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Letter Report for Characterization of Biochar

JE Amonette, Ph.D.

April 2013



Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
Richland, Washington 99352

Introduction

On 27 November 2012, a bulk biochar sample from Babcock & Wilcox Volund in Denmark was received from Hamilton Maurer International, Inc. for characterization of selected physical and chemical properties. The main purpose of the characterization was to help determine the degree to which biochar would be suitable as a soil amendment to aid in growth of plants. Towards this end, analyses to determine specific surface, pH, cation-exchange capacity, water retention, and wettability (i.e. surface tension) were conducted. A second objective was to determine how uniform these properties were in the sample. Towards this end, the sample was separated into fractions based on initial particle size and on whether the material was from the external surface or the internal portion of the particle.

Materials and Methods

The sample was divided into five fractions. Initially, biochar particles were separated into three size fractions: those greater than 2 cm in size, those between 1 and 2 cm in size, and those less than 1 cm in size. A portion of the > 2-cm size fraction was further fractionated into two sub-fractions which contained material taken either from the outer shell of the particle or from the inner core of the particles. The outer shell was separated by grating the particles by hand using a fine-toothed cheese grater. The five fractions are summarized in Table 1.

Sample ID	Particle Size	Bulk/Sub-fraction
V2B	> 2 cm	Bulk
V2O	> 2 cm	Outer shell
V2I	> 2 cm	Inner core
V12	1-2 cm	Bulk
V1M	< 1 cm	Bulk

Sample homogenization. About 20 g of each char fraction was gently crushed by hand using a mortar and pestle until the particles passed through a 2-mm sieve. Subsamples of these homogenized samples were then taken for each analysis.

Moisture content. The specific moisture content of the char fractions was determined by weighing 1.2-g sample (as received) into an aluminum weighing tin and then drying in an oven overnight at 110°C. The fraction of moisture present was calculated in terms of the oven-dry weight of the sample using

$$\% \text{ moisture} = 100 * (W_{AR} - W_{OD}) / W_{OD}$$

where W_{AR} is the weight of the sample as received and W_{OD} is the weight of the oven-dried sample.

Surface area determinations. The specific surface ($m^2 g^{-1}$) of the chars was determined by sorption of ethylene monoethyl ether (EGME) using the method of Carter et al. (1986) as modified by Cerato and Lutenegger (2002). Briefly, subsamples of the homogenized chars sufficient to yield about 1 g (oven-dry weight) were dried overnight at 110 °C in a tared 3”-diameter Al weighing tin and then cooled to room temperature in a desiccator. About 1.5 g of EGME were added and mixed with the char, and then the tin was placed in a vacuum desiccator containing an EGME/ $CaCl_2$ buffer mixture and allowed to equilibrate. The weight of the char/EGME in the tin was monitored daily for several days until equilibration had been achieved (about 1 mg or less in weight change from the previous weighing). The amount of EGME sorbed to the char was then calculated, and based on the known weight of EGME required to form a monolayer ($0.286 mg m^{-2}$), the specific surface of the sample was calculated. In addition to the char samples, a standard sample of porous silica (Sigma-Aldrich 236845, Davisil Grade 646, nominal $300 m^2 g^{-1}$) was included in each run for calibration purposes.

pH determinations. The as-received equivalent of 0.75 g of homogenized oven-dry sample was weighed into a tared glass vial. Fifteen mL of deionized water were then added to achieve a 20:1 solution:solid ratio, and the suspension shaken on a reciprocating shaker for 210 minutes. The sample was filtered through a 0.22- μm pore-size syringe filter and the pH of the filtrate was determined immediately using a glass pH electrode that had been calibrated at pH 4, 7, and 10 using standard calibration solutions.

Cation-exchange capacity. The “maximum” cation-exchange capacity was determined, using the proton, H^+ , or hydronium ion, H_3O^+ , as the exchange cation. The procedure was modified from that of Boehm (1994), Goertzen et al. (2010) and Oickle et al. (2010). However, because a full Boehm titration involves several separate titrations and measures acidity of a wide range of functional groups, most of which are not active at typical soil pH values, the analysis was further constrained to a single type of functional group (carboxylic acid) using a single titrant (0.05 M $NaHCO_3$, pH~8.4). The procedure thus determines proton exchange capacity (titrateable acidity) at a pH of about 8.4. The exchange capacity of the char at lower pHs would be smaller than the value given by this analysis.

