic C at 160–190 ppm. After subtraction of the upfield spin sidebands at 210–260 ppm, only low amounts of alkyl-C at a chemical shift from 0 to 45 ppm were found for the BC samples. No systematic changes of molecular properties

could be discerned as a function of MAT, MAP, PET, or MAP-PET.

4. Discussion

4.1. Carbon Storage in BC-Containing Soils

[26] The significant and substantially greater OC storage and concentration in the BC-containing soils, even 130 years after its application, indicated that BC is much more stable than non-pyrogenic OC. OC storage in the BC-containing soils surpasses that of most histosols [*Davidson and Lefebvre*, 1993; *Johnson and Kern*, 2003] or bog soils [*Mowbray and Schlesinger*, 1988; *Moorhead et al.*, 2000] in the eastern U.S. These high OC contents of the BC-containing soils as compared to the adjacent soils are not due to lower temperatures or water-logging conditions but entirely due to the specific chemical properties of BC.

[27] OC storage in the adjacent soils is in the range of other reported data from forest soils in the eastern U.S. [*Davidson and Lefebvre*, 1993; *Johnson and Kern*, 2003]. Some adjacent soils, such as PA-1 and PA-3, have higher OC storage than reported data under similar climatic and edaphic conditions. This may be because of the presence of small amounts of BC in these adjacent soils, since the soils were collected at about 100 m distance from the BC-containing sites.

4.2. Climate and Carbon Storage

[28] The significant relationship between MAT and OC storage of BC-containing soils and the lack of a relationship between effective precipitation (MAP - PET) and OC storage suggest that soil warming increased BC decomposition (r = −0.62, P < 0.01), whereas moisture did not affect BC decomposition for the range of moisture conditions investigated (P > 0.05). The positive effect of warming on organic matter decomposition is well documented [*Jenkinson and Ayanaba*, 1977]. *Puri* [1961] and *Cheng et al.* [2006, 2008] also reported that higher temperature
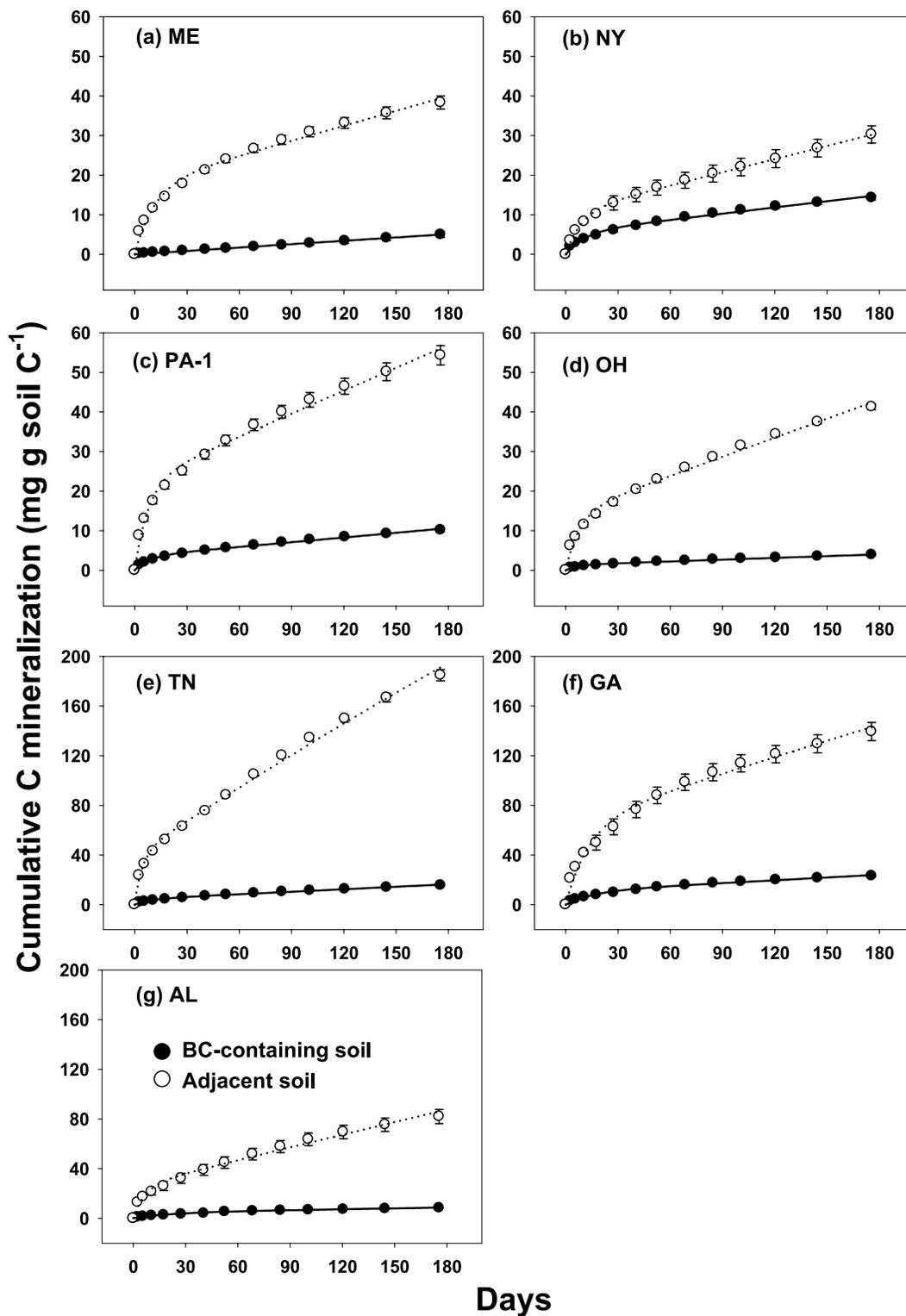
Figure 1. Cumulative carbon mineralization (mg CO_2-C g^{-1} soil OC) of the BC-containing soils and the adjacent soils incubated at 30°C for 177 days.

