Evaluation and implementation of methods for quantifying organic and inorganic components of biochar alkalinity

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Evaluation and implementation of methods for quantifying organic and inorganic components of biochar alkalinity

by

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CHAPTER 1. LITERATURE REVIEW

Biochar Production and Chemical Properties

Many definitions of biochar have been put forward in the literature, but it is generally agreed that biochar is pyrolyzed organic matter produced primarily for application to the soil (Lehmann et al., 2006; Spokas et al., 2011; Woolf et al., 2010). Pyrolysis is defined as the thermochemical transformation of carbonaceous materials at high temperature under oxygen-limited conditions. Pyrolysis results from incomplete combustion; and pyrolyzed organic matter can therefore be found in soils as a result of natural fires. Pyrolyzed organic matter, including biochar and non-anthropogenic pyrolyzed organic matter, found in soil is often referred to as black carbon (Spokas et al., 2011). Both natural black carbon and biochar are composed of a condensed aromatic carbon framework intermixed with inorganic compounds such as oxides, hydroxides and carbonates of base cations collectively referred to as “ash,” (Amonette and Joseph, 2009). A variety of feedstocks including various woods, crop residues and manures can be made into biochar via slow pyrolysis, fast pyrolysis, or gasification. Different techniques for achieving the thermal decomposition of organic materials vary in retention time and temperature. Slow pyrolysis can take hours to days, and is usually performed on individual batches between 350-800ºC; these conditions allow for maximum biochar yield. Fast pyrolysis is a continuous process usually performed between 400-600ºC, with the peak temperature reached in seconds, and it maximizes bio-oil production while still producing biochar. Gasification occurs in seconds to minutes at higher temperatures, ~700-
1500°C, in the presence of a controlled amount of oxygen. These conditions maximize the conversion of feedstocks into a combustible gas called syn-gas, which usually results in a low-C ash product, but the process can be engineered to produce biochar instead (Brewer, 2012; Brown, 2009).

Biochar pyrolysis parameters and feedstock can have a profound effect on biochar chemical properties (Spokas and Reicosky, 2009). Most notably, the degree of aromatic condensation has been shown to increase with increasing pyrolysis temperature and retention time. Consequently, fast pyrolysis biochars tend to be comprised of the small aromatic ring clusters, while gasification biochars contain relatively larger clusters (Brewer et al., 2009) (Figure 1.1). The arrangement of these clusters changes as temperature increases, starting as an amorphous matrix at lower temperatures to a more graphite-like, hard carbon structure at higher temperatures, with middle temperature biochars containing a mixture of these components (Franklin, 1951; Keiluweit et al., 2010). Ash content has been shown to be affected by both peak pyrolysis temperature and the chemistry of the feedstock. As the peak pyrolysis temperature increases, more organic components are volatilized, leaving behind a higher proportion of ash. Biochars made from feedstocks with relatively high concentrations of inorganic elements, including Si, Ca, Mg, K, P, Cl, and various metals, tend to have higher ash contents. As a result, crop residue and manure biochars have higher ash contents than wood biochars (Amonette and Joseph, 2009; Spokas and Reicosky, 2009; Spokas et al., 2011). Feedstock also affects the types of organic functional groups found in biochars. Biochars made from feedstocks with higher nitrogen contents, such as manures and dried distillers grains, have a higher proportion of nitrogen-based functional groups than those
produced from feedstocks with lower nitrogen contents, such as sawdust (Amonette and Joseph, 2009). The interactions between feedstock chemistry and pyrolysis temperature are not well understood, although grass is known to begin thermal decomposition at lower temperatures than wood (Keiluweit et al., 2010).

Although much progress has been made towards systematically characterizing biochar, the connections between biochar chemistry and how biochar interacts with soil is unclear. This knowledge gap is in part due to lack of quantitative research into intrinsic biochar properties that are the most relevant to soil chemical interactions. Because most soil chemical processes are aqueous and pH-dependent, relevant biochar properties would include concentrations of inorganic alkalis and organic functional groups that are reactive in pH range of soil (~4-9).

**Interactions of Biochar with Soil**

A plethora of studies have documented the effects of a wide variety of biochars on different soils, but relatively few studies have definitively elucidated the mechanisms underlying biochar-soil interactions (Joseph et al., 2010). Following application to the soil, biochar has been shown to increase crop yields, cation exchange capacity, microbial activity, soil organic carbon, and pH, and to decrease agroecosystem greenhouse gas emissions, nutrient leaching, and aluminum toxicity (Joseph et al., 2010; Major et al., 2010; Pietikäinen et al., 2000; Spokas et al., 2011; Steinbeiss et al., 2009). However, the effects biochar has on
soil vary with the soil and biochar type, and without mechanistic knowledge, it is difficult to predict how specific biochars will affect specific soils (Kimetu and Lehmann, 2010).

Many mechanisms have been postulated to explain soil-biochar interactions. Short-term pH increases are attributed to the dissolution of soluble inorganic and organic compounds, whereas long-term pH changes (increases or decreases) are due to the interaction of insoluble organic functional groups on biochar surfaces with the soil solution (Joseph et al., 2010). Long-term increases in cation exchange capacity and reductions in nutrient leaching are thought to be due to oxidation of biochar surfaces and subsequent formation of negatively charged acidic functional groups. Differences in the amount of biochar retained between coarse and fine textured soils have been attributed to the greater aeration of coarse textured soils, which allows for higher rates of chemical and biological oxidation of the biochar (Cheng et al., 2006; Joseph et al., 2010; Zimmerman et al., 2011). Lastly, effects on microbial and plant growth have been correlated with increases in pH, CEC and other effects. pH can affect all of the soil-biochar interactions discussed here, and therefore the soil and biochar pH values should be measured in any study investigating these interactions (Joseph et al., 2010).

**The Importance of Consistent, Accurate Methodology in Biochar Analysis**

Much of the lack of understanding of biochar-soil interaction mechanisms stems from a lack of consistency and/or accuracy of methodologies used in different studies (Spokas et al., 2011). Many of the methods used to analyze biochar were adapted from methods used to
analyze soil, coal, carbon black, or activated carbon, and it remains unclear whether these methods are also accurate for use with biochar. For example, biochar pH has been measured using saturated paste methods originally developed for use with soil. These methods often use different water-to-biochar ratios than the original soil methods, and it is not clear how the biochar-to-water ratio influences pH measurements (Gaskin et al., 2008; Singh et al., 2010; Van Zwieten et al., 2010). Fresh biochar is often hydrophobic whereas aged biochar is hydrophilic and may absorb large amounts of water. The amount of water adsorbed during saturated paste pH measurements could lead to bias in pH measurements (Karhu et al., 2011).

The Boehm titration (Boehm, 1994) was designed to measure reactive organic functional group concentrations of activated carbons and carbon blacks in discrete pK$_a$ ranges, and has recently been applied to biochar characterization (Boehm, 1994; Mukherjee et al., 2011; Singh et al., 2010). Although activated carbons and carbon blacks are, like biochar, made from pyrolyzed organic matter, the feedstocks and production parameters used to make them are different. Biochar can be made from a wide range of carbonaceous feedstocks, whereas activated carbon is made primarily from wood and carbon black is made from aromatic oils; activated carbon and black carbon are typically made at higher temperatures than biochar (Fulcheri and Schwob, 1995). Because the Boehm titration has not been standardized for use with biochars, it is not clear whether measurements of biochar functional groups made using the Boehm titration are accurate (Goertzen et al., 2010; Oickle et al., 2010). In addition, different authors take different approaches to adapting the Boehm titration for use with biochars. Consequently, Boehm titration results from different studies may not be comparable.
Several methods have been used to characterize organic functional groups on surfaces of biochar. Several studies have use Fourier-transform infrared spectroscopy (FTIR) to characterize organic functional groups on biochar surfaces, while other studies take a more quantitative approach with $^{13}$C nuclear magnetic resonance ($^{13}$C NMR) or Boehm titrations (Chun et al., 2004; Singh et al., 2010; Xu et al., 2011). In part, differences in approach are due to the expense involved with obtaining and operating FTIR and NMR instruments. Whichever method is chosen, the types of data yielded by each method are fundamentally different. The peaks in an FTIR spectrum represent bond vibrations at specific frequencies, and provide qualitative information about the functional groups being analyzed. Functional groups that can be distinguished using FTIR include carboxylic acids, esters, alcohols, and ketones (Solomons and Fryhle, 2008). The peaks in a $^{13}$C-NMR spectrum, on the other hand, represent the vibrations of $^{13}$C nuclei at specific frequencies determined by the structural environment of the nuclei producing the signal. The area under each peak is proportional to the number of $^{13}$C nuclei producing the signal; therefore, careful analysis of $^{13}$C-NMR spectra can allow for quantification of certain functional groups if the signals are sufficiently strong. Groups that can be quantified include alkene, alkyne, and aromatic C bonds, as well as C-O and C=O bonds. However, $^{13}$C-NMR alone is not capable of distinguishing quantitatively between carboxylic acids and esters, between lactones and non-cyclic esters, or between alcohols and ethers (including phenols and anisoles) (Solomons and Fryhle, 2008). Distinguishing among these groups is especially important to understanding biochar’s chemical interactions with soil, because some will react with acids or alkalis in the soil (carboxylic acids, lactones, lactols, and phenols), while others will not (ethers and non-cyclic esters). Unlike FTIR and $^{13}$C-NMR, the Boehm titration offers an opportunity to quantify
carboxylic acids, lactones, lactols, phenols, and other functional groups with similar pK$_a$ values that might react under soil conditions. Examples of functional groups that can be quantified with $^{13}$C-NMR and the Boehm titration can be found in Figures 1.1 and 1.2. The Boehm titration employs equilibration with the conjugate bases of weak acids to enable the quantification of functional groups in discrete pK$_a$ ranges (Boehm, 1994). In this way, non-reactive groups that do not have pK$_a$ values are excluded from quantification with the Boehm titration. Thus, FTIR, $^{13}$C-NMR and the Boehm titration are each capable of detecting and/or quantifying a distinct suite of functional groups. Methods used for characterizing biochar functional groups must therefore be chosen carefully to make the results as relevant as possible to the experimental hypothesis and as comparable as possible to the results of similar studies.

With regards to quantifying sources of alkalinity in biochar, some studies quantify the total and inorganic alkalinity only, whereas other studies quantify organic and inorganic alkalinity (Chun et al., 2004; Singh et al., 2010; Yuan et al., 2011). Similar differences in approach exist for other properties, such as the stability of biochar in soil, and its effect on crop yields. Such differences in approach can make comparisons between studies that explore the same biochar properties very difficult.

In summation, differences in the way methods are executed and in methods chosen to analyze specific properties often prevent direct comparison of results among biochar studies. Therefore, there is a need for the development and standardization of methods adapted from other disciplines for use with biochar, and for the development of a centralized list of methods to be used for the characterization and/or quantification of specific biochar
properties. This study will help to meet those needs by evaluating modified Boehm titrations for use with biochar and developing a suite of methods for assessing biochar alkalinity.

**Figure 1.1** Possible structures of aromatic clusters in switchgrass biochars made via fast pyrolysis at 500°C (left), slow pyrolysis at 500°C (middle), and gasification at 760°C (right) based on $^1$H and $^{13}$C-NMR data (Brewer, 2012).

**Figure 1.2** Hypothetical structures for wood biochar (left) and a manure biochar (right) showing aromatic clusters. The structures are based on data in Amonette and Joseph, 2009.

*Can be quantified with the Boehm titration.

*Can be quantified with the Boehm titration and likely to react in soil.
CHAPTER 2. EVALUATION OF MODIFIED BOEHM TITRATION METHODS FOR USE WITH BIOCHARS

Abstract

The Boehm titration, originally developed to characterize carbon blacks and activated carbons, has earned growing attention as a method for characterization of acid and base properties of biochar (Boehm, 1994; Goertzen et al., 2010). The method is based on the principle that strong acids and bases will react with all bases and acids, respectively, whereas the conjugate bases of weak acids will accept protons only from stronger acids (i.e. acids with lower pK\textsubscript{a} values). However, properties that distinguish biochar from carbon black and activated carbon, including greater carbon solubility and higher ash content, may violate integral assumptions of the Boehm titration. Three key assumptions are: (1) carbonates (as carbonate and bicarbonate) originating from atmospheric CO\textsubscript{2} are not present during titration, (2) solid-phase reactive compounds, including oxides, hydroxides, carbonates, and other conjugate bases of weak inorganic acids such as orthophosphate and sulfate have been removed prior to equilibration with Boehm reactants, and (3) the Boehm reactants do not dissolve significant amounts of organic molecules that contain reactive functional groups. Here we use three biochars to evaluate three modified Boehm titration methods for removing carbonates and dissolved organic compounds (DOC) from Boehm extracts. Our results indicate that the original Boehm titration method for measurement of functional groups with pK\textsubscript{a} values > 10.3 is not reliable when used with biochars containing significant levels of ash or soluble organic compounds. None of the modified Bohem titration methods developed and
tested here were able to fully resolve problems associated with soluble organic and inorganic components found in biochars. Therefore, more research will be needed to develop a robust Boehm titration method for use with biochar.