The procedure itself involved first acidifying the chars to protonate all exchange sites and dissolve any bases that might interfere with the analysis. Sufficient char to yield at least 1 g (oven-dry weight) was reacted with 20 mL of 0.05 M HCl on an oscillating shaker for 24 h at room temperature, then filter-washed with water until no Cl^- could be detected in the filtrate using a drop of $AgNO_3$ solution. The acidified char (pH 3.5-4.5) was then dried for 36 h at 40 °C.

Duplicate aliquots (500 mg) of dried acidified char were then reacted with 20 mL of 0.05 M NaHCO_3 in sealed plastic vials for 24 h. At the end of this period, the samples were filtered (0.22- μm pore-size syringe filter) into fresh plastic vials. Ten-mL aliquots of the filtrate were transferred immediately to 60-mL Teflon vessels containing 20 ml of freshly standardized 0.0500 M HCl and two drops of phenolphthalein as the end point indicator. The acidified solutions were then back-titrated with freshly standardized 0.0500 M NaOH to the first permanent pink endpoint. Blank samples, with no char, were carried through the same procedure. The proton exchange capacity was then calculated from the difference in NaOH consumed by the char sample and blank sample.

Water holding capacity. The intent of this measurement is to determine the *plant-available* water that could be held by the chars. A classic method for determination of “maximum available moisture” based on direct determination of “soil moisture equivalent” (Briggs and McLane, 1907; Briggs and Shantz, 1912) was modified to obtain values for the char samples. First, the char was diluted in a matrix of silt-sized (ca. 30 μm diameter) borosilicate glass beads (Spherglass 3000E, Potters Industries LLC, Valley Forge, PA) to simulate incorporation into soil. About 1.5 g of a mixture of 1 part char and 5 parts glass beads by weight was packed into the top of a tared 2-mL centrifuge filter tube (64520-CA, Sun-Sri, Rockwood, TN) and the total weight of tube and char/glass mixture taken. The contents of the filter tube were then saturated with 5 mM CaSO_4 and allowed to equilibrate overnight. The next day, the top of the filter tube was capped, attached to the bottom receiver tube, and centrifuged at 1023 RCF for 30 minutes using a Beckman GS-15 centrifuge equipped with a swinging-bucket rotor. The final weight of the top filter tube containing the char/glass mix was then determined and the net water retained was calculated. Controls consisting of 1) the same volume of glass beads in the filter tube (thus a higher weight) and 2) the empty filter tube were also run. The moisture equivalent for each sample (i.e., the net water retained as a fraction of the dry weight of the sample) was calculated, and then normalized by subtracting the control result and dividing by the char content of the mix to estimate the moisture equivalent of the pure char. The maximum available moisture content was then calculated by adding 0.21 to this value as described by Briggs and Shantz (1912).

Wettability. The wettability of the chars was determined by the “molarity of ethanol drop” (MED) method of Roy and McGill (2002). Briefly, air-dry homogenized char was placed in the bottom of an Al weigh boat in sufficient amount to uniformly cover the bottom to a depth of at least 6 mm. Drops from a series of aqueous ethanol solutions that ranged in concentration from 0 to 6 M ethanol were then gently added to the surface of the char and the time required for them to be absorbed was measured. The goal was to identify the least-concentrated ethanol solution that yielded a drop-absorption time of 10 s or less. Correlation of this concentration with known surface tension data for the aqueous ethanol solutions allows calculation of the surface tension of the char. The higher this value, the more wettable the surface.

Results and Discussion

The results of the analyses are summarized in Table 2. Overall, the five biochar fractions were similar in their physical and chemical properties, although the variability was surprising. The specific surfaces ranged from 260-330 m² g⁻¹, values that are reasonably high. The lowest specific surfaces were obtained for the subsamples of the >2-cm fraction, i.e., the outer shell (V2O) and inner core (V2I) fractions. For comparison, quartz sand has a specific surface of about 0.1 m² g⁻¹, soils typically range from 25-250 m² g⁻¹ depending on their clay content, montmorillonite clays range from 600-800 m² g⁻¹, and activated carbons range from 500-1500 m² g⁻¹. All five biochar fractions were moderately alkaline, having pHs between 9.8 and 10.4.