enhances oxidation of BC, and given the trend of decreasing proportions of BC along a climate sequence in the Great Plains of the U.S. [*Glaser and Amelung*, 2003], a significantly enhanced BC decay with increasing MAT is plausible.

[29] If the difference in OC storage between BC-containing and adjacent soils was assumed to be the contribution of BC and potentially occurring export of BC be independent of MAT, then a decomposition rate of BC at different MAT can be obtained. Based on the regression models (Figure 4),
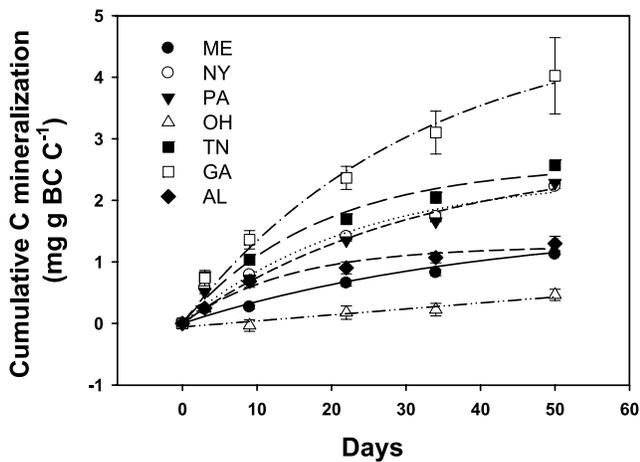
Figure 2. Cumulative carbon mineralization (mg CO_2-C g^{-1} BC C) of the historical BC particles incubated at 30°C for 50 days.

we use the BC storage at 0°C as the baseline (23.6 kg m^{-2}; i.e., 39.4 kg m^{-2} in the BC-containing soils minus 15.8 kg m^{-2} in the adjacent soils). Then, OC storage at 5°C and 15°C would amount to a 2.3 and 7.0 kg m^{-2} loss, respectively. Since BC in this study was deposited to soil on average 130 years ago, the relative decomposition rate constant of BC storage through first-order kinetics calculates to 0.0008 and 0.0027 year^{-1} at 5°C and 15°C, respectively. The resulting Q_{10} (increase in the rate of decomposition with a 10°C increase in temperature) of 3.38 is higher than that obtained for fresh plant materials of 2.6 for leaves and 2.1 for roots from a 5-year incubation in the field [*Gholz et al.*, 2000], or at the upper end of the Q_{10} values (2.1–3.4) for several plant materials obtained from a short-term laboratory incubation [*Fierer et al.*, 2005].

