

# Influence of Pyrolysis Temperature on Cadmium and Zinc Sorption Capacity of Sugar Cane Straw-Derived Biochar

Leônidas C. A. Melo,<sup>a,\*</sup> Aline R. Coscione,<sup>b</sup> Cleide A. Abreu,<sup>b</sup> Aline P. Puga,<sup>b</sup> and Otávio A. Camargo<sup>b</sup>

The effect of pyrolysis temperature on the characteristics and metal sorption capacity of sugar cane straw derived-biochar (BC) was investigated. Biochar was produced at four temperatures (400, 500, 600, and 700 °C) before characterization for yield, ash and moisture content, pH, EC, pH<sub>PZC</sub>, elemental composition, nutrient content, CEC, TGA, and functional groups (FT-IR). Biochar alone and in mixtures containing 10%, w/w biochar with one of two different tropical soils (Entisol and Oxisol) was shaken for 24 h with a 2.0 mM solution (pH 4.5) of Zn or Cd in a batch sorption test. Increasing the pyrolysis temperature led to a reduction in the O/C and H/C molar ratios. The sorption capacity of biochar pyrolyzed at 700 °C was nearly four times greater than that produced at 400 °C. In the Entisol mixture, there was an increase up to seven-fold in the sorption of both Cd and Zn compared with the control (without BC). In the Oxisol mixture, there was a maximum 20% increase in sorption compared with the control. For the remediation of Cd- and Zn-contaminated substrates, the use of higher pyrolysis temperature biochars are recommended because of their higher metal sorption capacities.

*Keywords:* Heavy metals; Biomass; Tropical soils; Zinc

*Contact information:* a: Departamento de Solos, Universidade Federal de Viçosa, CEP 36570-000, Viçosa, MG, Brazil; b: Centro de Solos e Recursos Ambientais, Instituto Agronômico de Campinas, CEP 13020 902, Campinas, SP, Brazil; \*Corresponding author: leonidas.melo@ufv.br

## INTRODUCTION

Biochar (BC) is pyrolyzed biomass produced under limited oxygen or oxygen-absent conditions, the specific intention being application to soil to improve its agronomic and bio-chemical quality (Maia *et al.* 2011) and/or to enhance carbon sequestration (Lehmann *et al.* 2006). Most recently, biochar has been considered as an option for remediation of heavy metals and organic pollutants from contaminated soils, as reviewed by Beesley *et al.* (2011).

Chemically, biochar is difficult to define because of the wide variety of biomass and charring conditions used in its production, which results in materials with a wide range of final characteristics (Lehmann and Joseph 2009). Pyrolysis temperature is critical in determining the final characteristics of biochar, and the carbonization of vegetative materials starts at temperature as low as 190 °C (Song and Guo 2012). For the range of temperature in which biochar is produced (usually < 700 °C), after an extensive characterization of grass- and wood-based biochar, Keiluweit *et al.* (2010) proposed a

categorization based on its chemical and physical states during pyrolysis: (i) transition chars—the crystalline character of the feedstock is preserved; (ii) amorphous chars—heat-altered molecules and incipient aromatic polycondensates are randomly mixed; (iii) composite chars—poorly ordered graphene stacks embedded in amorphous phases; and (iv) turbostratic chars—dominated by disordered graphitic crystallites.

Biochar has the ability to retain metals on protonated functional groups, which correspond to the release of  $H^+$  and also metal exchange with other cations (*e.g.* Na, Ca, K, and Mg) (Uchimiya *et al.* 2010). However, there is evidence that adsorption of transition metals, such as  $Cd^{2+}$ , occurs predominantly on uncharged functional groups via cation- $\pi$  bonding mechanisms, either with  $-C=O$  functional groups or on graphene-like structures (Harvey *et al.* 2011).

Uchimiya *et al.* (2011a) assessed the metal sorption efficacy of cottonseed hull-derived biochar prepared at five temperatures (200, 350, 500, 650, and 800 °C), and concluded that the properties of the surface functional groups of biochars (volatile matter, oxygen contents, and  $pH_{PZC}$ ) control the heavy metal sequestration ability from the soil. In another study employing a set of biochars (activated and non-activated), Uchimiya *et al.* (2011b) observed that biochars containing high amounts of oxygen functional groups were generally the most effective for stabilizing heavy metals (*e.g.*,  $Pb^{2+}$ ,  $Cu^{2+}$ ) in acidic, low CEC (cation exchange capacity), and low TOC soils. An increase in pyrolysis temperature is a way to produce biochar with high stability in the environment, which could be advantageous in avoiding field re-applications. Another mechanism of stability is the formation of mineral-biochar complexes related to increasing surface oxidation of the biochars during aging, as observed by Lin *et al.* (2012) after incubation of an Fe-rich soil (ferrosol) with biochars produced at 550 °C.

Chen *et al.* (2011) verified that corn straw-derived biochar pyrolyzed at 600 °C adsorbed about twice as much Cu(II) and Zn(II) from aqueous solution than a hardwood-derived biochar pyrolyzed at 450 °C. On the other hand, Cao *et al.* (2009) observed that manure-derived biochar produced at 200 °C (BC200) showed higher Pb sorption than biochar formed at 350 °C (BC350). This was mainly attributed to the precipitation of lead with soluble P, which was higher in BC200 than in BC350. Such research findings show that the use of biochar as a metal sorbent depends strongly on the feedstock and pyrolysis conditions and should be evaluated case by case.

