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The Cation-Exchange Capacity of Crete silt loam soil compared to charcoal.

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ABSTRACT

Black carbon's (BC) cation-exchange capacity (CEC) is one reason why charcoal amended soils in the humid tropics possess increased element retention, fertility, and crop production. Using charcoal as a soil amendment may build more sustainable soils due to BC's refractory nature which promotes the retention of soil organic matter (SOM). The purpose of this study was to verify the soil type to be used in the study and to determine the CEC of this soil type and that of charcoal. A soil texture analysis verified that the soil type used in this study was Crete silt loam. The CEC of the Crete silt loam soil and charcoal was determined by Cu saturation and Cu extraction with 1.0 N HCl. The results show that the CEC of the Crete silt loam soil was greater than that of the charcoal sample. Because the results were the reverse of what was expected, future studies should consider the source of the charcoal and the quality of the soil type before determination of the CEC.

Keywords: *cation-exchange capacity, charcoal, soil organic matter, soil texture analysis.*

INTRODUCTION

Soil organic matter (SOM) acts as a reservoir for essential elements needed for plant growth. The sustainability and productivity of a soil largely depends on the amount of SOM available and the elements it is capable of retaining (Mapfumo et al., 2007). For optimal plant growth, the SOM must contain an adequate supply of the 16 essential elements needed for plant growth. Carbon dioxide and water contribute hydrogen (H), oxygen (O), and carbon (C) to the soil. Above ground biomass decomposition is the main naturally occurring contributor of the other 13 essential elements found within SOM. The locality of SOM is found in the A horizon of soil or otherwise known as topsoil. This is also the horizon with which leaching occurs (Loynachan et al., 1999). Leaching and varying decomposition rates are two factors that account for the depletion of SOM making soils less fertile, productive, and sustainable (Steiner et al., 2007).

Organic amendments to soils by the addition of manure, mulch, or compost are ways of supplying necessary elements to leached soils in order to retain a high percentage of SOM while preserving fertility (Uphoff et al., 2006). The elements contained in these amendments are beneficial to the soil; however, repetitive applications are needed in order to maintain a sufficient level of SOM over a short period of time due to the relatively rapid decomposition rate of the organic amendments when added to tropical soils.

Charcoal amendments may be used as an alternative additive to soil (Steiner et al., 2007). Charcoal is a form of biomass-derived black carbon (BC) resulting from the incomplete combustion of organic materials. Pyrolysis and gasification are the two most popular BC production methods being used throughout the world today. The best feedstocks for the production of BC are cellulosic biomass wastes such as wood chips or rice hulls. The process of using BC as a soil amendment not only potentially improves a soil's elemental composition but also acts as a mechanism for carbon sequestration (International Biochar Initiative, Production). BC is structurally comprised of numerous aromatic rings resulting in a polycyclic aromatic hydrocarbon with potential carbon concentrations of about 70 to 80% (Liang et al., 2006). Polycyclic aromatic hydrocarbons are capable of intercalating with DNA molecules. This ability makes BC a potential carcinogenic substance. Unlike other soil amendments, BC is a polycyclic structure exceptionally resistant to microbial attack and decomposition (Uphoff et al., 2006; Mapfumo et al., 2007). Carbon to nitrogen (N) ratios increase as black carbon is added to the soil. An increase in C may significantly lower the N availability in the soil which notably decreases microbial decomposition. Due to BC's refractory nature, microbes are only able to metabolize a very small portion of the BC. Initially as C is added to the soil, microbes rapidly extinguish the available N within the soil to compensate for the increased C levels introduced into the soil. Because of the C to N ratio required by a microbe for decomposition, increased levels of N may need to be added to the soil after BC input in order for plants to have adequate N levels available for plant uptake (Steiner et al., 2007). These characteristics aid in the retention of SOM and may improve soil stability.

Black carbon's cation-exchange capacity (CEC) may be a pivotal reason that charcoal-amended soils possess such good element dynamics (Liang et al., 2006). Even though BC as a whole does not undergo oxidation, the carboxyl outer groups of the aromatic ring are capable of being oxidized which in turn yield carbonyl groups containing a net negative charge. The net negative charge allows adsorption reactions to occur with essential elements. Earlier experiments with soils containing BC revealed increased oxygen to carbon, chloride to carbon, and potassium to carbon ratios on the surface of the BC particles. These reactions explain the enriched element affinity of black carbon (Liang et al., 2006) (Mapfumo et al., 2007). The surface area of BC may also aid in the CEC found in charcoal containing soils. Experiments testing Anthrosols and adjacent soils in Manaus, Brazil found both increased CEC and increased soil surface area for the Anthrosol samples compared to the adjacent soil samples (Steiner et al., 2007). Decreased levels of water contamination can also be contributed to the increased CEC of BC amended soils by decreasing the concentration of elements being leached from the soil and entering groundwater (International Biochar Initiative, Biochar).