[30] In contrast to findings by *Glaser and Amelung* [2003], OC stocks in our BC-containing soils decreased with greater MAP and were not related to effective precipitation (MAP - PET). This can be explained by the fact that in our experiment, the disappearance of BC is decoupled from BC accumulation, whereas the production of BC in the grasslands studied by *Glaser and Amelung* [2003] is itself a function of MAP through its effect on biomass production and possibly burning frequency and BC formation. The influence of MAT studied here may obscure a relationship between soil moisture conditions and OC storage. It is also possible that the effect of moisture would affect BC decomposition only at sites with particularly dry or wet

conditions that may have been outside the range of moisture conditions investigated in our study.

[31] The reason for the decrease in OC storage with increasing pH (r = −0.51, p < 0.05) may involve interactions with soil type, vegetation, and microbial composition [*Fierer and Jackson*, 2006]. Our data show that this relationship disappeared once the sites under the conifer vegetation were excluded, which showed low pH values and high OC contents. In a separate study, we found that individual BC fragments from the conifer sites displayed the least oxidation, i.e., low oxygen content and low atomic O/OC ratios, which indicate lower decomposition of BC under acid soil conditions [*Cheng et al.*, 2008]. Possible direct effects of pH on BC stability have to be investigated in the future.

[32] Despite the significant relationship between MAT and OC storage in BC-containing soils, it is difficult to assert that lower BC contents can be solely explained by higher BC degradation, since the original BC contents could not be obtained. Similar initial BC accumulations are likely but remain unverifiable. However, the clear trend across the climate gradient is a compelling indication that warrants research into temperature effects on BC decay. Given the high stability and hence long half-life of BC, the present approach may indeed be one of few opportunities to show the temperature sensitivity of BC decomposition in soil. The adjacent soils show a similar general trend of soil OC that is strongly affected by temperature, as higher OC storage was found in colder areas rather than in warmer areas. However, OC storage in adjacent soils is the function of both net primary productivity and decomposition and these multiple effects are not focus of this study.

4.3. Stability of BC

[33] The higher level of mineralized OC on a soil basis (mg g^{-1} soil) found in the BC-containing soils compared to the adjacent soils indicates that there is no observable limitation on potential biological activity in the BC-containing soils by factors other than OC quality. Indeed, not only higher biological activity, but also higher reproduction rates and greater bacterial species richness and diversity can be found in BC-containing soils [*Pietikäinen et al.*, 2000; *Steiner et al.*, 2004; *Kim et al.*, 2007]. However, on an OC basis (mg g^{-1} soil OC), only a small fraction of the OC was mineralized in the BC-containing soils, significantly less than in the adjacent soils. Similar low levels of mineralized OC have only been reported when soils were incubated under conditions that reduce microbiological activity, such as low temperature [*Rasmussen et al.*, 2006], water deficiency [*Kelliher et al.*, 2004], or anaerobic

Table 5. Carbon Mineralization and the Kinetic Parameters Based on an Exponential Model of the BC Particles After 50 Days Incubation at 30°C

	Mineralized C, mg g^{-1}	Fraction of Mineralized C, mg g^{-1} C	C_0, mg g^{-1} C	k, day^{-1}	$t_{(1/2)}$, days	P-Value
ME	0.78	1.12	1.15	0.022	31	0.0002
NY	1.36	2.23	2.41	0.042	17	0.0004
PA-1	1.23	2.28	2.76	0.032	22	0.0004
OH[a]	0.26	0.46	C(t) = −0.0564 + 0.0097 t			0.0081
TN	1.29	2.57	2.59	0.055	13	0.0007
GA	1.81	4.02	4.89	0.032	22	<0.0001
AL	0.61	1.30	1.25	0.071	10	0.0002

[a]Linear regression for C mineralization.

