Supplementary Information

Ammonium, Nitrate and Phosphate Sorption to and Solute Leaching from Biochars Prepared from Corn Stover (Zea mays L.) and Oak Wood (Quercus ssp.)

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Physical differences between Corn-BC and Oak-BC with temperature

A previous study (Rajkovich, 2012) analyzed elemental concentrations (Ca, H, Mg, N, O, P) of these BCs including surface area and pore volume of Corn-BC and Oak-BC pyrolyzed at 400° and 600° C HTT using nitrogen gas (N₂) and CO₂ adsorbates. The N₂ measured surface area and pore volume for the Corn-BC shows an inverse relation to increasing HTT yet CO₂ measured surface area and pore volume increase with increasing HTT (Table 1). The Corn-BC micropore volume (measured with CO₂ adsorbate) doubles between 400-600 °C.

The ash content between Corn-BC and Oak-BC are markedly different across the HTT range (S.I. figure 1). The Oak-BC ash content does not increase with HTT whereas the Corn-BC shows a steady increase in ash content with increasing HTT. The higher ash content of the Corn-BC might be related to lower lignin content, whereas Oak-BC has higher lignin and would dilute the ash content on a weight basis. As Corn-BC loses mass in volatiles, percent ash content increases. Ash content can also be a surrogate for pH, where BC produced at higher HTT have higher pH (Nguyen et al., 2009).
S.I. Figure 1: Mean ash content (%) of Corn-BC and Oak-BC. ASTM 750º C method used, ash content equals (1 - % mass lost after combustion at 750º C in oxic conditions), compared to 105º C dry weight under oxic conditions. Error bars represent standard deviation, n=3. Data is compiled from a previous study (Rajkovich, 2012).

The nitrogen content of char remains fixed over the HTT range (S.I. Figure 2). For the 350º and 550º C chars of each feedstock, there does not appear to be any difference in their nitrogen contents between the two temperatures. The nitrogen must be changing in the same proportion as the overall mass of the char in order to maintain the same percent content over the HTT series.
S.I. Figure 2: Mean nitrogen content of Corn-BC and Oak-BC. Error bars represent standard deviation, n=3. Data is compiled from a previous study (Rajkovich, 2012).

The P content of the two chars is very different. Looking across the HTT range, Corn-BC shows an increasing P content with increasing temperature (S.I. Figure 3) whereas the P content of Oak-BC is constant throughout the entire temperature series. The pyrolysis reaction does not release much P from the feedstock as it is converted into BC (Bridle et al., 2004).
Ca could be an important element for P sorption as it is associated with the largest fraction of P in some chars (Bridle et al., 2004). In both Corn-BC and Oak-BC, Ca appears to increase with increasing HTT (S.I. Figure 4). Differences in Mg content of the Corn-BC and Oak-BC are large across the HTT range (S.I. Figure 5). For the temperature range of this study, the Mg content of the Corn-350-BC and Corn-550-BC is 150 and 200 times the Mg content of Oak-350-BC and Oak-550-BC respectively.
S.I. Figure 4: Mean calcium content of Corn-BC and Oak-BC. Error bars represent standard deviation, n=3. Data is compiled from a previous study (Rajkovich, 2012).
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S.I. Figure 5: Mean magnesium content of Corn-BC and Oak-BC. Error bars represent standard deviation, n=3. Data is compiled from a previous study (Rajkovich, 2012).

Ammonium sorption

Ammonium sorption was performed using biochar prepared by Alterna Biocarbon (Prince George, British Columbia) from a mixture of softwoods (Spruce, Pine and Fir; referred to as “SPF-BC”), which came from a chipped waste stream of the logging and sawmill industry. The wood mixture was slow-pyrolyzed at 400°C. Sorption experiments were prepared with SPF-BC and solution concentrations ranging: 1; 10; 100; 1000; 10,000 mg NH₄⁻N L⁻¹. Equilibrium concentrations were analyzed using the phenate colorimetric method (AWWA, 1999). Absorbance was measured at 640 nm on a Hewlett Packard diode array UV-Vis spectrophotometer. Results were analyzed using the Freundlich isotherm model (S.I. Equation 1 and 2).

Strong sorption was observed with unwashed, ground SPF-BC. The data fit the linearized Freundlich model well. The equation for the best fit line through the data had an R² value of 0.949, yielding a Kᵢ value of 0.129 and an n value of 1.423 (S.I. Figure 6). It was also confirmed that the solid to liquid ratio in the sorption experiments was suitable for the ammonium concentration range.
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S.I. Figure 6: Ammonium sorption results using raw, ground SPF-BC. Data was linearized according to the Freundlich model: $K^*_f = 0.129$, $n = 1.423$.

The Freundlich adsorption isotherm was chosen to model NH$_4$ sorption to SPF-BC:

\[ q^* = K^*_f C_e^{1/n} \]  \hspace{1cm} (S.I. eq. 1)

Where:
- $q^*$ = mass of NH$_4$ adsorbed per mass of BC at equilibrium
- $K^*_f$ = experimentally derived constant
- $C_e$ = equilibrium concentration of NH$_4$ in solution
- $1/n$ = experimentally derived constant

A least square regression of log($q^*$) versus log($C_e$) gives:

\[ \log(q^*) = \log(K^*_f) + \frac{1}{n} \log(C_e) \]  \hspace{1cm} (S.I. eq. 2)

Where:
- $\log(K^*_f) = y$-intercept
- $n^{-1}$ = the slope