The quantity of charcoal supplied to a soil reflects the ability of element sorption and SOM content within the amended soil. The benefits of charcoal amendments increase as charcoal additions increase up until a specific point at which the charcoal is most effective. Additional amounts beyond this usually cause a decrease in the SOM element supply pool (Uphoff et al., 2006). Additionally, past experiments have revealed that the particle size of the added charcoal does not make a significant difference in its ability to adsorb elements (Steiner et al., 2007).

Soil sustainability and element retention are areas of active research. Continued research is needed to uncover possible measures for rejuvenating the Earth's soils. The sustainability of element rich agricultural soils that continually yield productive and nutritious crops is a challenge in today's growing society with its growing agricultural needs. Therefore, through my research I will address the following objectives: (i) verify Crete silt loam as the soil type through soil texture analysis (ii) compare the CEC of the soil to the CEC of charcoal.

MATERIALS AND METHODS

Soil for this experiment was obtained from a field in McPherson County, KS (38°23'16.00''N, 97°41'06.23''W) owned by Paul Hoffman. The soil type of the field where the soil was collected is Crete silt loam, 0 to 1 percent slopes (NRCS). Alfalfa was being grown in the field during the time of soil collection.

The soil sample was taken to the agriculture laboratory at McPherson College and thinly spread out on a large sheet of paper to air dry for three days. The air-dried soil was manually crushed with a mortar and pestle to break up large clods of soil. The sample was then passed through a 1.19-mm sieve. The sieve was #16 from the U.S. standard sieve series. The 1.19-mm fraction of the soil sample was used for the experiments. An additional sample from the air-dried 1.19-mm portion of soil was dried in a 105° C oven for 24 hours. Both samples were placed in sealed containers and manually mixed for 5 minutes.

A soil texture analysis was performed to verify the soil sample type. A 50.0004-g sample of oven-dried soil was placed in a 250-ml beaker. 125 ml of Calgon® solution was added to the beaker and allowed to slake for at least 16 hours. The sample was transferred to an electrical blender and mixed for five minutes. The mixed sample was washed with deioinized (DI) water into a sedimentation cylinder and filled with DI water to the 1,000-ml mark. The cylinder was inverted repeatedly for one minute and immediately placed on the lab counter and the time noted. A hydrometer reading was taken at 40 seconds, 60 minutes, and 120 minutes along with the temperature. Correction values were obtained by adding 125 ml of Calgon® solution to a sedimentation cylinder. The cylinder was filled with DI water to the 1,000-ml mark. The cylinder was left undisturbed for two days before the temperature was measured. Using the actual measurements and correction factor, the fractions of sand, silt, and clay in the sample were found (Cox, 1967).

To prepare the soil for the determination of the CEC, a total of 160 g of soil was subjected to hydrogen peroxide digestion for removal of organic matter. Hydrogen peroxide with 35 wt% solution in water was used for this procedure. For each peroxide digest, 10 g of air-dried soil was transferred to a 1,000-ml beaker. A transfer pipette was used to transfer 10 ml of H_2O_2 to the sample. The beaker was immediately covered with a watch glass. Violent frothing occurred initially. Once the frothing subsided, another 5 ml of H_2O_2 was added to the sample. After frothing subsided for the second time, the sample was transferred to a hotplate and heated around 90°C. A total of 15 ml of H_2O_2 was added to the sample in 5-ml aliquots. Each aliquot was added once the previous was done frothing. After all the aliquots were added, DI water was used to rinse down the sides of the beaker. The sample was heated until all liquid was evaporated. After evaporation, the beaker was removed from the hotplate and left to cool. The sample was removed from the beaker and placed into a 125-ml screw top vial (Carter, 1993).

A standard curve of five known Cu concentrations (0.004mol/L, 0.008mol/L, 0.012mol/L, 0.016mol/L, and 0.02mol/L) was prepared using 0.2 N $Cu(C_2H_3O_2)_2$aq. Absorbances were measured using a Spectronic 20 by Spectronic Instruments, Inc. at 540nm wavelength.