In Brazil, sugar cane processing facilities convert the feedstock (sugar cane) into a variety of products, such as sugar, bioethanol, electricity, and other by-products (Cavalett *et al.* 2011). Brazil produced, in 2008, 415 million tons of sugar cane residues (wet biomass): 194 million tons of sugar cane bagasse and 220 million tons of sugar cane straw (Ferreira-Leitão *et al.* 2010). By applying a slow pyrolysis process, such residues can be used to generate electricity with a biochar recovery of between 31% to 33%, as reviewed by Quirk *et al.* (2012).

The present study was aimed at evaluating the influence of the pyrolysis temperature on sugar cane straw-derived biochar used as a metal sorbent and its application in two acidic tropical soils with contrasting attributes. It is hypothesized that by increasing the pyrolysis temperature, the metal retention capacity of biochar will be increased. Such an increase in sorption capacity is sought for future applications of biochar in reclaiming Zn-contaminated mine soils.

## EXPERIMENTAL

### Materials

Sugar cane straw was collected in a field experiment, just after the harvest of sugar cane. The material was oven-dried at 60 °C for 24 h and placed in a cylindrical pyrolyzer of 1.2 L of capacity, inside a muffle furnace. The pyrolyzer was sealed (to prevent oxygen flow) and heated to 400, 500, 600, and 700 °C at the rate of 10 °C/min. The desired temperature was held for about one hour (slow pyrolysis), after which the pyrolyzed material was left to slowly cool down to room temperature. The weights of the starting biomass and of the resulting material (biochar) were recorded to determine the BC yield. Biochar was ground to pass a stainless steel sieve (< 0.5 mm) and used for characterization and subsequent experimentation. A clay-rich Oxisol and an Entisol were used in the batch sorption experiments.

### Methods

#### *Biochar characterization*

The pH and electrical conductivity (EC) of the biochar were measured in the extracts (1:10 solid:solution ratio) after shaking with deionized water for 30 min and 24 h, respectively (Singh *et al.* 2010). Cation exchange capacity (CEC) was determined as described by Song and Guo (2012). Briefly, 0.5 g of BC was placed into 50-mL centrifuge tubes, 40 mL of 1 M ammonium acetate was added, and the mixture was shaken for 20 min at room temperature. The material was filtered in a 0.45- $\mu$ m membrane under vacuum with two portions of 20 mL of the acetate solution. The excess solution (non-adsorbed  $\text{NH}_4^+$ ) was washed with three portions of 30 mL of isopropyl alcohol. The biochar was rinsed with four portions of 50 mL of 1 M KCl solution, the rinsate was collected and brought to a final volume of 250 mL, and the  $\text{NH}_4^+$  was determined by the Kjeldahl method.

Prior to the analysis of the point of zero charge ( $\text{pH}_{\text{pzc}}$ ), the ash of biochar samples was removed by washing with 0.1 M HCl at the proportion of 27 g biochar  $\text{L}^{-1}$  by constant stirring for 1 h; then, the material was rinsed three times with distilled deionized water (DDW) and dried overnight at 80 °C (Uchimiya *et al.* 2011a). The  $\text{pH}_{\text{pzc}}$  was determined as described by Yang *et al.* (2004). In 60 mg of BC, 20 mL of 0.01 M  $\text{CaCl}_2$  solution was added that had been previously adjusted with diluted HCl or NaOH solutions to pH 4, 6, 8, or 10. After shaking for 24 h, the pH was measured, and when the final pH was equal to the initial pH (line 1:1), it was considered to be  $\text{pH}_{\text{pzc}}$ . The CHN elemental composition was determined in an elemental analyzer (Perkin Elmer series II 2400). The oxygen contents were estimated by mass difference, *i.e.*, 100% - (C + H + N + ash) (Fuentes *et al.* 2010).

Ash and moisture contents were determined in an open crucible. First, 1.0 g of BC was weighed, in duplicate, placed in a muffle furnace previously heated to 105 °C, and kept for 1 h. The crucibles were left to cool at room temperature in a desiccator, and their weight was recorded. The difference in the mass loss was considered to be the moisture content. The crucibles were placed again in the furnace and heated to 500 °C within 1 h and to 750 °C by the end of the second hour and held at this temperature for 2 h more. After slow cooling down to room temperature inside the furnace, the crucibles were weighed, and the remaining mass was considered the ash content. There were no visible carbon residues.

### *FT-IR and thermal analysis*

Surface functional groups of BC were analyzed by Fourier transform-infrared spectroscopy (FT-IR, Spectrum One, Perkin Elmer) in the range of 4000 to 450  $\text{cm}^{-1}$  using 20 scans/min at 4  $\text{cm}^{-1}$  resolution. Measurements were performed in pellets of BC blended with KBr.

Thermogravimetric analysis of BC was performed in a TGA 2050 TA instrument. The measurements were obtained under  $\text{N}_2$  atmosphere from room temperature up to 950  $^\circ\text{C}$  at a heating rate of 20  $^\circ\text{C}/\text{min}$ . The sample mass varied from 5.1 to 5.7 mg.

### *Scanning electron microscopy*

Analysis with a scanning electron microscope (SEM) was carried out using a LEO Evo 40 XVP scanning microscope. Images were obtained at 200 $\times$  and 1000 $\times$  magnification. All samples were coated with Au to reduce charge effects.