**Introduction**

Biochar is a co-product of the pyrolysis of biomass to produce energy that can be used as a soil amendment. Due to the recalcitrant nature of its framework of condensed aromatic carbon, biochar is predicted to have soil residence times of 100-1000 years. Consequently, biochar application to soils is widely viewed as a means for sequestering carbon from the atmosphere (Kimetu and Lehmann, 2010; Woolf et al., 2010). Biochar also has been shown to increase cation exchange capacity, plant available water, and pH while decreasing nutrient leaching and greenhouse gas emissions (Laird et al., 2010a; Laird et al., 2010b; Rogovska et al., 2011). Growing interest in biochar chemical properties and their potential impact on soil-biochar interactions has created the need for methods capable of quantitatively characterizing biochar surface functional groups that are reactive under soil-relevant conditions. To fill this need, many researchers have turned to Boehm titrations, because, unlike spectroscopic methods, they measure only functional groups that are reactive in aqueous environments (Mukherjee et al., 2011; Singh et al., 2010; Xu et al., 2012).

The Boehm titration was originally developed in 1994 by Hans Peter Boehm for quantifying the oxygen-containing surface functional groups of carbon blacks (Boehm, 1994; Boehm, 2002). The titration’s underlying principle is that strong acids and bases will react with all bases and acids, respectively, whereas weak acids will only donate protons to the conjugate bases of acids with higher pKₐ values (Table 2.1). The traditional procedure calls
for equilibrating 0.05 M solutions of the NaHCO$_3$, Na$_2$CO$_3$, and NaOH reactants with separate samples of carbon black or activated carbon. The solid analyte is then separated from the solution, and the solution is acidified and boiled to remove CO$_2$. Finally, aliquots of the resulting solutions are back-titrated with NaOH to determine the quantity of the reactants that had been reacted during equilibration.

**Table 2.1.** The pK$_a$ values, approximate pH values, and examples of functional groups determined by the three alkaline Boehm reactants. Functional groups listed are those that will donate the greatest number or protons to each Boehm reactant, but due to the equilibrium nature of the acid-base reactions, small amounts of other functional groups may also donate protons. For example, a small percentage of phenols may react with Na$_2$CO$_3$.

<table>
<thead>
<tr>
<th>Boehm Reactant</th>
<th>Reactant pK$_a$</th>
<th>Reactant pH (0.05M)</th>
<th>O-containing functional groups</th>
<th>N-containing functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaHCO$_3$</td>
<td>6.4</td>
<td>~8</td>
<td>Carboxylic acids</td>
<td>Pyridines and amines with pK$_a$ &lt;6.4</td>
</tr>
<tr>
<td>Na$_2$CO$_3$</td>
<td>10.3</td>
<td>~10</td>
<td>Carboxylic acids, lactones, lactols, and low pK$_a$ phenols</td>
<td>Pyridines and amines with pK$_a$ &lt; 10.3</td>
</tr>
<tr>
<td>NaOH</td>
<td>13.8</td>
<td>~13</td>
<td>Carboxylic acids, lactones, lactols, and all phenols</td>
<td>Pyridines and amines with pK$_a$ &lt; 13*</td>
</tr>
</tbody>
</table>

*NaOH has been reported to react with all functional groups with pK$_a$ values as high as 15.7, but here we cite a more conservative estimate given by Rutherford et al. (2008).
Equilibration with HCl can be used to quantify basic functional groups and/or acidic functional groups with pK$_a$ values less than that of the biochar as well, but many studies only use the alkaline Boehm reactants to address acidic functional groups.

Researchers generally assume that NaOH accepts protons from all Brønsted acids (including phenols and carboxylic acids) while hydrolyzing lactones and lactols, Na$_2$CO$_3$ accepts protons from groups with pK$_a$ values less than 10.3 (carboxylic acids) while hydrolyzing lactones and lactols, and NaHCO$_3$ accepts protons from groups with pK$_a$ values < 6.4 (carboxylic acids). This differentiation allows for the calculation of functional group quantities in discrete pK$_a$ ranges via subtraction (Contescu, 1997; Goertzen et al., 2010; Oickle et al., 2010).

Since its inception, many studies have used the original Boehm procedure or developed modified procedures, resulting in great variability among published procedures. Modifications include changes in the solution-to-solid ratio, reactant concentration, titrant concentration, methods of removing CO$_2$, type of filter, endpoint determination, pre-wash procedure to remove ash, and the type of carbonaceous material being analyzed. Solution-to-solid ratios generally fall within the range of 25-75:1 mL:g (Cheng and Lehmann, 2009; Cheng et al., 2006; Goertzen et al., 2010). Reactant and titrant concentrations range from ~0.01 M to 0.1 M. Acidification has been followed by boiling, refluxing, or sparging (i.e. bubbling or degassing) with an inert gas to remove dissolved CO$_2$ and thereby prevent interference from carbonates – and some studies do not specify whether CO$_2$ was removed (Chun et al., 2004; Contescu, 1997; Goertzen et al., 2010; Mukherjee et al., 2011). Filters are usually ashless, but the filtration method is not always specified, because the original Boehm
method only called for “separation” of solid from solution (Boehm, 1994; Cheng and Lehmann, 2009; Taghizadeh-Toosi et al., 2012). Acid or other aqueous pre-washes are used in some, but not all, studies for removing soluble ash and organic compounds (Cheng and Lehmann, 2009; Chun et al., 2004). Lastly, despite having been developed for carbon blacks and activated carbons, the Boehm titration has also been used on carbon nanotubes, black carbon isolated from soil, and biochar (Cheng and Lehmann, 2009; Kim et al., 2012; Mukherjee et al., 2011).

It is not clear whether the use of the Boehm titration on materials other than carbon blacks and activated carbons is justified. Carbon black can be made by pyrolyzing aromatic oils and/or natural gas, and activated carbon is traditionally made via the pyrolysis of hardwood or other low-ash, lignin-rich feedstocks followed by activation using steam and/or other chemical treatments. Peak pyrolysis temperatures of carbon blacks are often >1000°C, and activated carbons can be pyrolyzed at temperatures ranging ~300-800°C and activated at 700-1000°C. Due to the carbon-rich nature of these feedstocks and the high temperatures used for thermochemical processing, the resulting materials are typically >60% carbon, with ash contents of 10% or less (Carrier et al., 2012; Fulcheri and Schwob, 1995; Menéndez, 1996). Carbon nanotubes, black carbon, and biochar, however, can be made under a wider range of conditions, and have a wider range of C, H, O, and ash contents (Table 2.2). Therefore, these materials may not respond to equilibration with the Boehm reactants in a manner consistent with the underlying principles and assumptions of the Boehm titration.

Recently, the Boehm titration has been standardized for use with carbon blacks (Goertzen et al., 2010; Oickle et al., 2010). CO₂ and carbonate removal, endpoint
determination, titrant concentration, and filtration methods were all addressed. Reactant concentration and pre-washes were not addressed because Boehm later specified that 0.05M solutions should be used, and because carbon blacks are inherently low in ash (International Carbon Black Association, 2006; Boehm et al., 2008).

Table 2.2. A comparison of activated carbon and biochar properties relevant to the Boehm titration.

<table>
<thead>
<tr>
<th>Property</th>
<th>Carbon Black</th>
<th>Activated Carbon</th>
<th>Biochar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis or gasification temperature</td>
<td>~800-1500°C</td>
<td>~300-800°C</td>
<td>~300-800°C</td>
</tr>
<tr>
<td>Activation temperature</td>
<td>-</td>
<td>~700-1000°C</td>
<td>-</td>
</tr>
<tr>
<td>Feedstock</td>
<td>Aromatic oils or natural gas</td>
<td>Hardwood or other lignin-rich material</td>
<td>Biomass or other organic waste</td>
</tr>
<tr>
<td>Degree of aromatic condensation</td>
<td>Very high</td>
<td>Very high</td>
<td>Low to high</td>
</tr>
<tr>
<td>Solubility in alkali</td>
<td>Negligible</td>
<td>Negligible</td>
<td>Low to high</td>
</tr>
<tr>
<td>Ash content</td>
<td>~0-5%</td>
<td>~0-10%</td>
<td>~0-60%</td>
</tr>
<tr>
<td>Application</td>
<td>Rubber reinforcing agent, pigments, coatings</td>
<td>Sorbent</td>
<td>Soil enhancement, carbon sequestration, and more</td>
</tr>
</tbody>
</table>
Goertzen et al. (2010) and Oickle et al. (2010) determined that CO$_2$ and carbonates were best removed by sparging with N$_2$ gas for 2h, that the endpoint could be determined using a pH meter or indicator dye, and that neither titrant concentration nor type of filter influenced the results. However, because neither ash removal nor type of pyrolyzed organic matter was addressed, there is a need for research and development of Boehm titration methods for carbon materials other than carbon black and activated carbon.

Despite the lack of research in method-development, Boehm titrations have already been applied extensively to biochars due to the need to quantitatively assess potential soil-biochar interactions in a cost-effective manner. The Boehm titration has distinct advantages over other quantitative methods like $^{13}$C-NMR. The Boehm titration method is inexpensive, and it quantifies functional groups that are reactive in the soil, whereas $^{13}$C-NMR is not as effective at distinguishing between reactive and non-reactive organic functional groups. Specifically, $^{13}$C-NMR can estimate the concentration of carboxylic acids, but aromatic ethers and esters cannot be quantitatively distinguished from phenols, and esters cannot be distinguished from lactones. Furthermore, the Boehm titration may help distinguish between groups that will interact with alkaline versus acidic soils, while providing an indirect measure of CEC. However, because biochar differs from carbon black in several ways, it may interact with the Boehm reactants in ways that violate the principal assumptions of the method (Table 2.2). Most important of these differences are the higher ash content and greater carbon solubility of biochar compared with carbon black and activated carbon. If the ash fraction were to dissolve in the Boehm reactants, it would violate the assumption that the reactants are only interacting with organic surface functional groups (Cheng et al., 2006). Secondly, if
biochar carbon were to partially dissolve in the reactants, it would violate the assumption that the carbon and reactant phases were fully separated prior to titration (Kim et al., 2012).

Here we evaluate three different modifications of the original Boehm titration method developed by Goertzen et al. (2010) and Oickle et al. (2010). The modifications were developed in an effort to overcome problems noted above in the use of the Boehm titration with biochars. The goal of the research was assess the effectiveness of modified Boehm titration methods in the presence of (1) carbonates, (2) other inorganic forms of alkali commonly found in biochar, and (3) dissolved organic compounds (DOC) derived from alkali-soluble organic compounds present in biochar.

**Methods**

**Biochar Preparation**

The biochars used in this study were generated at 500°C from three different feedstocks: cellulose, red oak, and corn stover. For the cellulose biochar, cellulose powder (Sigma Aldrich) was slow-pyrolyzed in a N₂-purged muffle furnace for ~1 h. The red oak and corn stover biochars were generated via fast pyrolysis by Avello Bioenergy and the Center for Sustainable Energy Technologies at Iowa State University, respectively. Both of the fast pyrolysis biochars were produced in a fluidized bed reactor that used N₂ as a carrier gas and ~0.5 mm sand particles as fluidization media (Pollard et al., 2012).

The biochars were pre-treated for the removal of reactive ash components, including carbonates, phosphates, oxides and hydroxides. The two fast-pyrolysis biochars were sieved
to <0.417 mm. The cellulose feedstock was comprised of sufficiently small particles (<50 μm) that sieving the biochar was not necessary. After sieving, the biochars were shaken for 24 h with 0.05 M HCl, then washed twice with 1 M CaCl₂ and four times with deionized water, all at a 50:1 solution:biochar ratio. The final filtrates consistently had an electrical conductivity <10 μS/cm and a pH ~5 (this pH set the lower limit for the pKₐ values of the reactive functional groups measured). Preliminary studies showed that this treatment removed all of the soluble ash (see Chapter 3). Lastly, the samples were dried for >60 h at 50°C. The pre-treated cellulose, red oak, and corn stover biochars will henceforth be referred to as CE, RO and CS.