Table 6. Relationships Between Incubation Parameters and Environmental Factors for the BC-Containing Soils and the BC Particles[a]

	BC-Containing Soils (n = 7)					BC Particles (n = 6)[b]			
	Min C[c]	Frac C[d]	OC_0	k	h	Min C[c]	Frac C[d]	OC_0	k
MAT	−0.40	0.41	0.50	−0.54	0.27	0.13	0.40	0.35	0.68
MAP	−0.44	0.12	0.15	−0.51	0.07	−0.34	−0.08	−0.15	0.73*
PET	−0.43	0.41	0.49	−0.49	0.29	0.15	0.41	0.35	0.69
MAP-PET	−0.28	−0.23	−0.26	−0.60	−0.19	−0.74*	−0.59	−0.63	0.48
Clay	−0.17	0.31	0.20	0.20	0.33	0.20	0.36	0.26	0.65
pH	−0.12	−0.02	−0.06	0.65	−0.02	0.09	0.13	0.08	0.60

[a]Significant at P < 0.05 (*) probability level.
[b]OH site was excluded.
[c]Min C: mineralized OC (mg g^{-1} soil in BC-containing soils and mg g^{-1} BC in BC particles).
[d]Frac C: fraction of mineralized OC (mg g^{-1} soil OC in BC-containing soils and mg g^{-1} BC C in BC particles).

conditions [*Bridgham et al.*, 1998]. This was not the case for this study since optimum temperature and moisture were maintained throughout the entire incubation.

[34] Based on the double-exponential model for fitting C mineralization kinetics, the BC-containing soils have a higher amount of recalcitrant OC and also a longer half-life (60 years on average) than the adjacent soils (9 years on average). The half-life of OC in BC-containing soils is affected by both non-BC and BC organic material. Assuming that the half-life for non-BC organic materials in the BC-containing soils is the same as in the adjacent soil, then the half-life for BC in the BC-containing soils should be longer than the average of 60 years calculated for the mixture of BC and non-BC. Depending on the proportion of BC, which may amount to more than two-thirds of the OC (72% estimated by the difference in OC between BC-containing and adjacent soils from Table 2) but was not directly determined, the half-life for the BC portion may then calculate to 80 years at 30°C and optimum water content. In the natural environment, the decomposition of BC is expected to be slower than in our laboratory incubation, due to temperature and moisture conditions that are less conducive to optimum decay as well as due to less physical disruption and thus greater stability of OC. Assuming a Q_{10} of 3.4 as estimated above, the half-life of BC at a site with 10°C MAT may be as high as 925 years. Due to systematic overestimation of long-term BC decay by short-term incubations [*Lehmann*, 2007b], the true half-life of BC is most likely greater than calculated here. This agrees well with the C-14 ages of BC which have been reported to lie in the hundreds to thousands of years [*Pessenda et al.*, 2001; *Schmidt et al.*, 2002; *Gavin*, 2003; *Krull et al.*, 2006].

[35] The low OC mineralization rate of the studied BC particles, as well as their solid-state ^{13}C NMR spectra, suggests that the long half-life of the studied BC-containing soils is primarily due to the inherently recalcitrant chemical composition of BC. Low mineralization rates of BC were also reported by *Hamer et al.* [2004] and *Baldock and Smernik* [2002]. Their research showed that from 3 to 20 mg C per g C of fresh BC samples were mineralized. In our study, an even smaller portion of mineralized OC (from 0.46 mg to 4 mg per g C) was found than in the cited studies, even though the physically isolated BC particles in
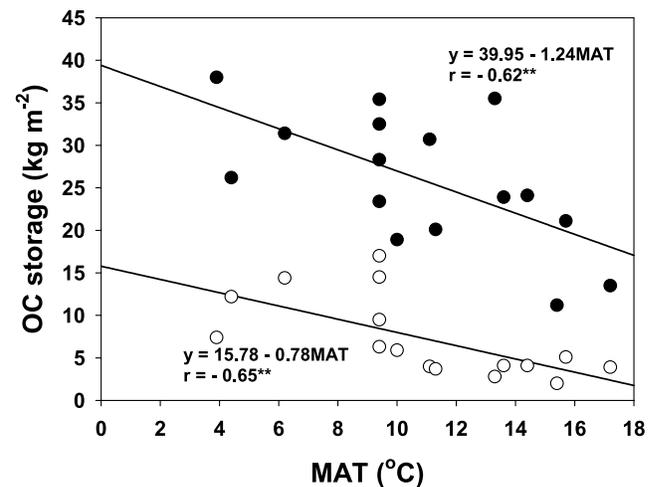

Figure 3. Solid-state cross polarization ^{13}C NMR spectra of the historical BC particles. SSB refers to spinning sidebands located approximately 100 ppm from their parent resonance.