### *Soil characterization*

Soil material was air-dried and sieved (2 mm) for characterization according to van Raij *et al.* (2001). The soil pH was determined in a 0.01 M  $\text{CaCl}_2$  solution (soil-to-solution ratio 1:2.5 v/v); soil organic matter was obtained following oxidation with sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), and determination was made colorimetrically.

Exchangeable aluminum was extracted with a 1 M KCl solution and measured by titration with a 0.025 M NaOH solution. Phosphorus, Ca, Mg, and K were extracted by ionic exchange resin and determined by ICP OES. The cation exchange capacity (CEC) was calculated as the sum of cations (Ca + Mg + K + H + Al). Total acidity (H + Al) was estimated at pH 7.0 with buffer SMP solution.

Available sulfur was extracted by  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  0.01 M and determined turbidimetrically, after reaction with  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . Soil available concentrations of Cu, Fe, Mn, and Zn were extracted with DTPA pH 7.3 (Lindsay and Norvell 1978).

Boron was extracted by hot water and determined colorimetrically. Soil physical fractionation was performed by the densimeter method (Gee and Or 2002). For a more detailed characterization of these soils, see Melo *et al.* (2011).

### *Batch sorption experiments*

Sorption experiments were carried out following the procedures described by Uchimiya *et al.* (2011c), with modifications. Briefly, 0.2 g of BC or 2.0 g of soil + BC mixture (1.8 g of Oxisol or Entisol + 0.2 g of BC) were weighed into 50-mL centrifuge tubes, in duplicate. Then, 20 mL of synthetic rainwater (SR) (obtained by addition of 10 mM  $\text{H}_2\text{SO}_4$  to deionized water until pH 4.5 was reached) was added to the sample, which was then shaken horizontally for 24 h at 100 oscillations/min. Afterward, 200  $\mu\text{L}$  of a 0.2 M stock solution of Cd or Zn was added to reach a final concentration of 2 mM, and the tubes were shaken for another 24 h and subsequently filtered. In the equilibrium solution, Cd or Zn was measured by ICP-OES. Control treatments were achieved using blank reagents in all batch procedures. Tests of sorption using longer times (*i.e.*, 48 h and 96 h) were performed and showed no significant difference from the 24-h treatment (data not shown), confirming the duration (24 h) was adequate for equilibration.

## RESULTS AND DISCUSSION

### Effect of Pyrolysis Temperature on Biochar Characteristics

Increasing the pyrolysis temperature led to a substantial reduction in the yield of BC, which decreased from 45% of total raw biomass at 400 °C to 31% at 700 °C (Table 1). Similar results (*i.e.*, yields of 43% at 400 °C and 37% at 700 °C) were observed by Wu *et al.* (2012) in rice straw-derived biochar. Also, increasing the temperature led to an increase in the pH and electrical conductivities, probably reflecting the greater ash content of biochar obtained at higher pyrolysis temperatures.

**Table 1.** Characterization of the Biochar

Parameter	Pyrolysis Temperature (°C)			
	400	500	600	700
Yield (% w/w)	45±2	38±1	35±1	31±5
EC (mS cm <sup>-1</sup> )	3.3±0.1	3.8±0.1	3.4±0.1	5.1±0.1
pH <sub>H2O</sub>	8.6±0.1	9.8±0.1	9.7±0.1	10.1±0.1
CEC (mmol <sub>c</sub> kg <sup>-1</sup> )	29±1	31±2	18±5	13±2
pH <sub>PZC</sub>	5.03	4.97	5.34	4.03
C (% w/w)*	67±0.1	71±0.1	74±0.8	73±0.5
H (% w/w)*	3.5±0.1	2.6±0.1	1.7±0.1	0.9±0.1
N (% w/w)*	1.3±±0.1	1.2±0.1	1.2±0.1	1.1±0.1
O (% w/w)*	13.8±0.8	10.7±0.6	6.3±1.5	6.7±0.9
O/C (molar ratio)	0.15	0.11	0.06	0.07
H/C (molar ratio)	0.63	0.44	0.27	0.15
Ash (% w/w)	11.3±0.7	11.7±0.1	13.1±0.1	13.2±0.1
Moisture (% w/w)	3.4±0.1	3.4±0.1	3.4±0.3	5.2±0.2
Ca (g kg <sup>-1</sup> )	6.8±0.3	7.4±0.8	9.1±0.3	9.5±0.4
Mg (g kg <sup>-1</sup> )	1.9±0.1	2.4±0.2	2.6±0.1	2.8±0.2
K (g kg <sup>-1</sup> )	15±1	19±2	18±1	22±1
P (g kg <sup>-1</sup> )	1.1±0.1	1.2±0.1	1.1±0.1	1.1±0.1
S (g kg <sup>-1</sup> )	3.2±0.1	3.8±0.2	4.3±0.3	5.0±0.4
Zn (mg kg <sup>-1</sup> )	23±1	26±1	29±1	30±1