Fourier-Transformed Infrared Spectroscopy (FTIR)

Samples of the pre-treated CE, RO, and CS biochars were ground for 3 min in a ball mill, then 5-6 mg of biochar were diluted to 1.7-2.0% in 294 mg spectroscopic-grade KBr and re-ground. The sample chamber was purged with inert gas for 10 min prior to sampling to prevent interference from H₂O and CO₂. For each sample spectra, 200 scans were collected using a Nicolet Magna-IR 560 FTIR spectrometer equipped with a deuterated triglycine sulfate detector and a diffuse reflectance accessory. These spectra were used as a qualitative reference for comparison to the Boehm titration results.
Equilibration with Boehm Reactants

Triplicate 0.500-g samples of the pre-treated biochars (see Biochar Preparation) were shaken with 25.00 mL of each of the three alkaline 0.05M Boehm reactants (NaHCO$_3$, Na$_2$CO$_3$, and NaOH) for 24 h in Nalgene centrifuge tubes enclosed in an insulated container at ~26°C. The equilibrated Boehm reactants were separated from the biochar by filtration using 0.45-μm nitrocellulose filter paper and either treated (as follows) immediately, refrigerated for ≤24 h before analysis, or frozen and then thawed to room temperature for later analysis.

Extract Treatment

Three different procedures were employed to remove DOC and carbonates prior to titration. All treatments were also performed on blanks – that is, equivalent volumes of Boehm reactants that were not equilibrated with biochars. For the first method, samples were treated as recommended by Goertzen et al. (2010). Briefly, to lower the pH to < 2, 0.05 M HCl was added at a 2:1 HCl-to-sample ratio by volume to the NaHCO$_3$ and NaOH extracts and at a 3:1 ratio to the Na$_2$CO$_3$ extract. Then, to remove CO$_2$ and carbonic acid, the acidified samples were sparged with N$_2$ for 2 h in glass scintillation vials prior to titration. Goertzen et al. (2010) recommended that NaOH extracts also be degassed during titration. However, dissolution of atmospheric CO$_2$ during the titration of preliminary samples did not affect the titration curves measured in this study, so samples were only sparged before and not during titration (see blank titration curves in appendix).
For the second method, extract aliquots were equilibrated with an equivalent volume of 1 M BaCl₂ to precipitate CO₃²⁻ and to coagulate DOC. Aliquots of NaOH and 1 M BaCl₂ were combined with the NaHCO₃ and Na₂CO₃ extracts in a 1:1:1 ratio (by volume) to ensure that all carbonates were in the CO₃²⁻ form and would precipitate with the Ba. The concentrations of the NaOH aliquots added to NaHCO₃ and Na₂CO₃ were 0.05 M and 0.01 M, respectively. Following equilibration, the samples were centrifuged to separate solids from the extracts. Any cloudy supernatants were also filtered with 0.02 μm Anatop filters. Aliquots of the supernatant were acidified to pH <2.

The third method was the same as the first, except that extracts were passed through solid-phase extraction ENVI-ChromP cartridges to remove DOC prior to acidification. The cartridges contain fine particles coated with a styrene-divinylbenzene resin and are designed to adsorb nonpolar DOC, with or without polar moieties, over a wide range of pHs. Under alkaline conditions, the cartridge is especially effective for adsorbing phenols, which would cause measurement bias if present (Kim et al., 2012). Before use, cartridges were pre-treated with methanol followed by water to ensure wetting. For the NaOH and Na₂CO₃ extracts, two cartridges were stacked on top of each other, and a single ~7 mL aliquot of extract was pulled through them into a glass tube via vacuum three times. The cartridges were washed with methanol and water following each sample run through the cartridge, and two new cartridges were used for each sample. For the NaHCO₃ extracts, the same procedure was performed only as many times as it took for the absorbance of the extract at 250 nm to fall below 0.05 absorbance units (see absorbance measurement section), because preliminary tests revealed that some NaHCO₃ was adsorbed each time an extract was passed through the cartridge (see
appendix). This approach resulted in passing CE, RO, and CS extracts through the cartridge 1, 2 and 3 times each, respectively.

Henceforth, these three methods, utilizing sparging only, barium, and the ENVI-ChromP cartridge with sparging, are referred to as the sparge, barium, and cartridge methods, respectively. A summary of the three methods used for treating extracts is found in Table 2.3.

Table 2.3. Boehm reactants and equations used to calculate the concentration of functional groups in each discrete pH range that donate protons to each Boehm reactant. The high end of each pKₐ range is determined by the pKₐ of Boehm reactant 1, and the low end by Boehm reactant 2, such that each formula is in the format of F⁻_{pKₐ(BR1)} – F⁻_{pKₐ(BR2)}.

<table>
<thead>
<tr>
<th>Step</th>
<th>Sparge Method</th>
<th>Cartridge Method</th>
<th>Barium Chloride Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pre-Treatment</td>
<td>Washed biochars with 0.05M HCl, 1M CaCl₂ 2x, and H₂O 4x at a 50:1 solution:biochar (volume:mass) ratio and dried at 50°C for 60 h. A final pH of ~5 was achieved.</td>
<td>Sorption to ENVI-Chrom P cartridge</td>
<td>Precipitation with 1M BaCl₂</td>
</tr>
<tr>
<td>2. Reaction</td>
<td>Pre-treated biochars were shaken for 24h with 0.05M NaHCO₃, Na₂CO₃, and NaOH solutions at 50:1 solution:char ratio, and extracts were filtered to &lt;0.45μm.</td>
<td>Sorption to ENVI-Chrom P cartridge</td>
<td>Precipitation with 1M BaCl₂</td>
</tr>
<tr>
<td>3. DOC Removal</td>
<td>None</td>
<td>Acidification and sparging</td>
<td>Acidification and sparging</td>
</tr>
<tr>
<td>4. Carbonate Removal</td>
<td>Acidification and sparging</td>
<td>Acidification and sparging</td>
<td>Precipitation with 1M BaCl₂</td>
</tr>
<tr>
<td>5. Titration</td>
<td>NaOH</td>
<td>NaOH</td>
<td>NaOH*</td>
</tr>
</tbody>
</table>
Titrations

All treated extracts were titrated with 0.01 M NaOH using a digital burette (Titrette). To avoid adsorption of CO$_2$ from the atmosphere, all samples were stored in glass scintillation vials sealed with Parafilm, and each batch of 0.01 M NaOH was stored for no longer than 3 days before use. The NaOH titrant was standardized within 24 h of each use using potassium hydrogen phthalate (KHP), and if a decline of >10% in measured NaOH concentration occurred, a fresh batch was made. Samples were titrated both with a pH meter (Fisher) equipped with a H$^+$ electrode and with phenolphthalein indicator. One sample of each reactant-biochar-treatment combination was arbitrarily chosen for incremental titration using the pH meter. Titrant was added in aliquots that varied from 0.03 to 1.00 mL, such that each addition raised the pH by 0.1-0.5 pH units until the pH reached ~11. Sufficient time was allowed for each pH reading to remain stable for ~5 s before recording the pH and the total amount of titrant added. Care was taken to keep all titrations less than 35 min to minimize the amount of atmospheric CO$_2$ that was adsorbed by the solutions. Any curves showing an inflection point near pH 6.4 were repeated with fresh titrant. In this way, the presence of carbonates in the titrant could be distinguished from carbonates and/or carboxylic acids present in the samples. These incremental titration curves were measured to detect inflection points qualitatively and not to quantify functional groups on biochar surfaces.

To quantify reactive organic functional groups, the treated extracts were titrated with phenolphthalein, and the endpoint was recorded when the solution took on a faint but permanent pink color (pH ~8.2).
Absorbance Measurements

Absorbance at 250 nm ($A_{250}$) was measured for all treated extracts and blanks using an Evolution 60S UV-Visible Spectrophotometer. This wavelength was chosen because it correlates strongly with the concentration of aromatic DOC such as phenols and anisoles (Weishaar et al., 2003). Before measurement, Ba-treated samples and blanks were diluted with deionized water so that the dilution factor would be equivalent to that of the sparge and cartridge-treated samples. A pH of <2 was maintained for all measurements.

Calculations

The amount of alkaline Boehm reactant that accepted protons from the biochars was calculated as the difference between the mmol of NaOH needed to titrate the blanks and the mmol of NaOH needed to titrate the samples. Because the blanks and extracts were acidified to pH <2 with a known volume of HCl first, this difference was effectively the mmol of H$^+$ donated to the Boehm reactants. The resulting number of mmol was converted to mmol g$^{-1}$ using the general equation:

$$F_x = \frac{V_{ex} - V_{bx}}{m} \times M_t \times DF$$

where $F_x$ represents the functional groups donating protons to the Boehm reactant with a pK$_a$ of x in meq g$^{-1}$, $V_{ex}$ is volume of titrant (0.01 M NaOH) used to titrate the extract in mL, $V_{bx}$ is the volume of titrant used to titrate the blank (mL), $m$ the mass of the biochar in grams, $M_t$ the molarity of the titrant in mol L$^{-1}$ (as measured via standardization with KHP), and $DF$ is
the dilution factor. To calculate the concentration of functional groups in each discrete pKₐ range, the following formula was used:

\[ F_{x_1-x_2} = F_{x_2} - F_{x_1} \]  \hspace{1cm} (2)

where \( F_{x_1-x_2} \) is the concentration of functional groups ranging from a pKₐ of \( x_1 \) to \( x_2 \) (each pKₐ corresponds to that of a Boehm reactant), \( F_{x_2} \) is the concentration of functional groups with pKₐ less than or equal to about \( x_2 \), and \( F_{x_1} \) is the concentration of functional group with pKₐ less than or equal to about \( x_1 \) (where \( x_1 < x_2 \)). A graphic representation of this equation can be found in Figure 2.1, and equations specific to each Boehm titrant can be found in Table 2.4. It should be noted that, because the pre-treated biochars had a pH of ~5, functional groups with pKₐ < 5 were not quantified.

Measured functional group concentrations are henceforth given in the format \( F_x \), where \( x \) is the approximate upper pKₐ limit for the functional groups based on the pKₐ of the Boehm reactant’s conjugate acid. For example, \( F_{13} \) refers to the functional groups that reacted with NaOH and have a pKₐ ~5-13.
Table 2.4. Boehm reactants and equations used to calculate the concentration of functional groups in each discrete pH range that donate protons to each Boehm reactant. The lower limit of the lowest pK\textsubscript{a} range is determined based on the pH of the pre-treated biochar (~5).

<table>
<thead>
<tr>
<th>pK\textsubscript{a} range</th>
<th>Boehm Reactant 1 (pK\textsubscript{a} = x\textsubscript{1})</th>
<th>Boehm Reactant 2 (pK\textsubscript{a} = x\textsubscript{2})</th>
<th>Equation to calculate functional group concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5-6.4</td>
<td>None</td>
<td>NaHCO\textsubscript{3}</td>
<td>(F_{5.6.4} = F_{6.4})</td>
</tr>
<tr>
<td>~6.4-10.3</td>
<td>NaHCO\textsubscript{3}</td>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>(F_{6.4-10.3} = F_{10.3}) - (F_{6.4})</td>
</tr>
<tr>
<td>~10.3-13</td>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>NaOH</td>
<td>(F_{10.3-13} = F_{13}) - (F_{10.3})</td>
</tr>
</tbody>
</table>

Figure 2.1 Illustration of the acidic functional groups donating protons to each Boehm reactant and how they can be used to calculate the functional group concentration in each pK\textsubscript{a} range (from Rutherford et al. 2008).
Results and Discussion

FTIR Characterization

The FTIR spectra revealed a wide variety of functional groups on the biochar surfaces (Figure 2.2). All three biochars had peaks corresponding to carboxylic acids (1690-1700 cm⁻¹), carboxylate salts (1590-1600 cm⁻¹), aromatic C=C bonds (1430-1440 cm⁻¹), aliphatic alcohols (950 cm⁻¹), and substituted aromatic rings (870-750 cm⁻¹). Although they were derived from different feedstocks and rates of pyrolysis, the CE and RO biochars had similar spectra. The spectra for these two biochars differed primarily in the intensity and number of peaks between 3000-2700 cm⁻¹, whereas all other peaks were nearly equivalent in position and intensity. In contrast, the spectrum of CS biochar differed from the spectra for the CE and RO biochars primarily by its strong peak ~1100 cm⁻¹. Because corn stover is known to contain large amounts of SiO₂, the 1100 cm⁻¹ peak could represent residual SiO₂, but it could also correspond to C-O stretching from unpyrolyzed carbohydrates (Kloss et al., 2011; Lee et al., 2010). Furthermore, the spectra for the CE and RO biochars displayed three peaks between 820-700 cm⁻¹, where CS spectrum had only one. This might be due to different pyrolysis conditions, as these peaks are associated with the extent of pyrolysis (Brewer et al., 2011; Brewer et al., 2009). Although FTIR spectra are minimally quantitative at best, the high degree of similarity between the CE and RO spectra suggests that these two biochars might have similar functional group distributions.
The carboxylic acid peaks (and, to some extent, the carboxylate salt peaks) indicate that all three biochars should react with NaHCO₃. The broad peaks from 1300-1100 cm⁻¹ present in the RO and CE spectra may be indicative of phenols, lactones and/or lactols. However, this region is also associated with other functional groups (including ethers and aliphatic alcohols), so the peaks may also represent groups that would not react with the Boehm titrants.