The titrateable acidities at pH 8.4, which serve as a proxy for cation-exchange capacity assuming that cations are retained only by carboxylic acid functional groups, ranged from about 140-240 μmol g⁻¹, which is substantially higher than published values for fresh chars but comparable to

Property	Units	Biochar Fraction				
		V2B	V2O	V2I	V12	V1M
Specific Surface	m ² g ⁻¹	315	270	260	330	285
Surface Tension (Wettability)	mN m ⁻¹	71.3	71.3	71.3	71.3	71.3
Moisture Content As-Received	g g ⁻¹	0.57	0.68	0.55	0.29	0.91
Maximum Available Moisture	g g ⁻¹	0.303 (0.007)	0.139 (0.016)	0.273 (0.021)	0.534 (0.005)	-0.084 (0.008)
Total C Content	g g ⁻¹	0.772 (0.012)	0.779 (0.010)	0.830 (0.003)	0.761 (0.050)	0.769 (0.016)
pH		10.29	10.32	10.22	10.42	9.78
Titrateable Acidity at pH 8.4	μmol g ⁻¹	198 (36)	143 (10)	209 (118)	179 (7)	239 (7)



values for oxidized chars. For example, Goertzen et al. (2010) reported a value of $14 \mu\text{mol g}^{-1}$ for the freshly prepared carbon black sample they analyzed whereas Boehm (1994) reported a value of $181 \mu\text{mol g}^{-1}$ for graphite wear dust oxidized in air at 420°C . Cation exchange capacities (CEC) for soils ($100\text{-}400 \mu\text{mol g}^{-1}$) are comparable to the Volund biochar results, whereas those for montmorillonite clays ($750\text{-}1200 \mu\text{mol g}^{-1}$) are substantially higher. Given the close correspondence to the value for oxidized graphite wear dust, it is not clear whether the values for the Volund biochar would be expected to increase further with prolonged exposure to the air.

The total C content of the fractions was similar at about 77%, except for the V2I fraction, which contained 83% C. The higher value obtained for this fraction suggests that it is less oxidized than the other fractions.

All five biochar fractions were wet as received (moisture contents ranged from 29-91 % on an oven-dry basis) and thus were initially assumed to have surface tensions of 71 mN m^{-1} . This was verified subsequently by testing with deionized water droplets after the samples were allowed to air dry overnight.

The maximum available moisture capacities of the chars varied substantially, from 0.53 for the V12 fraction to -0.8 for the V1M fraction. Only two of the fractions (V2B and V12) yielded higher available moisture capacities than the silt-sized glass beads (0.28) that proxy for soil having no organic matter. Lower values for the V2O, V2I, and V1M fractions suggests that with handling (grating) and comminution to smaller particle sizes (as in the V1M fraction) the available moisture capacities decrease. This is quite interesting, given that the V1M fraction had the highest moisture content as received, but the lowest plant-available moisture capacity. Evidently, the larger structures in the biochar, which are lost with comminution, are critical to moisture retention at energies accessible to plants. The negative plant-available moisture capacity of the V1M fraction suggests that the small biochar particles either actually repel water or at least prevent its retention in the $20\text{-}40 \mu\text{m}$ sized pores between the glass beads by filling the pores with similarly or smaller-sized biochar particles. On the positive side, addition of the V12 char at $50 \text{ metric tonnes ha}^{-1}$ (about 2.5% by weight) would be expected to increase the maximum available moisture capacity of soil by about 4.6% (i.e., from 0.281 to 0.294). This increase could be significant with some crops in some years, but would likely decrease over time as the biochar weathered into smaller particles.

In summary, the Volund biochar has significant liming potentials, significant cation-retention capacities, and highly variable plant-available moisture retention properties that, under the most favorable circumstances, could be helpful to plants. As a consequence, it would be quite suitable for addition to acidic soils and should enhance the fertility of those soils.

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