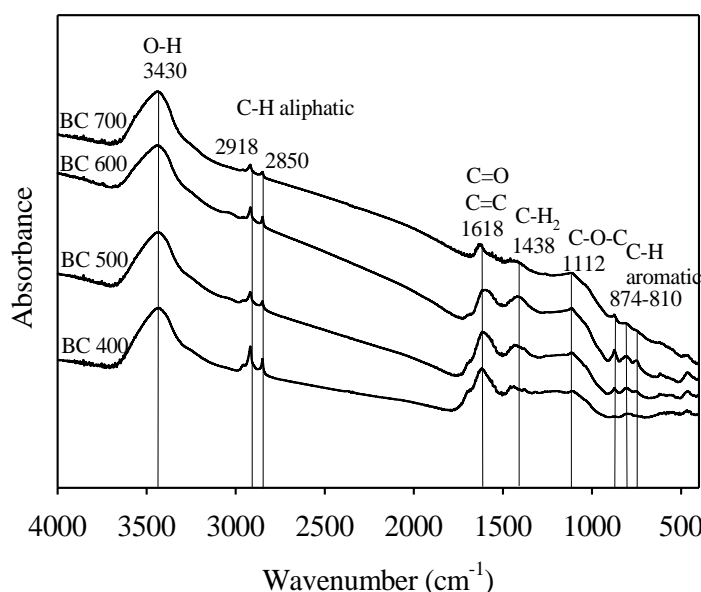
Values are mean (n = 3) ± standard deviation. \*Measurements performed in duplicate

The cation exchange capacity (CEC) was decreased, while the increase of the carbon content corresponded to a decrease of O and H, at higher pyrolysis temperatures. Consequently, there was a reduction in the O/C and H/C molar ratios. The reduction in CEC is probably related to loss of O-containing functional groups. Such findings are in agreement with other work (Singh *et al.* 2010; Mukherjee *et al.* 2011; Uchimiya *et al.* 2011a; Song and Guo 2012) that showed similar results for the effect of temperature on these biochar parameters produced from various biomasses, suggesting that variations in these parameters with temperature occur regardless of the parent biomass and seem to be a general rule.

Molar ratios obtained from the elemental analysis are commonly used to determine the degree of aromaticity (H/C) and polarity (O/C) of coal and have been used for biochar characterization (Uchimiya *et al.* 2011a) because, with increasing pyrolysis temperature, the plant-derived biomass undergoes dehydration reactions and depolymerization to form volatile lignin and cellulose that condensate to form graphitic structures (Keiluweit *et al.* 2010). Lower O/C ratios in biochars formed at higher temperatures increase its stability in the environment. For instance, if the O/C ratio is less than 0.2, the resulting biochar is predicted to have a half-life greater than 1000 years (Spokas 2010).

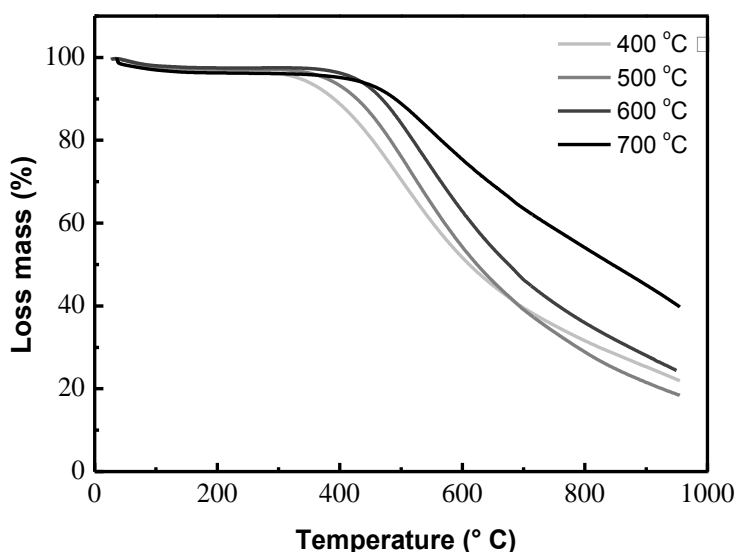
Increasing the pyrolysis temperature of sugar cane straw led to a relative increase in the concentrations of Ca, Mg, K, P, S, and Zn in the resulting BC (Table 1). This is likely to be related to the higher ash content as the temperature increased, making these elements more available. The relatively high levels of Ca, Mg, and K in all BCs tested are due to the sugar cane straw's initial composition, which is rich in such elements, mainly K (Oliveira *et al.* 2002). It should be noted that because of this, BC presents an alkaline reaction (pH ranging from 8.6 to 10.1) and is rich in nutrients; such factors indicate its good potential for reclaiming contaminated land, as it could act as a metal immobilizer and a nutrient supplier, allowing the growth of plants in bare soils. Such characteristics make this particular biochar an attractive option for this purpose. Al-Wabel *et al.* (2013) reported enrichments of 232%, 199%, and 304% for Ca, Mg, and K, respectively, for biochar produced from conocarpus wastes at 800 °C. They concluded that this increase in alkaline elements could be responsible for liming effects induced by biochar pyrolyzed at high temperatures.

The FTIR spectra revealed, in all cases, bands in the region of 3500 to 3400  $\text{cm}^{-1}$ , which relate to stretching of hydroxyl groups and indicate hydrogen bonds (Fig. 1). The bands between 2900 and 2800  $\text{cm}^{-1}$  are related to the elongation of CH aliphatic chains. Bands at 1600  $\text{cm}^{-1}$  represent aromatic systems in double bonds between carbons, but they may also be related to the double bonds between carbon and oxygen in amides. At 1430  $\text{cm}^{-1}$ , the band related to the deformation of  $\text{CH}_2$  groups is observed, but such a band is observed only at BC500 and BC600, which is acceptable because the bands between 874 and 810  $\text{cm}^{-1}$  observed in these BCs represent aromatic CH bonds. Finally, the band at 1112  $\text{cm}^{-1}$  represents C-O-C groups, which are related to cellulose aliphatic ethers, because cellulose is one of the main components of the feedstock. This interpretation is based on Chen *et al.* (2011). With increasing pyrolysis temperature the loss of intensity in bands due to O-H and aliphatic C-H stretching, and the increase in the intensity of bands due to aromatic C-H implies that dehydration and aromatization reactions occurred. The same behavior was observed by Wu *et al.* (2012) in rice straw-derived biochar produced from 300 to 700 °C.