**Figure 2.** FTIR spectra of CS (dark grey), RO (light grey), and CE (medium grey) biochars.
**Titration Curves**

The incremental titration curves showed little or no evidence of carbonates or carboxylic acids (Figure 2.3), as no equivalence points could be distinguished from noise (aside from that of $\text{H}_2\text{O}$ at pH 7) in the titration curves for any of the blanks or samples. The greatest slopes were consistently observed between pH 4 and 8, as expected for an aqueous sample with negligible levels of carbonates and carboxylic acids. General titration curve shape was similar between samples and blanks, although the slopes for the pH 4-8 region were usually greater for the blanks than for the samples. Although no inflection points were detected, the slopes of the titration curves in the pH 4-8 range for the samples were less than the slopes of the titration curves for the blanks, suggesting that some proton donating groups were present in the Boehm extracts. Judging from the difference in slopes of the titration curves for the blanks and samples we estimate that these proton donating functional groups in the extracts accounted for less than 10% of the total functional groups estimated for the biochar samples by the Boehm titration method. Although no inflection points were observed above pH 8 or below pH 4, it is possible that inflection points for minor peaks were masked by the large inflection point for water. Therefore, we infer from the titrations that the samples probably did not contain significant amounts of carbonates or carboxylic acids, but bias due to other functional group-bearing molecules such as phenols could not be ruled out.
Figure 2.3. Example incremental titration curves made using a sparge method blank (black, solid line) and samples prepared via the sparge (blue, dashes), barium (red, dash-dot), and cartridge (green, dots) methods.

**Titrations with Phenolphthalein**

Functional group quantification ($F_x$, in meq g$^{-1}$, where $x =$ the pK$_a$ of the conjugate acid of the Boehm reactant) was influenced by biochar type and procedure for all Boehm reactants. There was no correspondence between the method used and the measured functional group concentration for any Boehm reactant, but measurements made with different procedures on extracts of the same biochar from the same reactant differed by as much as a factor of 10. In other words, the choice of procedure had a substantial but inconsistent effect on $F_x$. 
No primary standards exist that can be used to judge the accuracy of results obtained with the various Boehm procedures. Here we will identify a method as biased if the measurements made using that method contradict the underlying principle of the Boehm titration. Specifically, for each method, the measured functional groups concentrations should follow the order $F_{13} > F_{10.3} > F_{6.4}$ if they are accurate. Furthermore, it is anticipated that bias could arise via one or more of the following mechanisms: (1) DOC in the Boehm extracts accepting protons from $HCl$ during acidification of the sample and not subsequently donating them to the solution during titration (this can occur in any method if reactive DOC is present), (2) DOC reacting with NaOH during titration of a Boehm extract (any method), (3) protonation or deprotonation of DOC during the addition of $BaCl_2$ and NaOH, and precipitation of $BaCO_3$ with DOC that is not reversed during titration in the barium method, and/or (4) direct or secondary sorption of the Boehm reactants to the cartridges in the cartridge method. Henceforth, these mechanisms will be referred to as “acidification,” “direct titration,” “$BaCO_3$,” and “sorption,” respectively.

The $F_{13}$ values followed a pattern that best fit the acidification mechanism. The largest $F_{13}$ values were generally obtained with the cartridge method followed by the Ba and sparge methods (Figure 2.4a). However, RO was the only biochar for which $F_{13}$ varied $<10\%$ with respect to the method used. The CE and CS biochars, on the other hand, had $F_{13}$ values that varied greatly with respect to method. For CE, the measurement of $F_{13}$ made with the cartridge method was about 10x greater than the measurements made with the Ba and sparge methods, whereas for CS, the Ba and cartridge method measurements were both over 2x greater than the sparge method measurements. The sparge method $F_{13}$ values for the CE and
CS biochars were similar to or less than the $F_{10.3}$ values measured with the same method, thereby violating the defining principle of the Boehm titration wherein more alkaline reactants should accept protons from greater quantities of acidic functional groups. Therefore, the results suggest that the sparge method can cause an underestimation of $F_{13}$. The underestimation of $F_{13}$ could have been caused by the acidification mechanism because this mechanism is the only one of the four proposed mechanisms that would consistently result in an underestimate of $F_{13}$ and would be prevented when reactive DOC with $pK_a > 8$ was removed. The differences in the apparent accuracy of each method among biochars suggest that inherent differences in DOC chemistry between biochars may have influenced the results. Namely, the Ba method may be more effective at removing the high-$pK_a$ DOC originating from CS than from CE, and the DOC solubilized from RO may have a minimal influence. Assuming that a greater $F_{13}$ value indicates less interference from DOC, the cartridge method was the most effective at removing DOC from NaOH extracts and preventing the acidification mechanism of bias from taking effect.

The $F_{10.3}$ results supported the sorption mechanism of bias when the cartridge method was used, but it is unclear whether the other two methods were biased (Figure 2.4b). The sparge method yielded the highest $F_{10.3}$ values for the CS biochar, while the Ba and cartridge methods yielded 30% lower $F_{10.3}$ values. In contrast, the $F_{10.3}$ values for the CE and RO biochars were 3x higher when the cartridge method was used as when the sparge and Ba methods were used. The $F_{10.3}$ value for the RO biochar made using the cartridge method was greater than all of the $F_{13}$ values for the RO biochar regardless of method, thereby violating the basic principle of the Boehm titration and suggesting that the cartridge method is
unreliable for Na$_2$CO$_3$ extracts. For the CE biochar, the $F_{10.3}$ value obtained with the cartridge method was approximately equal to the $F_{13}$ value obtained with the same method, an outcome that seems unlikely although it does not directly violate the basic principles of the Boehm titration. One possible explanation for apparent over-estimates of $F_{10.3}$ values by the cartridge method is that carbonates in the extract (either Na$_2$CO$_3$ or NaHCO$_3$) could be adsorbed by the cartridges to a greater extent from the samples than from the blanks. This might occur if DOC adsorbed to the styrene-divinylbenzene cartridge surface were to attract Ca$^{2+}$ left over from the pre-treatment, which in turn would attract CO$_3^{2-}$. In other words, the DOC might be acting as a “bridge” between the cartridge surface and carbonates in solution. This phenomenon would be an example of the sorption mechanism in action.

The $F_{6.4}$ results best fit the BaCO$_3$ mechanism of bias. The $F_{6.4}$ values were lower on average than the $F_{10.3}$ and $F_{13}$ values, and they varied depending on the method and biochar being analyzed (Figure 2.4c). The CE and CS extracts had similar $F_{6.4}$ values, while the RO extracts showed a variable response. Both CE and CS extracts yielded the low $F_{6.4}$ values when the Ba method was used, while the sparge and cartridge methods yielded $F_{6.4}$ values that were ~2x greater in magnitude than that of the Ba method. The RO extracts showed the opposite relationship, wherein the sparge and cartridge methods yielded low $F_{6.4}$ values, and the Ba method results were ~40% greater. The coefficient of variation for the RO $F_{6.4}$ values measured using the cartridge method were > 50%, suggesting that the cartridge method analysis of RO was imprecise relative to the other methods. Assuming that the absence of diagnostic inflection points on the titration curves indicates minimal interference from carboxylic acids or other functional groups in the extracts with pK$_a$ values <6.4, the results
suggest a systematic bias associated with the Ba method relative to the sparge and cartridge methods. The previously proposed BaCO$_3$ mechanism would fit these parameters if DOC with pK$_a$ values $>$6.4 were deprotonated upon addition of NaOH and precipitated with BaCO$_3$, if functional groups with pK$_a$ values $<$6.4 were protonated upon addition of BaCl$_2$ and subsequently precipitated with BaCO$_3$, and/or if DOC with pK$_a$ values $>$8 were not sufficiently removed by precipitation with BaCO$_3$. 
Figure 2.4. Functional groups measured (F, a-c) and absorbance at 250 nm ($A_{250}$, d-f) for different Boehm reactants, biochars and methods.
Absorbance Measurements and Comparison with Titration Results

The absorbance at 250 nm ($A_{250}$) was used as a qualitative index of aromatic DOC concentrations in the Boehm extracts. Because $A_{250}$ values for the CE extracts were consistently <0.02 absorbance units, here we only discuss the $A_{250}$ results for RO and CS. These data are used to elucidate the influence of DOC on $F_5$ values and to evaluate the effectiveness of the various methods for removing DOC. Because biochar is considered to be primarily composed of aromatic C, and $A_{250}$ correlates well with aromatic DOC (Weishaar et al., 2003), we will assume for the purposes of this study that $A_{250}$ correlates with total DOC for RO and CS extracts.

Although $A_{250}$ values varied with respect to the method, variations in $F_5$ values were not systematically related to $A_{250}$ overall (Figure 2.4). Among these extracts, $A_{250}$ was generally highest for the NaOH extracts (Figure 2.4d) and for extracts prepared via the sparge method. On average, CS extracts had higher $A_{250}$ values than the RO extracts. Relative to the sparge method, both the Ba and cartridge methods reduced the $A_{250}$ values considerably for the RO extracts; for the CS extracts, the cartridge method also reduced $A_{250}$ considerably, but the Ba method had a more moderate impact. These results indicate that the Ba and cartridge methods were both capable of removing DOC from the extracts before titration, but their effectiveness varied with respect to the biochar from which the extracts were obtained.

The $A_{250}$ results for the NaOH extracts best supported the acidification mechanism of bias (see Titrations with Phenolphthalein). Despite the substantial differences in $A_{250}$, the RO extracts had similar $F_{13}$ values determined by all three methods. The CS extracts, on the other
hand, exhibited increased $F_{13}$ values as $A_{250}$ was reduced. This behavior would be expected if the DOC were causing an underestimate of $F_{13}$, and removing this DOC prevented the underestimate. However, in the case of the Ba method, the dramatic increase in $F_{13}$ relative to the sparge method was disproportionately large relative to the slight decrease in $A_{250}$, and the additional large decrease in $A_{250}$ achieved using the cartridge method only brought a slight increase in $F_{13}$. The apparent effect of DOC on $F_{13}$ values for the CS extracts, in contrast with the lack of such an effect on the RO extracts, implies that not all DOC that absorbs at 250 nm is reactive under the conditions of the sample preparation and titration. Furthermore, the relatively small decrease in $A_{250}$ for the CS extracts relative to the sparge method that corresponded to a relatively large increase in $F_{13}$ suggests that some of the DOC absorbing at $A_{250}$ has a disproportionately large functional group concentration relative to its absorptivity at 250 nm. Such DOC could include aromatic compounds with more than one functional group each, such as benzenediols, and aliphatic compounds such as acetic acid that have a low absorbance at 250 nm (NIST, 2011). When compared with the $F_{13}$ results, these $A_{250}$ results support the acidification mechanism because it is the only mechanism in which a reduction in DOC should consistently result in an increase in $F_{x}$.

The $A_{250}$ results for the Na$_2$CO$_3$ extracts supported the sorption mechanism of bias. The Na$_2$CO$_3$ extracts generally had $A_{250}$ values that were between those of the NaOH and NaHCO$_3$ extracts (Figure 2.4e). The Na$_2$CO$_3$ extracts of CS had $A_{250}$ values that were higher on average than those of RO, suggesting that CS was more soluble in Na$_2$CO$_3$ than RO. For both biochars, the Na$_2$CO$_3$ extracts prepared with the sparge method had the highest $A_{250}$ values, and these values were only slightly less than that of the NaOH extracts prepared with the sparge method. For both RO and CS, the Ba and cartridge methods reduced $A_{250}$ by
>50% relative to the sparge method. The fact that $A_{250}$ varied relatively little between the Ba and cartridge method samples for both biochars suggests that the two methods are comparable in their effectiveness for removing DOC solubilized from these biochars. In spite of the disparity between the $A_{250}$ values obtained by the sparge and Ba methods for RO, the $F_{10.3}$ results were similar. Consequently, the observed difference in $F_{10.3}$ between the Ba and cartridge methods for RO could not be linked to differences in DOC content, but only to other processes occurring during removal of the DOC. This is consistent with the previously proposed bias mechanism related to sorption of $\text{CO}_3^{2-}$ to the cartridges.

