Characterization and quantification of biochar alkalinity

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HIGHLIGHTS

- We present a suite of methods for quantifying biochar alkalinity in four categories.
- Total biochar alkalinity and distribution of alkalis varied widely among biochars.
- Base cation concentration was a good predictor of total biochar alkalinity.
- Inorganic alkalis comprised >55% of lignocellulosic biochar alkalinity.

GRAPHICAL ABSTRACT
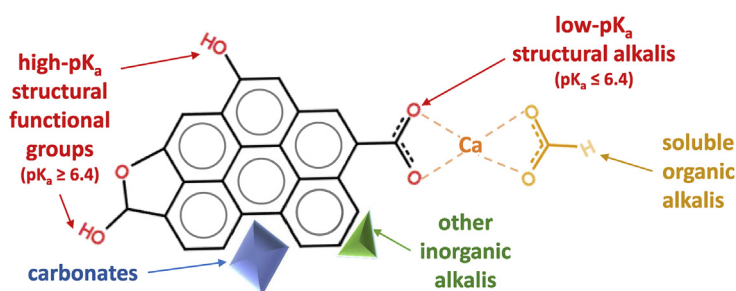
ABSTRACT

Lack of knowledge regarding the nature of biochar alkalis has hindered understanding of pH-sensitive biochar-soil interactions. Here we investigate the nature of biochar alkalinity and present a cohesive suite of methods for its quantification. Biochars produced from cellulose, corn stover and wood feedstocks had significant low-pK_a organic structural (0.03–0.34 meq g^{-1}), other organic (0–0.92 meq g^{-1}), carbonate (0.02–1.5 meq g^{-1}), and other inorganic (0–0.26 meq g^{-1}) alkalinities. All four categories of biochar alkalinity contributed to total biochar alkalinity and are therefore relevant to pH-sensitive soil processes. Total biochar alkalinity was strongly correlated with base cation concentration, but biochar alkalinity was not a simple function of elemental composition, soluble ash, fixed carbon, or volatile matter content. More research is needed to characterize soluble biochar alkalis other than carbonates and to establish predictive relationships among biochar production parameters and the composition of biochar alkalis.

1. Introduction

Biochars, the solid co-products of the pyrolysis biomass-to-bioenergy pathway suitable for use as a soil amendment (Lehmann et al., 2006; Schimmelpfennig and Glaser, 2012), are diverse materials with a wide range of chemical and physical properties (Brewer et al., 2011; Kloss et al., 2012; Singh et al., 2010; Wang et al., 2014). Application of biochar to soil can sequester carbon (C) by both increasing soil carbon directly and by increasing yields of biomass, but such benefits are dependent on properties of both the soil and the biochar. Biochar application has been shown to increase soil cation exchange capacity (CEC), water-holding capacity, nutrient retention, and pH, and also to decrease soil bulk density and net greenhouse gas emissions from soil

agroecosystems (Fidel, 2015; Joseph et al., 2010; Laird et al., 2010). However, the effects of biochar amendments on soils arise from many complex-interactive processes, often resulting in strongly context-specific and method-dependent results (Joseph et al., 2010; Simek and Cooper, 2002). Alkalinity is one of the most influential biochar properties, because changes in pH have cascading impacts on many soil processes, including nitrogen mineralization, mineral precipitation, ion exchange, and greenhouse gas emissions (Joseph et al., 2010; McCormack et al., 2013). Many studies have shown that biochar amendments increase and buffer soil pH, but the nature of biochar alkalis, the influence of feedstock and biochar production conditions on biochar alkalinity, and the variability of alkali properties among biochars remain poorly understood (Xu et al., 2012; Yuan et al., 2011a, 2011b). A mechanistic understanding of how specific biochar alkalis interact with soil is therefore imperative to further pH-related biochar research.

Four broad categories of biochar alkalinity have been identified in the literature: surface organic functional groups (as conjugate bases), soluble organic compounds (also conjugate bases of weak acids), carbonates (salts of bicarbonate and carbonate), and other inorganic alkalis, which may include oxides, hydroxides, sulfates, sulfides, and orthophosphates (Cheah et al., 2014; Singh et al., 2010; Yuan et al., 2011a). Distinguishing between these categories is essential to understanding the short- and long-term impacts of biochar on soil pH, because soluble organic and inorganic alkalis contribute to short-term acid amelioration (Silber et al., 2010; Yuan et al., 2011b); while surface organic functional groups contribute to long-term soil CEC and pH buffering capacity (Mao et al., 2012). Furthermore, biochar surface functional groups with pK_as close to that of typical soil pHs (5–7) will be the most active ion donators and acceptors in soil.

