Long-term effects of black carbon on soil properties

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Abstract
Using biomass-derived black carbon (or biochar, BC) as soil amendment has been proposed to be a promising method for enhancing soil carbon (C) sequestration and fertility. However, in addition to the “terra preta” phenomenon, direct and available information about long-term effects of BC on soil properties is still scarce. In this study, we used the BC-containing soils collected from historical charcoal blast furnace sites where BC was deposited in the 19th century to examine the long-term effects of BC. A wide geographical distribution from Quebec to Alabama along the eastern part of the US was selected. Both BC-containing and adjacent soils were collected from soil layers at the depth of 0 to 10 and 10 to 20 cm. Our results showed that soil organic C and BC contents in the BC-containing soils were 9 and 21 times higher than those in the adjacent soils, respectively. Soil physical and chemical properties were significantly different between the BC-containing and adjacent soils, in which soil pH, total N, Mehlich-3 extractable phosphorus, cation exchange capacity, exchangeable cations, and percentage of base saturation were higher in the BC-containing soils. We also measured the chemical properties of BC particles in the size of 1 to 2 mm in order to represent the influences of BC itself and found more concentrated amounts on surface charge, exchangeable cations and available P in this portion. The results suggest that BC could play important roles in affecting long-term soil properties. Thus, BC itself could enhance C content, surface charge and available nutrients of soils through BC’s intrinsic refractory and surficial oxidation.

Key Words
Black carbon, surface charge, exchangeable cations, nutrients, charcoal blast furnace.

Introduction
The “terra preta” phenomenon provides a promising way of using biomass-derived black carbon (or biochar, BC) for enhancing soil C sequestration and fertility (Glaser et al. 2001; Lehmann 2007). However, in addition to the “terra preta” phenomenon, direct and available information about long-term effects of BC on soil properties is still scarce. In this study, we used the BC-containing soils collected from historical charcoal blast furnace sites where BC was deposited in the 19th century to examine the long-term effects of BC. Unlike the soils from terra preta, these soils from historical charcoal blast furnace had never been converted to crop production. Thus, this study could focus more on understanding the direct influence of BC itself on soil properties.

Since BC is thermally altered, BC can be resistant from microbial decomposition in nature for a long time. Nevertheless, surficial oxidation of BC can occur along its long-term exposure and render BC to develop surface negative charge (Cheng et al. 2008a). We tested three major soil properties of (i) BC contents, (ii) soil surface charge, and (iii) exchangeable cations and available phosphorus contents between BC-containing and adjacent soils to understand the roles of BC towards soil properties.

Methods
Sampling sites
High BC-containing soils were collected from the historical sites of 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). In the 19th century, every eastern state in the U.S. (except for Delaware) had at least one furnace. In this study, sixteen historical charcoal furnaces sites, spanning along a climosequence from Quebec (QC) to Alabama (AL), were selected. Dark black soil color and even large BC fragments are conspicuous in these BC-containing soils (Figure 1). Both BC-containing and adjacent soils were collected from soil layers at the depth of 0 to 10 and 10 to 20 cm.
Figure 1. Example of soil profile in the Fletcherville Furnace in NY. This furnace was abandoned since 1875 and there was no artificial disturbance and forest fire record after its decommissioning.

Soil properties
A serious of soil physical, chemical and biological properties were determined, but only soil organic C content, BC content, CEC, exchangeable cations, Mehlich 3 extract P, and pH-dependent surface charge were presented. Soil organic carbon was measured by dry combustion (Cheng et al. 2008b). BC content was measured by using 0.1N dichromate/2M H2SO4 oxidation method. The residue remaining from 60°C dichromate/H2SO4 oxidation was defined as BC (Wolbach and Anders, 1989). Exchangeable cation (Ca, K, Mg, Na) were extracted with 1N ammonium acetate (at pH 7.0) and the concentration of the individual nutrients were determined by ICP-AES. Exchangeable acidity was measured on a 1N KCl extraction with a 1:10 (w/v) ratio and titrated with 0.01N NaOH to an endpoint of pH 7.0. Cation exchange capacity was determined by the content of the adsorbed ammonium after replaced by 2N KCl. Available P was determined by Mehlich 3 extraction and measured by ICP-AES. In addition, BC particles in the size between 1 mm and 2 mm were handily picked. The chemical properties of picked BC particles were also measured in order to examine surface charge, exchangeable cations and available P of BC itself.

pH-dependent surface charge
The pH-dependent surface charge for both BC-containing and adjacent soils were determined by “index” or “indifferent” ion adsorption method (Uehara and Gillman 1981; Chorover et al. 2006; Cheng et al. 2008). A KCl electrolyte (0.01 N) was used in this study, in which K and Cl ions were assumed to be bound by non-specific adsorption.