The $A_{250}$ results for the NaHCO$_3$ extracts best supported the BaCO$_3$ mechanism of bias. The NaHCO$_3$ extracts had the lowest $A_{250}$ values on average relative to the other Boehm reactant extracts, but still varied with respect to biochar and extract preparation method (Figure 2.4f). Relative to the Na$_2$CO$_3$ extracts, the NaHCO$_3$ extracts prepared with the sparge method were >50% lower for RO and CS biochars. The NaHCO$_3$ extracts had higher $A_{250}$ values for CS than for RO extracts, and the sparge method consistently yielded extracts with the highest $A_{250}$ values compared to the other two methods. Relative to the sparge method, the Ba and cartridge methods reduced $A_{250}$ values by >50% for RO and CS biochar Boehm reactant extracts. The $A_{250}$ values of the NaHCO$_3$ samples did not appear to vary with respect to the $F_{6.4}$ results in any consistent fashion. This lack of consistency may have been due to low DOC levels, as suggested by the relatively low $A_{250}$ values for the NaHCO$_3$ extracts had compared to the more alkaline extracts. Therefore, the observed differences in $F_{6.4}$ values between methods were likely due to processes occurring during the DOC removal procedure, which are independent of the amount of DOC in the resulting extracts. Such processes could include the BaCO$_3$ and sorption mechanisms, because they involve concurrent removal of
DOC along with the net addition or removal of protons from solution. Because the $F_{6.4}$ values were similar when measured with the sparge and cartridge methods, it is not clear whether the sorption mechanism may have influenced the results. Thus, the $A_{250}$ results best support the BaCO$_3$ bias mechanism for underestimating and overestimating $F_{6.4}$ with the Ba and cartridge methods.

Overall, the $A_{250}$ results for RO and CS showed a general trend of decreasing $A_{250}$ with decreasing Boehm reactant pKa. When the $A_{250}$ values are compared with the $F_x$ values, it becomes apparent that, the lower the pKa of the Boehm reactant the less responsive $F_x$ becomes to changes in $A_{250}$. Taken alone, this observation for RO and CS suggests that there may be a linear relationship between the influence of DOC and the amount of DOC. The $A_{250}$ values for CE were too low to confirm or deny this relationship. Because $A_{250}$ is an index of aromatic DOC content, regardless of functional group (Weishaar et al., 2003), the $A_{250}$ values are not able to explain differences observed between $F_x$ values measured with the different methods. A more suitable indicator of functional group chemistry in DOC will be needed to assess how robust a given Boehm method is to DOC in biochar extracts.

**Conclusions**

Although the results did not provide a clear indication as to which method or combination of methods examined here was the most accurate, they did identify methods that were inaccurate when used on specific Boehm reactant extracts. Inaccuracies were identified primarily on the basis that all accurate measurements should adhere to the rule that Boehm reactants with higher pKa values react with a greater number of functional groups, such that $F_{13} > F_{10.3} > F_{6.4}$. Any method or combination of methods violating this rule was considered
biased. However, bias in a given method is not positive proof that the remaining methods are accurate. Even when two out of three methods are proven biased, the third remaining method cannot be proven accurate by simple process of elimination.

The sparge and Ba methods underestimated $F_{13}$ for CE and CS biochars, and the cartridge method overestimates $F_{10.3}$ for the RO biochar, as evidenced by $F_x$ values that violated the basic principle of the Boehm method. Thus, the sparge and Ba methods were shown to be unsuitable for use with NaOH, and the cartridge method was shown to be unsuitable for use with Na$_2$CO$_3$. The underestimation of $F_{13}$ values is supported by FTIR spectra for the CE and RO biochars, which suggested that their functional group distributions should be similar, and by the A$_{250}$ data, which indicated that the cartridge method was more effective at removing DOC from the NaOH extracts than BaCl$_2$ treatments. The overestimation of $F_{10.3}$ is supported by the A$_{250}$ values for the RO extracts prepared with the Ba and cartridge methods, which were both very low, thereby implying that the elevated $F_{10.3}$ measurement was not caused by differences in DOC.

No inaccuracies were definitively identified for titration of the NaHCO$_3$ extracts, although the dependence of the amount of NaOH needed to titrate NaHCO$_3$ blanks on the number of times the blanks had been pulled through the cartridges casts doubt on the cartridge method. The sparge and Ba methods yielded different $F_{6.4}$ and $F_{10.3}$ results, but it was not clear which method was more accurate for making either measurement.

Therefore, it can be concluded that, with present knowledge, the original Boehm titration method is not reliable for determining functional group chemistry of biochars because it does not accurately measure $F_{13}$ values. Moreover, no one method evaluated here can be used with all three Boehm reactants. More research will be needed to determine
which, if any, combination of the evaluated methods is the most accurate for measuring the functional group concentrations in all three pKₐ ranges.
CHAPTER 3. QUANTIFYING ORGANIC AND INORGANIC COMPONENTS OF BIOCHAR ALKALINITY

Abstract

The soil liming capacity of biochar has been explored in several studies, but a holistic, quantitative understanding of the forms of organic and inorganic alkalis in biochar is lacking (Xu et al., 2012; Yuan, 2011; Yuan and Xu, 2011). This study aims to quantify the organic functional groups, carbonates, and other inorganic compounds that contribute to biochar alkalinity. A suite of methods, including acid reaction kinetics, carbonate analysis, thermal analysis, and Boehm titrations was used. Three biochars pyrolyzed at 500°C were analyzed: corn stover biochar and a red oak biochar made using fast pyrolysis, and a cellulose biochar made using slow pyrolysis. The sources of alkalinity in the biochars varied quantitatively and qualitatively with respect to feedstock. The corn stover biochar had the greatest total alkalinity. For the red oak and corn stover biochars, more than 50% of alkalinity was attributed to carbonates and other inorganic compounds, whereas the cellulose biochar’s alkalinity primarily originated from organic functional groups. The results indicated that when significant quantities of ash are present, inorganic alkalis dominate other sources of alkalinity. Furthermore, the wide diversity in the amounts of alkalinity originating from organic functional groups, carbonates, and other inorganic compounds observed in this study demonstrate the importance of considering all three of these biochar alkalinity components when conducting a holistic analysis of biochar alkalinity.
Introduction

Biochar is the solid residue of pyrolyzed organic matter that may be used as a soil amendment (Lehmann et al., 2006). Land application of biochar has been shown to have a wide range of positive effects on soil quality and nutrient cycling. Depending on the biochar feedstock and pyrolysis conditions, these effects can include increased cation exchange capacity (CEC), plant available water, soil aeration, carbon sequestration, microbial activity, and pH, and/or reduced nutrient leaching and greenhouse gas emissions (Laird et al., 2010a; Laird et al., 2010b; Major et al., 2010; Steiner et al., 2008; Woolf et al., 2010). Although these effects are often investigated independently, they interact with one another. In particular, changes in pH caused by biochar application can have cascading effects on several other soil properties that can confound the analysis of other effects (Joseph et al., 2010). The fact that some components of biochar alkalinity may have longer-lasting effects than others further complicates the distinction of pH-related effects from effects that arise independently from biochar alkalinity. For example, if the application of biochar to a soil increased both the soil pH and the abundance of actinomycetes, then it may be difficult to determine whether the increase in actinomycetes abundance was due to the increase in soil pH, or due to some other effect such as the biochar providing suitable habitat for actinomycetes colonization. Therefore, characterization and quantification of the different components of biochar alkalinity are of utmost importance. For the purposes of this study, biochar “alkalinity” will refer to the capacity of biochar to accept protons without significantly altering biochar’s chemical structure.
Three components of alkalinity have been identified in the literature: organic functional groups, carbonates (salts of carbonate and bicarbonate), and other inorganic alkalis (Singh et al., 2010; Yuan et al., 2011). The “other inorganic alkalis” category may include oxides, hydroxides, bisulfate, and phosphates (as orthophosphate or hydrogen phosphate), depending on the biochar. However, studies quantifying all three of these alkalinity components are lacking. Some studies quantify carbonates and other inorganic alkalis, while others quantify only the organic functional groups or the total alkalinity (Chun et al., 2004; Singh et al., 2010; Yuan et al., 2011). In other studies, the organic functional groups are characterized qualitatively without any attempt at quantification (Yuan et al., 2011).

Furthermore, the methods used to quantify each component vary from study to study. For example, Singh et al. (2010) quantified total alkalinity by shaking biochars with 1 M HCl and titrating the filtrate, whereas Yuan et al. (2010) titrated a biochar-water suspension directly with HCl at 0.05 mmol H⁺ per min to pH 2. Because standard biochars have not been developed for distribution, biochars are usually produced independently using local reactors and feedstocks, thereby increasing the variations between studies even further. Thus, arbitrary choice of methods and biochars has rendered studies of biochar individually limited in scope and collectively incomparable to each other. Therefore, the goal of this study was to implement a suite of methods to quantify the components of biochar alkalinity, with the assumption that these components are limited to organic functional groups, carbonates, and other inorganic alkalis.
Methods

Biochar Preparation

The biochars used in this study were generated at 500°C from three different feedstocks: cellulose, red oak, and corn stover. For the cellulose biochar, cellulose powder (Sigma Aldrich) was slow pyrolyzed in a N₂-purged muffle furnace for ~1 h. The red oak and corn stover biochars were generated via fast pyrolysis by Avello Bioenergy and the Center for Sustainable Energy Technologies at Iowa State University, respectively. Both of the fast pyrolysis biochars were produced in a fluidized bed reactor that used N₂ as a carrier gas and ~0.5 mm sand particles as fluidization media (Pollard et al., 2012). The two fast pyrolysis biochars were sieved to <0.417 mm. The cellulose feedstock was composed of sufficiently small particles (~50 μm) such that sieving the biochar was not necessary. Henceforth, the sieved cellulose, red oak, and corn stover biochars will be referred to as CE, RO, and CS, respectively.

Fourier-Transform Infrared Spectroscopy

Diffuse reflectance Fourier-transform infrared spectroscopy (FTIR) was used to qualitatively detect organic functional groups and carbonates in the three biochars. All three biochars were pre-treated for the removal of inorganic alkalis by shaking with either 1 M or 0.05 M HCl solution for 24 h, then washing twice with 1 M CaCl₂ and four times with deionized water using a 50:1 (volume:weight) solution-to-biochar ratio. Both 1 M and 0.05
M HCl were used to determine if HCl concentration affected the FTIR spectra. Samples of treated and untreated CE, RO, and CS biochars were ground for 3 min in a ball mill, then 5-6 mg of biochar were diluted to 1.7-2.0% in 294 mg spectroscopic-grade KBr and re-ground with the KBr. The FTIR sample chamber was purged with inert gas for 10 min prior to analysis to prevent interference from H2O and CO2. For each sample spectrum, 200 scans were collected using a Nicolet Magna-IR 560 FTIR spectrometer equipped with a deuterated triglycine sulfate detector and a diffuse reflectance accessory.

Ash Content and Solubility

Ash content was measured for acid-washed and untreated biochars by thermogravimetric analysis using a Mettler TGA/DSC 1 system. Biochar samples weighing 5-15 mg were heated to 900ºC in air, and the remaining mass was considered to be “ash.” Percent ash was calculated on a mass basis. Percent ash was compared among acid-washed and untreated biochars to assess the effectiveness of each acid washing treatment for solubilizing ash, where “soluble” ash was estimated as the difference in percent ash between untreated biochars and biochars washed with 1 M HCl.

Surface Area

Surface area was measured by the BET method using N2 adsorption isotherms. Particle density was measured with a Quantachrome Pentapycnometer prior to analysis. After degassing for over 19 hours at 300ºC, the isotherm was measured using a Quantachrome
NOVA 4200e Surface Area and Pore Size Analyzer, and the BET region of the isotherm was used to calculate the surface area. This procedure was repeated for untreated biochars and biochars pre-treated with 0.05 M HCl as described previously.

**Reaction with Acid and Ion Release**

Total alkalinity and acid reaction kinetics were analyzed by equilibration of biochar samples with HCl. In triplicate, 0.5 g of each untreated biochar was weighed into 30 mL Nalgene centrifuge tubes and 25 mL of dilute HCl were added. The tubes were shaken at ~26°C in an insulated, opaque container for 2, 4, 8, 16, 20, 24, 48, and 72 h, and then filtered using 0.45-µm nitrocellulose filter paper. A 10-mL aliquot of each filtrate was titrated with standardized, dilute NaOH of approximately the same concentration as the HCl. The endpoint was recorded when phenolphthalein turned the solution a faint, permanent pink color. This was repeated with three HCl concentrations for each biochar, such that the filtrates encompassed a wide pH range: 0.05, 0.01, and 0.001 M HCl for CE, 0.05, 0.01, and 0.004 M HCl for RO; 0.1, 0.05, and 0.029 M HCl for CS. Solutions of HCl that had not been shaken with biochar were titrated as blanks. The amount of acid reacted was calculated as the difference, in mmol, between the amount of NaOH used to titrate the sample and the blank. This number was multiplied by 2.5 to account for the fact that only 10 of 25 mL were titrated, and divided by 0.5 g to convert to mmol H⁺ g⁻¹ of biochar. In this way, the amount of acid reacted over time was calculated, and each data point represented a separate set of samples that were shaken for the same amount of time. Total alkalinity was estimated as the amount of 0.05 M HCl reacted after 72-h of shaking.
The HCl extracts of RO and CS biochars were analyzed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) to determine HCl-extractable concentrations of Ca, Mg, K, Mn, Fe, Si, P and S in these two biochars. Na was excluded from the analysis of the ICP-AES results due to low, inconsistent concentrations. The CE biochar extracts were not analyzed because the ash content was <2%, and hence only trace concentrations of inorganic elements were present in the CE biochar. The sum of equivalents for the base cations, Ca, Mg and K, in the 72-h, 1-M HCl extracts was compared with total alkalinity.