**Fig. 1.** FTIR spectra of sugar cane straw-derived biochar pyrolyzed at four temperatures

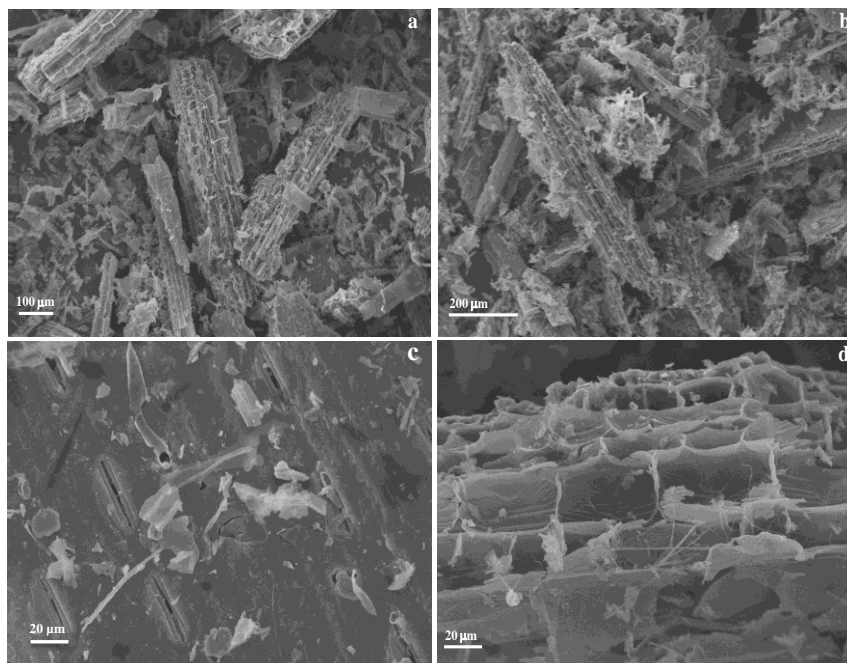
The mass loss at different TGA stages of analysis of the biochar samples is presented in Fig. 2. For all samples considered, Stage 1, around 100 °C, was observed and consistent with the loss of water (moisture) from the samples. With the increase of furnace temperatures, a plateau occurred until around 380 °C (BC400) and 450 °C (BC700), in which no effective loss of mass was observed. At Stage 3, there was a steep drop representing approximately 50% sample weight loss, up to  $\pm$  640 °C. An exception here was BC700, in which the mass loss was relatively low (23.7%), as compared with biochar samples obtained at lower temperatures. The mass loss at this range of temperature is related to the decomposition of the remaining organic content of the BC samples, including cellulose and hemicellulose. The latter starts to decompose from 220 °C up to 315 °C and is followed by cellulose decomposition (Yang *et al.* 2007).



**Fig. 2.** Mass loss by TGA for sugar cane straw biochar samples

Finally, a loss of approximately 20% of sample mass that occurred between 640 °C and 950 °C is attributed to the presence of carbonates. Increasing the pyrolysis temperature led to less pronounced BC weight losses, and the phase changes occurred more discreetly. Crombie *et al.* (2012) also observed that increasing pyrolysis temperature resulted in higher fractions of stable C due to an increased release of volatile matter. This may be interpreted as a stabilization effect of BC by pyrolysis at higher temperatures, which would probably also result in samples being more stable under field conditions, in agreement with the discussion of the O/C molar ratio. The stability of BC, associated with a greater ability to retain metals, is an important criterion for field application with respect to remediation of contaminated areas.

Furthermore, the surface properties of materials are also important in explaining reactivity. In general, the surface morphology of the sugar cane straw biochar samples, despite the temperature they are produced at, showed an irregular amorphous surface with a porous structure (Fig. 3). This effect could be the result of a melting and fusion process of the lignin and other small molecule compounds, such as pectin and inorganic compounds, as described by Liu *et al.* (2010) for pinewood biochar produced at 300 °C and 700 °C.



**Fig. 3.** Scanning electron microscope (SEM) images of biochar. The images show biochar produced at 400 °C (a; c) and 700 °C (b; d), at 200× (a; b) and 1000× magnification (c; d).

### Adsorption of Cd and Zn in Soils

The Oxisol and the Entisol used for experimentation were slightly acidic and had contrasting characteristics, mainly governed by the clay content/fraction (63% for the Oxisol *versus* 6% for the Entisol), CEC, and organic matter content (Table 2). The lower available P and micronutrient (*i.e.*, Cu, Fe, Mn, and Zn) contents in the Oxisol as compared with the Entisol indicate a naturally higher sorption capacity for the Oxisol.