Widely differing methods for defining and quantifying biochar alkalinity categories have been employed in previous experiments, thereby confounding comparisons among studies (Dai et al., 2014; Singh et al., 2010; Wan et al., 2014; Yuan et al., 2011b; Yuan and Xu, 2011). Existing methods for determining total alkalinity include: (1) directly titrating a biochar-water slurry with 0.1 M HCl (Wan et al., 2014), (2) equilibrating biochar with 0.03 M HCl and titrating the filtered extracts with NaOH (Yuan and Xu, 2011), and (3) shaking biochar with 1 M HCl for 2 h, followed by titration of extracts with NaOH (Singh et al., 2010). Determining carbonate alkalinity in biochars typically requires quantification of CO_2 liberated during equilibration with HCl by using a manometer or NaOH trap. However, recommended HCl concentrations have varied from 1 to 4 M and equilibration times have ranged from 1 to 5 days (Wan et al., 2014; Wang et al., 2014). The NaOH trap method was determined to be the most accurate for quantification of carbonates, but the effects of HCl concentration and equilibration time on carbonate and total alkalinity determination have not been examined (Wang et al., 2014). Silber et al. (2010) showed that the release of ions and neutralization of H^+ by biochar is both pH- and time-dependent, signifying total alkalinity and carbonate alkalinity should be measured under the same conditions to facilitate quantitative comparisons; however, no single study has done so. Lastly, most studies use Boehm titrations to quantify weak organic acid functional groups that are directly bonded to biochar surfaces. These functional groups can contribute to alkalinity when present as deprotonated conjugate bases. On the other hand, recent reports indicate that soluble alkalis can confound Boehm titration results (Fidel et al., 2013; Tsechansky and Graber, 2014). Although several studies have quantified one category – and in some cases two categories – of biochar alkalinity (Chen et al., 2015; Chun et al., 2004; Dai et al., 2014; Tsechansky and Graber, 2014; Wan et al., 2014; Wang et al., 2014; Yuan et al., 2011b), no study has systematically investigated the relative abundance of all four categories of

biochar alkalinity or considered method efficacy. Therefore, this study investigates the nature of biochar alkalis and presents a cohesive suite of methods for their quantification.

2. Materials and methods

2.1. Biochar preparation

Given the diversity of biochars, a full analysis examining biochars produced from all possible combinations of feedstock and pyrolysis conditions is beyond the scope of this study. Hence, eight biochars produced at three temperatures (300, 500 and 600 °C) and by three processes (slow pyrolysis, fast pyrolysis, and gasification) were chosen to encompass the anticipated range of total alkalinity and alkalinity distributions for cellulosic and lignocellulosic feedstocks (Table 1). Slow pyrolysis biochars made from cellulose (Sigma Aldrich) and corn stover (Zea mays; harvested in Boone, IA) were pyrolyzed in a N_2-purged muffle furnace. The muffle furnace temperature was first held at 105 °C for 1 h to remove any water present in the feedstock, then the furnace was heated to 100 °C below the highest treatment temperature (200 °C, 400 °C or 500 °C) at 10 °C per minute, and held at that temperature for 2 h before increasing to the highest treatment temperature at 0.5 °C per minute. The highest treatment temperature (300 °C, 500 °C, or 600 °C, see Table 1) was then maintained for 2 h before the furnace was allowed to cool overnight under N_2-purge. A hardwood slow pyrolysis biochar (HW5s), obtained from Royal Oak Enterprises, LLC (size #10 charcoal, 0.5–2 mm, http://royal-oak.com/), was produced using a traditional kiln. A mixed wood gasification biochar (MW6g), obtained from ICM, Inc. (http://www.icminc.com/), was produced using a auger bed gasifier at 550–650 °C from a blend of primarily oak (Quercus spp.), elm (Ulmus spp.) and hickory (Carya spp.) woodchips with particle sizes 0.1–2000 mm. Two fast pyrolysis biochars, RO5f and CS5f – produced from red oak wood (Quercus rubra) and corn stover (Zea mays) respectively at 500 °C – were obtained from the Center for Sustainable Energy Technologies at Iowa State University. Both of the fast pyrolysis biochars were produced in a fluidized bed reactor that used N_2 as a carrier gas and sand particles (0.5 mm average particle diameter) as fluidization media (Pollard, 2009; Pollard et al., 2012). These fast pyrolysis biochars were sieved to <0.50 mm to minimize the influence of sand particles. All slow pyrolysis and gasification biochars were ground to <0.50 mm to minimize the influence of particle size on chemical analyses.

2.2. Biochar pH

Biochar pHs were measured in duplicate by mixing biochar and deionized water in a 10:1 water:biochar (mL:g) ratio; the resultant slurries were equilibrated for 1 h, and then the pHs were measured by placing a glass H^+ electrode in the solution just above the settled

Table 1
Biochar abbreviation, feedstock, pyrolysis temperature, process type, and biochar pH (in H_2O and 1 M NaCl) expressed as means of two replicates (±0.1).

Biochar	Feedstock	T (°C)	Process	pH (H_2O)	pH (NaCl)
CE5s	Cellulose	500	Slow pyrolysis	6.4	6.4
RO5f	Red Oak	500	Fast pyrolysis	7.1	7.3
CS5f	Corn stover	500	Fast pyrolysis	8.4	7.6
CS3s	Corn stover	300	Slow pyrolysis	7.3	6.7
CS5s	Corn stover	500	Slow pyrolysis	10.1	9.2
CS6s	Corn stover	600	Slow pyrolysis	10.3	9.3
HW5s	Hardwood	~500	Slow pyrolysis	7.9	8.2
MW6g	Mixed wood	~600	Gasification	8.8	8.6

T = highest pyrolysis treatment temperature.