**Carbonate Analysis**

For each untreated biochar, 2.00 g were weighed into 125-mL glass French square bottles, and a stir bar was added to each bottle. Each bottle was placed, uncovered, in a Mason jar together with 15 mL of standardized 1M NaOH in a 50 mL French square bottle. The jars were sealed with lids equipped with septa, through which ~240 mL of air were withdrawn using a syringe and 18-mm gauge needle to create a vacuum. This same syringe and needle was used to inject 100 mL of HCl into the biochar-containing bottle. The Mason jars were placed on stir plates to mix the biochar and acid together. It was observed that stirring the biochar as acid was added aided the mixing process. After 24 h, the NaOH bottles were removed, and the NaOH was quantitatively transferred to a beaker to which 15 mL of 1 M BaCl₂ was added to precipitate carbonates. The solution was titrated with 1 M HCl using a digital titrator (Titrette) and phenolphthalein to indicate the endpoint when the solution turned from pink to white. The mmol of carbon dioxide (CO₂) evolved from the biochar-HCl
suspension was calculated as the difference, in mmol, between the amount of HCl needed to
titrage the blanks and the samples multiplied by two. This procedure was repeated using all
three biochars, with five different HCl concentrations such that the filtrate pH ranged from
about 0 to 6. In this manner, it was possible to compare the final solution pH with amount of
CO\(_2\) evolved for each biochar. The procedure was repeated with a set of 4 calcium carbonate
standards and a blank to calibrate the titration measurements of CO\(_2\) evolved with the amount
of carbonate.

**Organic Functional Groups**

The concentrations of different reactive organic functional groups that contributed to
biochar alkalinity were estimated using a method based on the Boehm titration (see sparge
method for treating NaHCO\(_3\) extracts in Chapter 2 for further details). Each of the three
biochars were first pre-treated by equilibrating them with 0.05 M HCl for 24 h by shaking,
then washing them twice with 1 M CaCl\(_2\) and four times with deionized water (50:1
solution:biochar ratio). Following each wash, the biochar suspensions were filtered with
nitrocellulose filter paper. The final water extracts obtained from filtering the fourth water
wash had a pH of about 5, which set the lower limit for the pK\(_a\) values of the functional
groups being measured. The pre-treated samples were then dried for >60 h at 50ºC. Of each
of the dried biochars, 0.5 g were shaken in centrifuge tubes with 25 mL of 0.05 M NaHCO\(_3\)
for 24 h. The samples were then filtered with nitrocellulose filter paper and a 5 mL aliquot of
the NaHCO\(_3\) extract was withdrawn, to which a 10 mL aliquot of 0.05 M HCl was added.
Acidified samples were then sparged for 2 h to remove carbonates, and titrated using 0.01 M
NaOH until an endpoint of ~8.2 pH was reached as indicated using phenolphthalein. The acidification, sparging and titration steps were repeated for aliquots of NaHCO$_3$ that had not been equilibrated with biochar to serve as blanks. The concentration of organic functional groups that had reacted with the NaHCO$_3$ was calculated from the difference between the mmol of NaOH required to titrate the samples and the blanks. Because the pK$_a$ of NaHCO$_3$ is 6.4, it was assumed that only functional groups with pK$_a$ values less than 6.4 reacted. Hence, based on the pH of the biochar and the pK$_a$ of bicarbonate, this estimate of reactive organic functional groups included groups with pK$_a$ values of 5-6.4. Henceforth the functional groups within the pK$_a$ range of 5-6.4 that are expected to react with NaHCO$_3$ will be described as “reactive.”

It is also possible to measure functional groups in the pK$_a$ ranges of 6.4-10.3, 10.3-13, and 1.3-5 by using Na$_2$CO$_3$, NaOH, and HCl, respectively (Boehm, 1994; Boehm, 2002). However, functional groups with pK$_a$ > 10.3 were excluded because they are not expected to be reactive under soil conditions (pH ~4-8.5). The number of protonated groups with pK$_a$ values between 6.4 and the initial biochar pH (8-9) could not be measured directly using the Boehm titration method because it only allows for the quantification of functional groups with pK$_a$ values between the pH of the biochar and the pK$_a$ values of the Boehm reactants, which are 6.4, 10.3, and 13. Because evidence from the analysis of activated carbon shows that the vast majority of functional groups with pK$_a$ values between 6.4 and 10.3 are concentrated in the pK$_a$ range 9-10.3 (Contescu, 1997), it was assumed for the purposes of this study that the concentrations of functional groups between 6.4 and the biochar pH were negligible. Furthermore, because most soils of agricultural interest do not have pH values
significantly below 5, a \( pK_a \) of 5 was deemed an appropriate lower limit for functional groups that would remediate soil acidity.

**Results**

**FTIR**

The FTIR spectra of the original and acid washed biochars were generally similar (Figure 3.1). The most notable difference was the decrease in intensity of a small, broad peak at 1437 cm\(^{-1}\) and small, sharp peak 876 cm\(^{-1}\) from the CS biochar spectrum after the biochar had been washed with 0.05 M and 1 M HCl. Both of these peaks have previously been attributed to the presence of carbonates (Kloss et al., 2011).

Peaks at \(~878\) cm\(^{-1}\) and \(~1435\) cm\(^{-1}\) were also present in the spectra of both the untreated and acid washed CE and RO biochars. In addition to carbonates, these peaks have previously been attributed to aromatic carbon (Kloss et al., 2011), which is present in all of the samples. Two peaks in the RO spectrum also diminished in intensity upon acid washing, these were located at about 2900 cm\(^{-1}\) and 2850 cm\(^{-1}\) and are associated with aliphatic C-H stretching vibrations (Kloss et al., 2011; Sharma et al., 2004).

All three biochars had FTIR spectral peaks corresponding to carboxylic acids (1690-1700 cm\(^{-1}\)), carboxylate salts (1590-1600 cm\(^{-1}\)), aromatic C=C bonds (1430-1440 cm\(^{-1}\)), aliphatic alcohols (950 cm\(^{-1}\)), and substituted aromatic rings (880-760 cm\(^{-1}\)) (Kloss et al., 2011). The CE and RO biochars had similar FTIR spectra although they were produced from different feedstocks and using different pyrolysis processes. The FTIR spectra of these two
biochars differed primarily in the intensity and number of peaks between 3000-2700 cm\(^{-1}\), suggesting that the CE biochar had lower levels of aliphatic hydrocarbons than the RO biochar. All other peaks in the CE and RO spectra were nearly equivalent in position and intensity, including a broad peak at ~1300-1100 cm\(^{-1}\) that includes wavenumbers attributed to aromatic and aliphatic groups including alcohols, ethers, and esters. In contrast, the spectra of the CS biochar had a strong peak ~1100 cm\(^{-1}\) which was absent in the spectra of the CE and RO biochars, and can be attributed to Si-O stretching and carbohydrates (Kloss et al., 2011; Reig et al., 2002). Furthermore, the spectra of the acid-washed CE and RO biochars displayed three peaks between 880-760 cm\(^{-1}\), whereas the spectra of the CS biochar had only one.

\[\text{Figure 3.1 FTIR spectra of CE, RO, and CS biochars that were untreated, washed with 0.05M HCl, and washed with 1M HCl.}\]
**Surface Area and Particle Density**

The untreated CE, RO, and CS biochars had surface areas determined by the N\textsubscript{2}-BET method of 236, 5, and 21 m\textsuperscript{2} g\textsuperscript{-1}, respectively. The particle densities of the biochars, as determined using a Quantachrome Pycnometer, were 1.44 1.55, and 1.64 g cm\textsuperscript{-3}, respectively. After being washed with 0.05M HCl their surface areas were 245, 4, and 48 m\textsuperscript{2} g\textsuperscript{-1}, and their particle densities were 1.44, 1.55, and 1.72 g cm\textsuperscript{-3}, respectively. Thus, acid washing had a minimal effect on the surface areas and particle densities of RO and CE biochars, but more than doubled the surface area and slightly increased the particle density of the CS biochar.

**Ash Content and Solubility**

Prior to acid washing, CE, RO and CS biochars had ash contents (determined by thermal analysis) of 1.8, 7.3 and 35\%, respectively (Table 3.1). The 0.05 and 1 M acid washing treatments reduced the ash content of the CE biochar by 55\% and 66\%, respectively. For the RO biochar, the 0.004, 0.05 and 1 M HCl washing treatments reduced the ash content by 65, 78 and 82\%, respectively, and the 0.02, 0.05 and 1 M HCl washing treatments reduced the ash of CS biochar by ~29\% relative to the untreated CS biochar. Thus, although CS had the highest ash content, it also had the highest proportion of insoluble ash.
Table 3.1 Percent ash of untreated and acid-washed biochar samples and pH ranges of biochar suspensions measured during acid washing. Soluble ash is calculated as the difference in ash content between the biochars washed with 1M HCl and the untreated biochars.

<table>
<thead>
<tr>
<th>treatment</th>
<th>pH</th>
<th>CE</th>
<th>RO</th>
<th>CS</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>8-9</td>
<td>1.8</td>
<td>7.3</td>
<td>35</td>
</tr>
<tr>
<td>0.004-0.02M HCl</td>
<td>3-4</td>
<td>n.d.</td>
<td>2.5</td>
<td>25</td>
</tr>
<tr>
<td>0.05 M HCl</td>
<td>1-2</td>
<td>0.8</td>
<td>1.6</td>
<td>26</td>
</tr>
<tr>
<td>1.00 M HCl</td>
<td>0</td>
<td>0.6</td>
<td>1.3</td>
<td>24</td>
</tr>
</tbody>
</table>

**Soluble Ash** | 1.2 | 6.0 | 11 |
Reaction with Acid and Total Alkalinity

All three untreated biochars reacted with the HCl rapidly at first, but after ~16 h the reaction rate slowed (Figure 3.2). The total amount of acid reacted after 72 h varied with respect to biochar and the HCl concentration of the reaction solution. For the CE and RO biochars, the amount of acid reacted increased as HCl concentration increased. However, for the CS biochar, the amount of acid reacted after 20 h in the HCl solutions increased for HCl concentrations in the order 0.05 M > 0.1 M > 0.029 M. This pattern was not evident for reaction times less than 16 h, wherein the amount of acid reacted increased in the order of 0.029 M < 0.05 M < 0.1 M. Total alkalinity, reacted after 72 h of equilibration with 0.05M HCl, was 0.229, 0.259 and 1.48 mmol g⁻¹ for the CE, RO and CS biochars, respectively.
Figure 3.2 Protons accepted by CE (a), RO (b) and CS (c) biochars over time. Units are in milli-equivalents of H\(^+\) per gram of biochar (meq g\(^{-1}\)). Error bars represent one standard deviation (smaller error bars may be hidden behind data points). Not to same scale.
Ion Release

The release of cations from the CS and RO biochars by reaction with dilute HCl generally decreased in the following order Ca = K > Mg >> Si > Al > Mn (Figures 3.3-3.4 and Tables 3.2-3.3). The amount of K and Ca released after 72 h from the CS biochar was 3-4x greater than from the RO biochar. Substantially larger amounts of Mg were released from the CS biochar (188-231 µmol g⁻¹) than from the RO biochar (2.1-3.3 µmol g⁻¹). Releases of Mn, Al and Si from the CS biochar were also greater than from RO biochar, but only by a factor of 2-5x.

Cations released from the RO and CS biochars followed a general pattern of increasing cation concentration with increasing HCl concentration, and increasing cation concentration over time (Figures 3.2 and 3.3). This trend was consistent for all cations released from the RO biochar, but for the CS biochar the amount of K released started decreasing after 16 h when 0.029 and 0.1M HCl were used, such that the amounts of K released after 20 h were actually similar to the amount of K released by 0.05M HCl. Furthermore, the amount of K released from the RO biochar continued to increase through the 72-h equilibration, whereas the amounts of Ca, Mg, P and S released leveled off after ~30h.