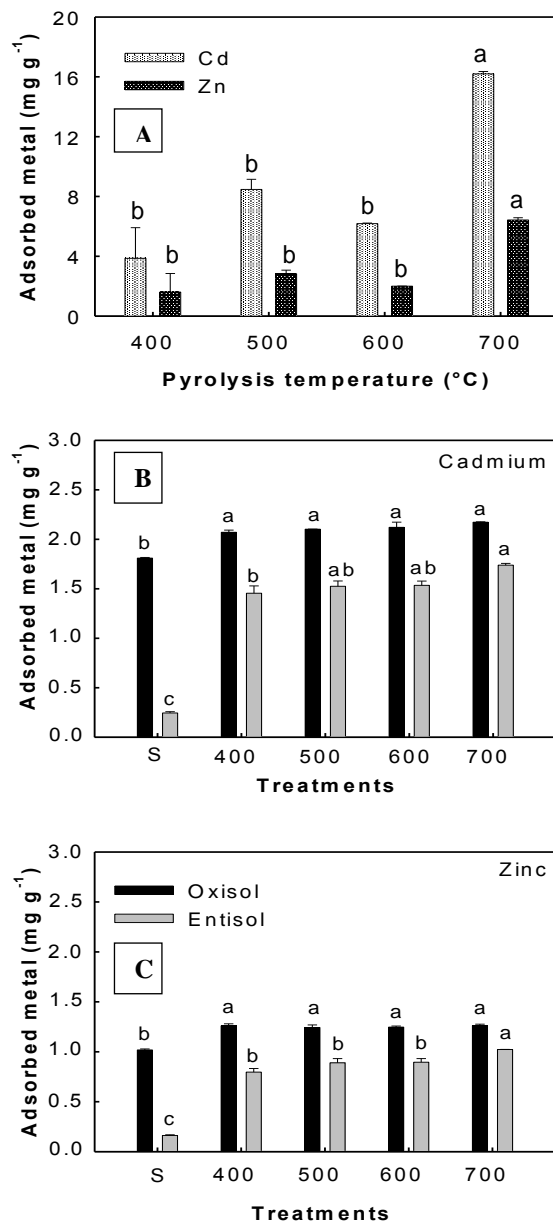
**Table 2.** Characterization of the Soils Used in the Sorption Experiment

Soil	pH	SOM	CEC	Al	Ca	Mg	K
	CaCl <sub>2</sub>	(g kg <sup>-1</sup> )	-----mmol <sub>c</sub> kg <sup>-1</sup> -----				
Oxisol	5.7 ± 0.0	37 ± 2	94 ± 7	-	39 ± 2	26 ± 2	1.4 ± 0.1
Entisol	5.2 ± 0.2	23 ± 2	69 ± 4	1.4 ± 0.1	28 ± 1	1.9 ± 0.8	0.6 ± 0.1
	P	S	Cu	Fe	Mn	Zn	B
	-----mg kg <sup>-1</sup> -----						
Oxisol	3.9 ± 0	60 ± 3	0.7 ± 0.1	39 ± 1	14 ± 2	0.5 ± 0.1	0.3 ± 0
Entisol	173 ± 6	15 ± 1	3.0 ± 0.1	130 ± 13	28 ± 1	11 ± 0.1	1.0 ± 0

SOM, soil organic matter; CEC, cation exchange capacity; -, not detected

When the batch adsorption experiment was performed using BC only, there was a remarkable increase in the adsorption of both Cd and Zn, as a function of pyrolysis temperature (Fig. 4A).





**Fig. 4.** Adsorption of cadmium and zinc in biochars prepared at different temperatures (A); and adsorption of cadmium (B) or zinc (C) in Oxisol or Entisol alone or mixed with 10% (w/w) biochar pyrolyzed at different temperatures. The Fig. 3C legend can be used also for Fig. 3B.

Pyrolysis of biochar at 700 °C increased the adsorption of both metals four-fold, as compared with the BC produced at 400 °C. The BC pyrolyzed at 500 °C and 600 °C showed similar and intermediate sorption capacities of metals. These results are in agreement with Chen *et al.* (2011), who found higher sorption capacities of Cu and Zn from aqueous solution in corn straw biochar produced at 600 °C than in hard wood biochar at 450 °C. This result was attributed to the higher surface area and porosity of the biochar formed at the higher temperature. Also, Jiang *et al.* (2012) observed that the application of rice straw-derived biochar in an Ultisol increased soil pH, making the surface charge more negative, and significantly decreasing the amounts of acid-soluble Cu(II) and Pb(II), as extracted by 0.11 M acetic acid in the BCR sequential extraction

method. They also found that the functional groups (*i.e.*, -COOH and -OH) of the biochar formed stable complexes, mainly with Cu(II), greatly enhancing its adsorption.

Interesting results were found when biochar was mixed into the soils, as related to cadmium (Cd) or zinc (Zn) sorption (Fig. 4B and 4C). The addition of 10% BC to the Oxisol increased the adsorption of both Cd and Zn up to 20%, as compared with the control. As discussed above, Oxisol is clay-rich and naturally exhibits a relatively high sorption capacity. Even so, BC played a role in increasing the metal sorption capacity in this soil.

When BC was applied to the Entisol, there was an increase up to seven-fold in the sorption of both cations, as compared with the control (without BC). Uchimiya *et al.* (2011c) also found similar results for Cu retention in two soils (Norfolk and San Joaquin), with distinct characteristics. In Norfolk soil, biochar enhanced Cu retention mainly by the cation exchange mechanism, while for San Joaquin soil, additional mechanisms such as electrostatic interactions, sorption, complexation, and precipitation were responsible for controlling Cu adsorption.