Results and Discussion
SOC and BC contents
Soil organic C and BC contents in the BC-containing soils were 9 and 21 times higher than those in the adjacent soils, respectively. Average BC percentage in the BC-containing soils was 87% of SOC, compared with 44 % in the adjacent soils (Table 1). High SOC and BC contents in the BC-containing soils imply the long-term persistency of BC in soils over a wide geographical range.

CEC, exchangeable cations and Available P
The BC-containing soils showed significantly higher values in CEC than that in the adjacent soils. Average CEC for the BC-containing soils measured by 1N NH4OAC at pH 7.0 were 1139 and 1015 mmole/kg in the surface and subsurface which were 4 and 3 times larger than those for the adjacent soils (284 and 223 mmole/kg), respectively (Table 1). Exchangeable bases of Na, K, Mg and Ca also displayed significantly higher contents in the BC-containing soils than those in the adjacent soils (Table 1). Average values for Na, K, Mg and Ca in the BC containing soils were 1.2, 8, 51, and 379 mmole/kg in the surface and 1, 7, 60, and 409 mmole/kg in the subsurface, respectively. Available P content in the BC-containing soils was 3 times higher than that in the adjacent soils. Moreover, BC particles that isolated from BC-containing soils in the size between 1 to 2 mm showed more concentrated amounts of CEC, exchangeable cations and available P
compared with the corresponding soils and indicated the crucial contribution of BC itself toward soils properties (Table 1).

The enhancements of all exchangeable cations in Na, K, Mg and Ca in the BC-containing soils could imply that these increases are promoted by the improvements of soil properties, not just by specific application of ash or lime (Rolando 1992). We propose ash content, high pH value, and high surface charge of BC would facilitate BC-containing soils to retain exchangeable bases. Phosphate may become repulsive when surface negative charge is increased. However, higher soil pH values in the BC-containing soils can reduce P fixation from adsorption or precipitation with iron or aluminium and lead to have higher available P.

Table 1. Soil organic carbon, black carbon, cation exchange capacity, exchangeable cations, base saturation, and available P contents in the BC-containing and adjacent soils (n=16)

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>SOC (g/kg)</th>
<th>BC (mmol/kg)</th>
<th>BC (mmol/kg)</th>
<th>PCEC (mmol/kg)</th>
<th>ECEC (mmol/kg)</th>
<th>Exch. Cation</th>
<th>BS %</th>
<th>Avail P (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 10 cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC-containing</td>
<td>228</td>
<td>-</td>
<td>1139</td>
<td>447</td>
<td>1.2</td>
<td>8</td>
<td>51</td>
<td>379</td>
</tr>
<tr>
<td>Adjacent</td>
<td>53</td>
<td>-</td>
<td>284</td>
<td>107</td>
<td>0.3</td>
<td>3</td>
<td>13</td>
<td>99</td>
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<tr>
<td>10 – 20 cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BC-containing</td>
<td>275</td>
<td>197</td>
<td>1015</td>
<td>495</td>
<td>1.0</td>
<td>7</td>
<td>60</td>
<td>409</td>
</tr>
<tr>
<td>Adjacent</td>
<td>31</td>
<td>12</td>
<td>223</td>
<td>94</td>
<td>0.1</td>
<td>2</td>
<td>14</td>
<td>68</td>
</tr>
<tr>
<td>BC particles</td>
<td>1612</td>
<td></td>
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<td>549</td>
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</tbody>
</table>

*p=9

**pH-dependent charge**

Surface negative charge measured by 0.01N KCl adsorption method showed surface negative charge of both BC-containing and adjacent soils increased with increasing pH (Figure 2). High surface negative charge was also observed in the BC-containing soils. However, negligible positive charge was found for both BC-containing and adjacent soils. Long-term natural oxidation renders BC to develop surface functional groups, such as carboxylic and phenolic groups, and increase surface negative charge or reduce surface positive charge (Cheng et al. 2008a).

![Figure 2](image)

**Figure 2. The values of surface positive (triangles) and surface negative charge (circles) versus pH of historical BC samples in NY of (a) BC-containing soil and (b) adjacent soil.**

**Conclusion**

Our results suggest that BC plays important roles in affecting long-term soil properties, in which C content, surface charge and available nutrients could be enhanced through BC’s intrinsic refractory and surficial oxidation. Our studies reinforce the promising application of BC for long-term C sequestration and soil fertility improvement.

**References**


sustainable agriculture in the humid tropics. Naturwissenschaften 88, 37-41.
Rolando VR (1992) 200 years of soot and sweat: the history and archeology of Vermont’s iron, charcoal, and
lime industries. Vermont Archaeological Society, Manchester Center, Vermont.
clays. Westview Press, Inc. CO.