Figure 4. Relationship between OC storage and MAT for the BC-containing soils (closed circle) and the adjacent soils (open circle). Slopes between BC-containing and adjacent soils were significantly different at P < 0.01.

our study certainly contained some adsorbed non-BC as shown by *Lehmann et al.* [2005]. It is possible that compared with BC from forest fire or from domestic use, the BC used in this study (metallurgical charcoal) was produced at a higher charring temperature [*Hollindale*, 1999] which may lead to a lower chemical and biological reactivity. However, differences as a function of production conditions may be small given the similar NMR spectra of BC produced at different temperatures investigated by *Czimczik et al.* [2002] and *Baldock and Smernik* [2002], but warrant further investigation. More likely is that the BC particles investigated in our study had already undergone loss of the more labile fractions of BC that can occur rapidly during the first months of exposure [*Cheng et al.*, 2006].

[36] These results suggest that over time periods studied here the proportion of a more labile fraction of BC may progressively decrease, rather than that the remaining BC becomes more vulnerable to biological decomposition. This conclusion is in contrast to interpretations of the C-14 ages of different BC fractions which showed that older BC was more easily oxidized by chemical treatment indicating that older BC was less stable [*Krull et al.*, 2006]. It is possible that 130 years of BC presence in soil were long enough to remove labile fractions of BC, but not long enough to degrade the most stable fractions of BC to a significant extent. These results also reiterate the point made by *Lehmann* [2007b] that incubations of fresh BC do not capture the turnover of aged BC which may indeed be up to one order of magnitude slower than fresh BC as shown here.

4.4. Climate Effects on BC Stability

[37] The lack of a relationship between climate variables such as MAT and effective precipitation and the observed stability of BC against microbial decomposition confirms the conclusions made above that properties of any remaining BC does not vary after exposure to different MAT over centennial timescales under the climatic conditions of this study. Higher temperatures certainly led to greater decomposition of BC as suggested by the lower OC stocks, but the recalcitrance of the remaining BC appears to have not been impacted. The properties of the remaining BC may be a result of its chemical and physical nature, not of climatic influences after 130 years. This result neither confirms nor refutes the hypothesis that BC as a chemically stable form of OC decomposes more rapidly with warming than more labile fractions of soil OC based on Arrhenius' law [*Davidson and Janssens*, 2006] and the Q_{10} of BC calculated above. But it suggests any warming or cooling has only immediate consequences for BC stocks and may bear little impact on BC forms and fate under a changing climate over the period studied here.

5. Conclusions

[38] High OC storage and OC concentration of soils that received BC additions over 130 years ago in conjunction with the low decomposition rates not only underpin the stability of BC in the global C cycles, but also reinforce the strategy of exploring BC production in form of biochar as a means to sequester atmospheric CO_2 in soils [*Lehmann et al.*, 2006; *Lehmann*, 2007a]. Our data from a wide range of

climatic conditions and soils further suggests that such biochar applications may be effective in increasing soil OC in many different geographic regions. While interactions between BC and soil minerals may significantly increase BC stability, direct measurements of BC particles by incubation and NMR indicate that the long half-life of BC in our study was primarily due to its inherently recalcitrant chemical composition. The lack of climatic effects on BC stability observed in this study suggest specific processes of BC decay rooted in its chemical and physical nature. Nevertheless, decreasing OC stocks with increasing MAT show as expected that BC is decomposing to a greater extent with warming, where soil water is not a limiting factor. The relatively high temperature sensitivity of BC decomposition (or Q_{10}) needs to be considered when predicting feedback of CO_2 emissions from soil due to global warming. Quantification of the magnitude of long-term decomposition over decadal and centennial timescales warrants further research.

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