It should be noted that BC at 700 °C was more effective in increasing the sorption of Cd as compared with BC at 400 °C (Fig. 4B) and significantly increased sorption of Zn as compared with all other BC (Fig. 4C). As the CEC reduces with the increase in pyrolysis temperature (Table 1), probably the dominant metal sorption mechanism between the metals and BC700 was cation- $\pi$  bonding, agreeing with the observations of Harvey *et al.* (2011). Another property of BC that could explain these results is the higher pH of the BC at 700 °C, which has a more pronounced liming effect (when BC is reacted with the soil), thus causing precipitation of Cd or Zn. This is in agreement with the findings of Kim *et al.* (2013), which observed that biochar produced from a giant *Miscanthus* at higher pyrolytic temperatures ( $\geq 500$  °C) increased the sorption of Cd from aqueous solution up to 13.24 mg g<sup>-1</sup> ( $\approx 59$  mmol kg<sup>-1</sup>) and they attributed the results due to the precipitation as Cd(OH)<sub>2</sub> as a consequence of the higher pH and also due to the higher surface area.

Results from Uchimiya *et al.* (2011a), on the other hand, show that biochar formed at a lower temperature (350 °C) was more effective in retaining heavy metals in acidic and eroded soil than biochar formed at higher temperatures. They concluded that “surface functional groups of biochars (which govern pH<sub>pzc</sub> and oxygen contents) control their ability to retain heavy metals in the soil.” Therefore, they stated that “biochar selection for soil amendment must be made case by case based on the biochar characteristics, soil property, and the target function.” In this particular case, the pH<sub>pzc</sub> of the BC at 350 °C was only one unit below the equilibrium pH. The higher the difference between pH<sub>pzc</sub> and equilibrium pH is, the higher the electrostatic interactions between cationic metal species and negatively charged surfaces (Uchimiya *et al.* 2011a), which in the current case is for BC at 700 °C, helping to explain the higher metal sorption.

In aqueous solution, Uchimiya *et al.* (2012), however, found that BC poultry litter pyrolyzed at 350 °C was better at retaining and stabilizing Pb in a contaminated soil than the BC produced at 650 °C. In this case, they found that the soluble P in larger concentrations in BC at lower temperatures was the main mechanism in retaining Pb. This reinforces the idea that the mechanisms of metal retention by BC are specific and depend on the conditions of the pyrolysis source biomass used and the metal.

## CONCLUSIONS

1. Biochar physicochemical properties were affected by the pyrolytic temperatures, with higher temperatures leading to more recalcitrant forms of the material.
2. The increase in the pyrolysis temperature increased the capacity of sugar cane straw-derived biochar to sorb Cd and Zn.
3. The effect of biochar in the sorption of Cd and Zn is much more pronounced in sandy soils, with their low natural ability to retain metal pollutants, than in clay soils.

## ACKNOWLEDGMENTS

The authors are grateful for the financial support of the São Paulo Research Foundation (FAPESP) (Grant No. 2011/12346-3) and for the postdoctoral fellowship (Grant No. 2011/02844-6) for the first author. The authors are also grateful to Prof. J. O. Brito (Esalq/USP) for kindly providing the biochar for the study and to Dr. Luke Beesley (The James Hutton Institute) for helpful comments on the article.

## REFERENCES CITED

- Al-Wabel, M. I., Al-Omran, A., El-Naggar, A. H., Nadeem, M., and Usman, A. R. A. (2013). "Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpus wastes," *Bioresour. Technol.* 131, 374-379.
- Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J. L., Harris, E., Robinson, B., and Sizmur, T. (2011). "A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils," *Environ. Pollut.* 159(12), 3269-3282.
- Cao, X., Ma, L., Gao, B., and Harris, W. (2009). "Dairy-manure derived biochar effectively sorbs lead and atrazine," *Environ. Sci. Technol.* 43(9), 3285-3291.
- Cavalett, O., Junqueira, T. L., Dias, M. O. S., Jesus, C. D. F., Mantelatto, P. E., Cunha, M. P., Franco, H. C. J., Cardoso, T. F., Maciel Filho, R., Rossell, C. E. V., and Bonomi, A. (2011). "Environmental and economic assessment of sugarcane first generation biorefineries in Brazil," *Clean Technol. Environ. Policy* 14(3), 399-410.
- Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., and Hay, A. G. (2011). "Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution," *Bioresour. Technol.* 102(19), 8877-8884.
- Ferreira-Leitão, V., Gottschalk, L. M. F., Ferrara, M. A., Nepomuceno, A. L., Molinari, H. B. C., and Bon, E. P. S. (2010). "Biomass residues in Brazil: Availability and potential uses," *Waste Biomass Valorization* 1(1), 65-76.
- Fuertes, A. B., Arbestain, M. C., Sevilla, M., Maciá-Agulló, J. A., Fiol, S., López, R., Smernik, R. J., Aitkenhead, W. P., Arce, F., and Macias, F. (2010). "Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover," *Aust. J. Soil Res.* 48(7), 618-626.