The amounts of P and S (assumed to be present as orthophosphate and sulfate) released by 0.05 M HCl were 2 and 1 orders of magnitude greater, respectively, for the CS biochar than for the RO biochar (Figures 3.5 and 3.6). The amount of P and S solubilized tended to increase with increasing HCl concentration, with a few exceptions. For the RO biochar, the amounts of S released by reaction with 0.05 M HCl and with 0.02 M HCl were
similar. For the CS biochar, the amount of P released on reaction with 0.05 M HCl was similar to the amount released with 0.1 M HCl at 48 and 72 h.

**Table 3.2** Trace cation concentrations of RO, in µmol g⁻¹, as measured after 72h of shaking with 0.004, 0.02 and 0.05M HCl. Standard deviations are in parenthesis.

<table>
<thead>
<tr>
<th>[HCl]</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004 M</td>
<td>0.47 (±0.03)</td>
<td>0.317 (±0.007)</td>
<td>2.1 (±0.8)</td>
</tr>
<tr>
<td>0.02 M</td>
<td>0.57 (±0.02)</td>
<td>1 (±1)</td>
<td>2.5 (±0.5)</td>
</tr>
<tr>
<td>0.05 M</td>
<td>0.7 (±0.05)</td>
<td>4 (±3)</td>
<td>4 (±1)</td>
</tr>
</tbody>
</table>

**Table 3.3** Trace cation concentrations of CS, in µmol g⁻¹, as measured after 72h of shaking with 0.029M, 0.05M and 0.1M HCl. Standard deviations are in parenthesis.

<table>
<thead>
<tr>
<th>[HCl]</th>
<th>Mn</th>
<th>Al</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.029 M</td>
<td>1.59 (±0.04)</td>
<td>9 (±2)</td>
<td>16.7 (±0.7)</td>
</tr>
<tr>
<td>0.05 M</td>
<td>3 (±2)</td>
<td>8 (±2)</td>
<td>17 (±2)</td>
</tr>
<tr>
<td>0.1 M</td>
<td>1.85 (±0.01)</td>
<td>10.4 (±0.6)</td>
<td>21.7 (±0.4)</td>
</tr>
</tbody>
</table>

The sum of equivalents for K, Ca, and Mg released from the CS and RO biochars by 0.05 M HCl were consistently greater than the amount of protons accepted by these biochars (Figure 3.7). For RO biochar, the meq of K, Ca and Mg released was greater than the meq of H⁺ reacted by about 50% on average, and for CS biochar this difference was about 25%.

After shaking with 0.05 M HCl for 72h, the sum of K, Ca and Mg solubilized from RO and CS were 0.45 and 1.8 meq g⁻¹, respectively.
Figure 3.3 Ca (a), K (b), and Mg (c) released by RO during equilibration with dilute HCl over time. Units are in µmol per gram of biochar (µmol g\(^{-1}\)). Error bars represent standard deviations. Not to same scale.
Figure 3.4 Ca (a), K (b), and Mg (c) released by the CS biochar during equilibration with dilute HCl over time. Units are in µmol per gram of biochar (µmol g\(^{-1}\)). Not to same scale.
Figure 3.5 P (a) and S (b) solubilized by RO during equilibration with dilute HCl over time. Units are in µmol per gram of biochar (µmol g\(^{-1}\)). HCl concentrations are given in the legends. Error bars represent standard deviations. Not to same scale.
Figure 3.6 P (a) and S (b) released by CS during equilibration with dilute HCl over time. Units are in µmol per gram of biochar (µmol g\(^{-1}\)). HCl concentrations are given in the legends. Error bars represent standard deviations. Not to same scale.
Figure 3.7 Protons accepted (diamonds) and the sum of K, Ca and Mg (triangles) released by RO (a) and CS (b) during equilibration with 0.05 M HCl over time. Units are in meq per gram of biochar (meq g$^{-1}$). Error bars represent standard deviations. Not to same scale.
Carbonate Analysis

The amount of CO$_2$ released from the biochars on reaction with HCl decreased with increasing pH of the equilibrated solution (Figure 3.8). The amount of CO$_2$ released from the various biochars followed the order CE < RO < CS for all HCl concentrations.

![Graph showing CO$_2$ evolved during carbonate analysis of CE (diamonds), RO (squares), and CS (triangles) when different concentrations of HCl were used. The final pH values achieved after 24 h of stirring the HCl solutions with the biochar are shown, and CO$_2$ units are in mmol per gram of biochar.]

**Figure 3.8** CO$_2$ evolved during carbonate analysis of CE (diamonds), RO (squares), and CS (triangles) when different concentrations of HCl were used. The final pH values achieved after 24 h of stirring the HCl solutions with the biochar are shown, and CO$_2$ units are in mmol per gram of biochar.

Organic Functional Groups

The estimated concentrations of reactive organic functional groups with pK$_a$ values from 5-6.4 were different with for each biochar. The CS biochar had the greatest concentration of reactive organic functional groups, followed by RO and CE biochars (Figure
3.9). The CE biochar, however, had about 20% more reactive organic functional groups than the RO biochar. Compared to the CE and RO biochars, the CS biochar had over twice as many reactive functional groups in total.

On a surface area basis (mmol m\(^{-2}\)), the RO biochar had the highest concentration of reactive organic functional groups (Figure 3.10), followed by CS and CE biochars. Furthermore, the magnitude of difference in reactive functional group concentration between the different biochars was greater on a surface area basis: the total functional group concentration for RO became ~6x greater and ~100x greater than that of CS and CE biochars, respectively.

![Figure 3.9](image)

**Figure 3.9** Reactive organic functional group concentrations in the pK\(_a\) range of 5-6.4 on a mass basis (per gram of ash-free biochar).
Contributions to Total Alkalinity

Each biochar had different proportions of total alkalinity originating from reactive organic functional groups, carbonates, and other inorganic compounds (Table 3.4). Here total alkalinity was estimated by first reacting alkalis with 0.05 M HCl and then back titrating the reaction solution to the phenolphthalein endpoint after 72 h with standardized NaOH (Figure 2). Carbonate alkalinity was estimated by the amount of CO₂ evolved during a 24 h reaction with 0.05 M HCl (Figure 3.8). Reactive organic functional group alkalinity was estimated by the Boehm titration method using bicarbonate (pKₐ range 5-6.4) after carbonates and other inorganic alkaline components had been removed by an initial acid treatment. Other inorganic components of total alkalinity were estimated by difference. The majority of total alkalinity for the CS and RO biochars was attributed to carbonate compounds, whereas the
majority of total alkalinity for the CE biochar was attributed to organic functional groups. Organic functional groups contributed 18% and 33% of the alkalinity of the CS and RO biochars, respectively, whereas inorganic alkalis contributed 30% and 0%, respectively. For the CE biochar, carbonates and other inorganic compounds were 17 and 0% of total alkalinity, respectively.

Table 3.4 Components of biochar alkalinity, where the organic functional groups with pKₐ 5-6.4 were estimated using the sparge method, and total alkalinity was estimated as the meq of H⁺ reacted after 72h of equilibration with 0.05M HCl. Other inorganic compounds were calculated by difference. Standard deviations are in parenthesis.

<table>
<thead>
<tr>
<th>Biochar</th>
<th>Organic functional groups</th>
<th>Carbonates</th>
<th>Other inorganic compounds</th>
<th>Total Alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CE</td>
<td>% 89%</td>
<td>17%</td>
<td>0%*</td>
<td>106%**</td>
</tr>
<tr>
<td></td>
<td>meq/g 0.2038 (±0.002)</td>
<td>0.045 (±0.007)</td>
<td>0*</td>
<td>0.229 (±0.007)</td>
</tr>
<tr>
<td>RO</td>
<td>% 33%</td>
<td>73%</td>
<td>0%*</td>
<td>106%**</td>
</tr>
<tr>
<td></td>
<td>meq/g 0.085 (± 0.009)</td>
<td>0.19 (±0.01)</td>
<td>0*</td>
<td>0.26 (±0.02)</td>
</tr>
<tr>
<td>CS</td>
<td>% 18%</td>
<td>53%</td>
<td>30%</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>meq/g 0.27 (± 0.01)</td>
<td>0.78 (±0.02)</td>
<td>0.44 (±0.03)</td>
<td>1.48 (±0.02)</td>
</tr>
</tbody>
</table>

*When the sum of the organic functional group and carbonate alkalinitities exceeded the total alkalinity, it was assumed that the contribution from other inorganic compounds was zero.

**The sum of the percent contributions from organic functional groups and carbonates.
Discussion

FTIR

The FTIR spectra provided qualitative insight into the nature of organic functional groups and evidence for the presence or absence of carbonates in the three biochars, as well as evidence for how these biochar components were influenced by acid washing (Figure 3.1). The decrease in intensity of the carbonate peaks at 876 cm\(^{-1}\) and 1437 cm\(^{-1}\) from the CS spectra upon washing with 0.05 M HCl suggests that this treatment was sufficient to remove the majority of the carbonates. However, peaks appearing at these positions on the CE and RO spectra were not diminished upon washing with HCl, suggesting that those peaks were attributed to aromatic C=C and C-H bonds. Furthermore, the fact that CO\(_2\) evolved from these biochars upon reaction with acid suggests that the two aromatic peaks might have been obscuring smaller carbonate peaks at the same wavenumbers. Therefore, FTIR may only be suitable for qualitatively detecting large quantities of carbonate ions in biochar samples.

The FTIR spectra revealed a wide variety of organic functional groups. Peak locations and intensities in the spectra of the untreated biochars were similar to those reported in the literature for biochars made using similar feedstocks and pyrolysis conditions (Brewer et al., 2011; Rutherford et al., 2008). Acid washing did not have a noticeable impact on the organic functional group peaks in spectra for the CE or CS biochars, suggesting that 0.05 M to 1 M HCl can be used as a pre-treatment to remove soluble ash from these biochars without causing major changes to the organic functional groups. However, the decrease in sharpness and intensity of the peaks in the RO spectra associated with aliphatic C-H stretching (~2920 and 2850 cm\(^{-1}\)) that occurred upon acid washing with 0.05M and 1M HCl
suggests that some aliphatic compounds may have been solubilized, hydrolyzed or otherwise altered during the acid washing process. Some biochars can contain precipitated lipids or other organic compounds on their surfaces that are not chemically bonded to the condensed aromatic matrix, and the disappearance of the peaks from the RO biochar spectrum may be due to the removal of such compounds. If this were the case, the organic molecules in question would contain little to no oxygen or nitrogen, and would therefore not contribute significantly to biochar alkalinity (Amonette and Joseph, 2009).

**Surface Area and Particle Density**

Surface area increased among biochars in the order of RO < CS < CE, and particle density increased in the order of CE < RO < CS. Differences in surface area among untreated biochars could be attributed to differences in particle size, because the CE biochar was a fine powder, whereas RO and CS biochars were coarser. As particle size was not analyzed, however, this relationship is uncertain.

The surface area and particle density of the CS biochar were greater for the acid-washed sample than the untreated CS biochar. Because CS was also the biochar with the highest ash content and the greatest 0.05 M HCl-extractable ion content, it is possible that dissolution of ash during the acid washing process led to the exposure of pore spaces, thereby increasing the total surface area. Additional evidence, such as SEM imagery, will be needed to confirm this conclusion.
Ash Content and Solubility

As expected, the CS biochar had a larger ash content than the CE or RO biochars (Brewer et al., 2011; Rutherford et al., 2008; Yuan et al., 2011) (Table 3.1). The RO biochar had an ash content about half that of CS biochar, and the CE biochar had negligible ash content. However, the ash contents of the RO and CS biochars were only about half of what has been reported in the literature (Basso, 2012; Brewer et al., 2009). The difference is attributed to the sieving of the biochars that was performed in this study but not in other studies. It has been observed that sand particles (~0.5 mm on average in this study) adhered to the feedstock and/or sand used to transfer heat to the feedstock in the fluidized bed fast pyrolysis reactor used to make the CS and RO biochars are often present in biochars made with this system. Hence, sieving to < 0.417 mm could remove the sand which otherwise may have contributed to the ash content of the fast pyrolysis biochars used in this study.

The amount of soluble ash, measured as the difference in ash content between untreated and 1M HCl-washed biochars, increased with increasing ash content, total alkalinity, and alkalinity attributed to carbonates and other inorganic compounds. This relationship is consistent with the direct relationship observed between the concentration of HCl-extractable ions and acid reacted for the RO and CS biochars. These results suggest that ash solubility could be used as an index of biochar alkalinity, especially alkalinity derived from inorganic compounds.
Reaction with Acid and Total Alkalinity

The amount of acid reacted generally increased with increasing ash content, HCl concentration, and equilibration time (Figure 3.2). The direct relationship between ash content and total alkalinity was probably due to alkali present in the ash fraction of the biochars. The trend of increasing acid reacted with increasing HCl concentration was likely caused by increased solubility of inorganic alkali at lower pH values. Solubilizing these alkalis may also have exposed occluded inorganic alkali and occluded conjugate bases of functional groups. The one exception to this pattern, which occurred for the 0.05 M and 0.1 M HCl equilibrations, may have been due to bias originating from titrating a stronger acid with a stronger base and/or from phosphates or carbonates in solution reacting with the titrant. The amount of acid reacted most likely increased with equilibration time because the longer the biochars were exposed to acid, the more H⁺ could diffuse through the biochar matrix to reach the organic or inorganic alkali within. Mechanical breakdown of biochar particles and the dissolution of occluding inorganic compounds may also have exposed organic functional group-containing surfaces over time. Overall, the shapes of the acid reaction curves resembled those measured by Silber et al. (2010), despite differences in methods.

Ion Release

The total amount of ions extracted increased with respect to both HCl concentration and time for both the CS and RO biochars (Figures 3.3-3.6 and Tables 1.2 and 1.3).
Individual ions did not always follow this pattern of increasing amount extracted with increasing HCl concentration, but the majority of exceptions to this pattern had relatively high coefficients of variation (>25%) (Figures 3.4 and 3.6a). The relative amounts of K, Ca, and Mg released from the RO and CS biochars by 0.05M HCl were similar to the relative concentrations of these elements measured by ultimate analysis of similarly produced red oak and corn stover biochars (Basso, 2012; Brewer et al., 2009), and the concentrations of 0.029M HCl-extractable (final pH ~3) cations in CS were similar to those measured by Silber et al. (2010) at a constant pH of 4.5. The amounts of P and S extracted using 0.05M HCl were similar to or slightly lower than total P and S contents reported in the literature for RO and CS biochars (Brewer et al., 2011; Brewer et al., 2009; Yuan et al., 2011).

The total quantity, in meq per gram of biochar, of K, Ca and Mg released consistently exceeded the meq of acid reacted (Figure 3.7). This apparent over-abundance of base cations can be attributed to anions that do not contribute to alkalinity, such as chloride or nitrate - that is, soluble anions that do not accept protons at pH > 1. Yuan et al. (2011) detected sylvite (KCl) via XRD analysis of a corn stover biochar, suggesting that chloride may indeed be present in the CS biochar. In addition, using the amount of acid reacted to estimate total alkalinity could have produced an underestimate if significant quantities of organic and/or inorganic compounds with pK_a values between the solution pH (1-6) and a pH of 8.2 (the pH at which phenolphthalein changes color) were solubilized during equilibration of the biochar with acid and remained in solution during the back titration used to quantify total alkalinity. Such compounds could include carboxylic acids, lactones, carbonates, orthophosphate and sulfate. Further research will be needed to determine if any of these compounds are
solubilized in sufficient quantities to interfere with the measurement of alkalinity, and if so, how they can be removed.

**Carbonate Analysis**

The observed direct relationship between ash content and carbonate content was expected because carbonates have been previously observed to constitute a significant portion of biochar ash (Yuan et al., 2011) (Figure 3.8). If we assume that the carbonates were mostly present as CaCO$_3$, then CaCO$_3$ would have comprised 17% of the soluble ash in the CE and RO biochars, and 40% of the soluble ash in CS biochar on a dry weight basis. However, Yuan et al (2011) detected both calcite and dolomite by XRD analysis of a corn stover biochar, suggesting that both CaCO$_3$ and CaMg(CO$_3$)$_2$ were present.

The observed trend of increasing CO$_2$ released with decreasing pH was also expected because, as pH decreases, the solubility of carbonates increases and the percentage of carbonates converted to CO$_2$ also increases. Previous evidence shows that soil organic matter was not mineralized using HCl concentrations of up to 2 M (Bundy and Bremner, 1971), so it is unlikely that organic carbon contributed to the CO$_2$ evolved in this study, although specific evidence is lacking for experiments with biochar. Therefore, further research will be needed to determine the optimal pH range for converting all of the carbonates in biochar to CO$_2$ without mineralizing any organic functional groups.
Organic Functional Groups

All three biochars had surface functional groups in the 5-6.4 range, reflecting the wide variety of reactive functional groups detected by FTIR (Figures 3.9 and 3.10). The functional group concentrations reported are within the range of values measured for other biochars (Mukherjee et al., 2011; Rutherford et al., 2008; Singh et al., 2010). Differences between the estimates given here and those in the literature are likely due to differences in feedstock, pyrolysis temperature, and Boehm titration method used. The Boehm titration is still in the process of being adapted for use with biochars; hence the estimates for functional group concentrations given here may not be accurate. As noted in Chapter 2, different results were obtained using the sparge, barium and cartridge methods for the 5-6.4 pK_a range, and it is not clear which method would be more accurate. Therefore, the Boehm titration data presented here should be interpreted as approximate estimations of organic functional group concentrations rather than exact values.

Contributions to Total Alkalinity

Organic functional groups, carbonates and other inorganic compounds all contributed to the total alkalinity of the CS biochar, and organic functional groups and carbonates contributed to the alkalinity of the CE and RO biochars, thereby validating the assumption that all three forms of alkali would contribute to the total alkalinity of biochar (Table 3.4). Variation in alkalinity distributions, from the organic functional group-dominated CE biochar to the carbonates-dominated RO and CS biochars, reflects the diversity of biochar chemical
properties observed in other studies (Rutherford et al., 2008; Spokas and Reicosky, 2009; Yuan et al., 2011). However, that the sum of the carbonates and organic functional groups contributing to biochar alkalinity slightly exceeded the total alkalinitities of the CE and RO biochars suggests that there may have been some negative bias in the estimation of total alkalinity. Negative bias may have been caused by the release of reactive anions such as carbonates, phosphates and/or carboxylic acids from the biochars during the reaction with HCl. If present in the acid extracts, these anions would have interfered with the titration of the extracts by donating protons to the solution as NaOH was added. Furthermore, without a continuous pK_a distribution or similar data for biochar (Contescu, 1997), the previously made assumption that biochar should not have a significant amount of functional groups with pK_a values from 6.4-9 cannot be verified. Therefore, further research will be needed to determine how to estimate the total alkalinity in a manner robust to the presence of phosphate and other anions, and how to estimate the concentration of functional groups with pK_a values between 6.4 and the biochar pH.
CHAPTER 4. GENERAL CONCLUSIONS

When used as a soil amendment, biochar has the potential to increase soil pH and provide several other benefits to soil quality, but scientific understanding of the mechanisms by which biochar influences the acid-base chemistry of soil is incomplete. Integral to this understanding is knowledge of the components of biochar alkalinity. However, methods for quantifying the components of biochar alkalinity vary greatly among biochar studies. Components of biochar alkalinity have been shown to include organic functional groups, carbonates, and other inorganic alkalis. Unfortunately, studies quantifying all three of these components are lacking, and of the studies that quantify at least one component, different methods are used from study to study. One method of particular concern is the Boehm titration, which was originally developed for quantifying reactive organic functional groups of carbon blacks and activated carbons in discrete pKₐ ranges (Boehm, 1994; Boehm, 2002). Given that the Boehm titration has only been standardized for use with carbon black and that the differences between biochar and carbon blacks are numerous, the Boehm titration may require modification before it can be relied upon to quantify reactive organic functional groups in biochars (Goertzen et al., 2010). Therefore, three modifications of the Boehm titration method for measuring functional group concentrations were evaluated, and a suite of methods was used to quantify the organic and inorganic components of biochar’s alkalinity.

To identify sources of bias and determine how bias could be prevented, two modifications of the traditional Boehm titration method were compared with the traditional method using acid-treated biochars. To remove soluble ash components that might interfere with the titration, an HCl-wash pre-treatment was applied to all biochars prior to conducting
the traditional and modified titration methods. Other than the pre-treatment, the original sparge method was implemented as recommended by Goertzen et al. (2010). In this approach, acidification with HCl and sparging with N2 gas are employed to remove carbonates, but interference from dissolved organic compounds (DOC) is not addressed. In an effort to remove DOC and carbonates from the Boehm extracts (which otherwise may bias the titrations), barium precipitation and cartridge methods were developed. The barium method uses BaCl2 to precipitate BaCO3 and flocculate DOC, followed by acidification and titration, whereas the cartridge method uses a solid-phase extraction to remove DOC, followed by acidification, sparging and titration. Additionally, the absorbance at 250 nm was measured at all treated extracts to provide an index of DOC.

From the results of the modified Boehm titrations and the absorbances of the extracts, it was not possible to determine which of the three methods tested (sparge, barium, or cartridge) was the most accurate. However, it was possible to identify methods that were likely to be inaccurate when used on specific pK\textsubscript{a} ranges. A method was considered definitively inaccurate if the results obtained with that method did not conform to an underlying principle of the Boehm titration, that is, more alkaline Boehm reactants should accept protons from more functional groups. Inaccuracies were identified when the sparge and barium methods were used to measure functional groups in the 5-13 pK\textsubscript{a} range, and when the cartridge method was used to measure functional groups in the 5-10.3 pK\textsubscript{a} range. Bias in the 5-6.4 pK\textsubscript{a} range results was not definitively identified, but results obtained with different methods were not the same. Possible bias mechanisms included (1) the potential for dissolved organic compounds to take up protons when the filtered samples were acidified and
(2) adsorption of carbonate anions to the cartridges at greater rates from the sample matrix than from the blank matrix because of cation-bridging between carbonate and the cartridge resin. Therefore, the evidence presented in this study shows that the original Boehm titration cannot be relied upon to quantify biochar surface functional groups in all of the intended pK_a ranges. Because the reliability of the modified Boehm titrations used in this study could not be proven, more research is required to prevent interference from dissolved organic compounds and carbonates present in biochar extracts.

Organic functional groups, carbonates (carbonate and bicarbonate), and other inorganic alkalis contributed to the alkalinity of at least one of the studied biochars, thereby verifying the assumption that these components could be contributors to the total alkalinity of biochar. The organic functional groups, carbonates, and other inorganic alkalis were measured using a procedure derived from the Boehm titration, a NaOH trap for capturing CO_2 evolved, and by difference from the total alkalinity, respectively. Total alkalinity was quantified by shaking the biochars with 0.05 M HCl solutions for 24 h and titrating the resulting extracts. Each component of this suite of methods had its own source of error, and so the results should be interpreted accordingly (see Chapters 2 and 3). The corn stover biochar had the greatest total alkalinity, followed by the red oak and cellulose biochars. The alkalinity of the cellulose biochar was dominated by organic functional groups, whereas carbonates constituted the majority of the alkalinity for the red oak and corn stover biochars. Organic functional groups constituted the second largest contribution to total alkalinity for the red oak biochar, whereas inorganic alkalis constituted the second largest contribution for the corn stover biochar.
The corn stover biochar was the only biochar to have any of its alkalinity attributable to inorganic alkalis such as oxides, hydroxides, and phosphates. HCl extracts of the red oak and corn stover biochars contained substantial amounts of K, Ca, Mg, Mn, Al, Si, P, and S. The rates of base cation release and acid reaction were rapid in the first 2-16h of shaking biochar with HCl, but generally slowed at times greater than 16h. In some instances, the rate slowed to what appeared to be equilibrium at times greater than 24h, whereas in other cases, the amount of acid reacted and/or cations released continued to increase between 24-72h. The total concentration, in meq per gram of biochar, of the K, Ca, and Mg released was greater than the amount of HCl reacted during the extraction process, suggesting that these cations were associated with non-alkaline anions such as Cl⁻ in addition to alkalis such as oxides, hydroxides, and carbonates. Thus, the results demonstrated that biochar can contain alkalis in the form of organic functional groups, carbonates and other inorganic alkalis associated with base cations, and that the quantities of each of these alkalinity components can vary greatly between biochars.

In summation, the results demonstrated that biochar alkalinity is present in diverse forms and quantities, but optimal methods for quantifying each component remain uncertain. Thus, more research will be needed to develop the Boehm titration and/or other methods for quantifying biochar’s alkalinity components that are robust to the presence of carbonates, dissolved organic compounds, and other soluble components of biochar.
LITERATURE CITED


Basso, A.S. 2012. Effect of fast pyrolysis biochar on the physical and chemical properties of a sandy soil. M.S., Iowa State University, Ames, IA.


APPENDIX

Figure 1 (a) Goertzen et al. (2010) showed that, following 2h of sparging with N₂ gas, further degassing during the titration can remove additional CO₂ from solution and thereby prevent a positive bias (CSF is defined as Carbon Surface Functionalities). (b) In this study, no evidence of dissolved CO₂ was found after 2h of sparging without further degassing during the titration. Dashed lines indicate pH 7.

Figure 2 Comparison between the number of times 0.05 M NaHCO₃ solution was run through an ENVI-Chrom P solid phase extraction cartridge and the amount of NaOH needed to back-titrated an acidified 5 mL aliquot. Aliquots were acidified using a 2:1 volume ratio of 0.05M HCl to cartridge-treated sample.
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