- Gee, G. W., and Or, D. (2002). "Particle-Size Analysis," in: *Methods of soil analysis. Part 4. Physical methods*, Dane, J. H., Toop, G. C. (eds.), American Society of Agronomy (ASA) and the Soil Science Society of America (SSSA), Madison. p. 255-293.
- Harvey, O. R., Herbert, B. E., Rhue, R. D., and Kuo, L.-J. (2011). "Metal interactions at the biochar-water interface: Energetics and structure-sorption relationships elucidated by flow adsorption microcalorimetry," *Environ. Sci. Technol.* 45, 5550-5556.
- Jiang, J., Xu, R., Jiang, T., and Li, Z. (2012). "Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol," *J. Hazard. Mater.* 229, 145-150.
- Keiluweit, M., Nico, P. S., Johnson, M. G., and Kleber, M. (2010). "Dynamic molecular structure of plant biomass-derived black carbon (biochar)," *Environ. Sci. Technol.* 44(4), 1247-1253.
- Kim, W. K., Shim, Y., Kim, Y. S., Hyun, S., Ryu C., Park, Y. K., Jung, J. (2013). "Characterization of cadmium removal from aqueous solution by biochar produced from a giant *Miscanthus* at different pyrolytic temperatures," *Bioresour. Technol.* 138, 266-270.
- Lehmann, J., and Joseph, S. (2009). *Biochar for Environmental Management: Science and Technology*, Earthscan Ltd., London.
- Lehmann, J., Gaunt, J., and Rondon, M. (2006). "Bio-char sequestration in terrestrial ecosystems—A review," *Mitigation and Adaptation Strategies for Global Change* 11(2), 395-419.
- Lin, Y., Munroe, P., Joseph, S., Kimber, S., and Zwieten, L. (2012). "Nanoscale organo-mineral reactions of biochars in ferrosol: An investigation using microscopy," *Plant Soil* 357(1-2), 369-380.
- Lindsay, W. L., and Norvell, W. A. (1978). "Development of a DTPA soil test for zinc, iron, manganese and copper," *Soil Sci. Soc. Am. J.* 42(3), 421-428.
- Liu, Z., Zhang, F.-S., and Wu, J. (2010). "Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment," *Fuel* 89(2), 510-514.
- Maia, C. M. B. F., Madari, B. E., and Novotny, E. H. (2011). "Advances in biochar research in Brazil," *Dynamic Soil, Dynamic Plant* 5(Special Issue 1), 53-58.
- Melo, L. C. A., Alleoni, L. R. F., Carvalho, G., and Azevedo, R. A. (2011). "Cadmium- and barium-toxicity effects on growth and antioxidant capacity of soybean (*Glycine max* L.) plants, grown in two soil types with different physicochemical properties," *J. Plant Nutr. Soil Sci.* 174(5), 847-859.
- Mukherjee, A., Zimmerman, A. R., and Harris, W. (2011). "Surface chemistry variations among a series of laboratory-produced biochars," *Geoderma* 163(3-4), 247-255.
- Oliveira, M. W., Trivelin, P. C. O., Boareto, A. E., Muraoka, T., and Mortatti, J. (2002). "Leaching of nitrogen, potassium, calcium and magnesium in a sandy soil cultivated with sugarcane," *Pesqui. Agropecu. Bras.* 37(6), 861-868.
- Quirk, R. G., Zwieten, L., Kimber, S., Downie, A., Morris, S., and Rust, J. (2012). "Utilization of biochar in sugarcane and sugar-industry management," *Sugar Tech* 14(4), 321-326.
- van Raij, B., Andrade, J. C., Cantarella, H., and Quaggio, J. A. (2001). *Chemical Analysis to Evaluate the Fertility of Tropical Soils*, Instituto Agronômico, Campinas (in Portuguese).

- Singh, B., Singh, B. P., and Cowie, A. L. (2010). "Characterisation and evaluation of biochars for their application as a soil amendment," *Aust. J. Soil Res.* 48(7), 516-525.
- Song, W., and Guo, M. (2012). "Quality variations of poultry litter biochar generated at different pyrolysis temperatures," *J. Anal. Appl. Pyrolysis* 94, 138-145.
- Spokas, K. A. (2010). "Review of the stability of biochar in soils: Predictability of O:C molar ratios," *Carbon Manage.* 1(2), 289-303.
- Uchimiya, M., Lima, I.M., Klasson, K.T., and Wartelle, L.H. (2010). "Contaminant immobilization and nutrient release by biochar soil amendment: Roles of natural organic matter," *Chemosphere* 80, 935-940.
- Uchimiya, M., Wartelle, L. H., Klasson, K. T., Fortier, C. A, and Lima, I. M. (2011a). "Influence of pyrolysis temperature on biochar property and function as a heavy metal sorbent in soil," *J. Agric. Food Chem.* 59(6), 2501-2510.
- Uchimiya, M., Chang, S., and Klasson, K. T. (2011b). "Screening biochars for heavy metal retention in soil: Role of oxygen functional groups," *J. Hazard. Mater.* 190(1-3), 432-441.
- Uchimiya, M., Klasson, K. T., Wartelle, L. H., and Lima, I. M. (2011c). "Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations," *Chemosphere* 82(10), 1431-1437.
- Uchimiya, M., Bannon, D. I., Wartelle, L. H., Lima, I. M., and Klasson, K. T. (2012). "Lead retention by broiler litter biochars in small arms range soil: Impact of pyrolysis temperature," *J. Agric. Food Chem.* 60(20), 5035-5044.
- Wu, W., Yang, M., Feng, Q., McGrouther, K., Wang, H., Lu, H., and Chen, Y. (2012). "Chemical characterization of rice straw-derived biochar for soil amendment," *Biomass Bioenergy* 47, 268-276.
- Yang, Y., Chun, Y., Sheng, G., and Huang, M. (2004). "pH-dependence of pesticide adsorption by wheat-residue-derived black carbon," *Langmuir* 20(16), 6736-6741.
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86, 1781-1788.

Article submitted: June 24, 2013; Peer review completed: July 31, 2013; Revised version received: August 6, 2013; Accepted: August 7, 2013; Published: August 12, 2013.