The total CEC of each sample was then determined by placing 1.0 g of soil or charcoal into a 50-ml beaker. 10 ml of 0.2 N $Cu(C_2H_3O_2)_2$aq or 10 ml of DI H_2O were added to the soil or charcoal and manually mixed for one minute by swirling. One soil and charcoal sample each were subjected to 0.2 N $Cu(C_2H_3O_2)_2$aq addition while one soil and charcoal sample each were subjected to DI H_2O addition. The soil or charcoal was poured into a funnel containing Whatman 9.0 cm #2 filter paper. DI water was used to wash all remaining matter into the filter. A total of 30 ml of DI H_2O was poured through the sample to wash all excess Cu from the soil or charcoal sample. Approximately 5 ml of DI water was added to the funnel at a time. Each aliquot was completely drained before adding the next aliquot. This solution was the first Cu elution fraction and was saved for analysis. The funnel was transferred to a 25-ml graduated cylinder and three, 5-ml portions of 1 N HCl were added to the sample with a transfer pipette. DI water was added until a total of 20 ml of solution was collected. 5 ml of this second Cu elution fraction solution plus 5 ml of concentrated NH_4OH were mixed together into a tube. All 10-ml samples were centrifuged in a Fisher centrific model 228 at 1294.72x *g* for seven minutes before being transferred to a ½" diameter test tube by Spectronic Instruments. The absorbance was measured for each 10-ml sample with a Spectronic 20+ (Thien and Graveel, 1997). For each soil or charcoal sample three different absorbances were measured. The first absorbance was measured from a solution consisting of 5 ml of concentrated NH_4OH, 4 ml of DI H_2O, and 1-ml of 0.2 N $Cu(C_2H_3O_2)_2$aq. This absorbance was multiplied by ten because the $Cu(C_2H_3O_2)_2$aq was diluted by a factor of ten. This represents the initial amount of Cu added to the soil or charcoal. The first absorbance for the soil or charcoal sample when DI H_2O was added initially consisted of 5 ml of concentrated NH_4OH and 5 ml of DI H_2O. The second absorbance was measured for each soil and charcoal sample from a solution consisting of 5 ml of concentrated NH_4OH, 4 ml of DI H_2O, and 1 ml of the first Cu elution fraction solution that was not held by the sample. This absorbance was multiplied by ten because the Cu solution was diluted by a factor of ten. The third absorbance was measured from a solution consisting of 5 ml of concentrated NH_4OH and 5 ml of the second Cu elution fraction solution. The concentration of this sample was multiplied by two because of a dilution factor. The only difference in measurements between the samples subjected to 0.2 N $Cu(C_2H_3O_2)_2$aq addition verse DI H_2O addition is in the first absorbance.

RESULTS

Standard Curve

In order to determine the concentration of the Cu present in each sample, a standard curve constructed from five known Cu concentrations was needed. A linear regression was used to find the line of best fit for the measured absorbances. The slope of the line is equal to 0.0295. The R^2 value of the line of fit was 0.9999. The equation along with my measured absorbances was used to determine the Cu concentration of my unknown samples.

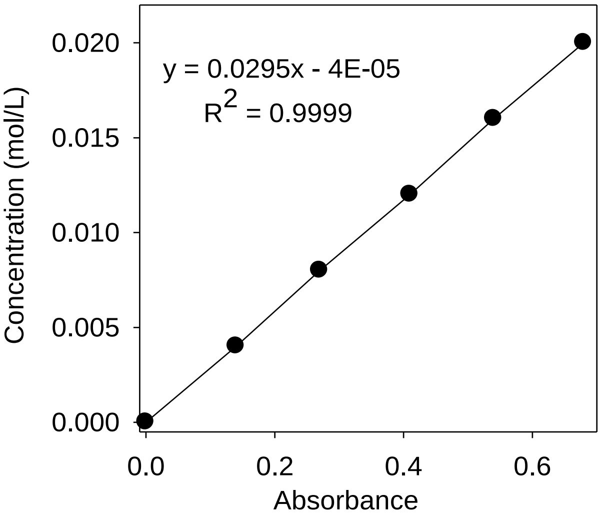

Figure 1. $Cu(C_2H_3O_2)_2$aq standard curve.

Experimental Results

The soil texture analysis allowed me to verify the soil type which I was using in my experiment. The analysis provided me with the different percent by weight particle classifications found within soil. (See Table 2) By using this data and a soil texture triangle, I found the texture of the soil to consist mostly of silt. (See Figure 2) This corresponds to the classification, Crete silt loam, found using the web soil survey (NRCS).

Table 2. Particle size distribution. The percent of sand, silt, and clay in the sample determined by soil texture analysis.

Particle Size	Percent Weight (%)
Sand	< 2.0
Silt	98
Clay	< 1.0

The first total CEC test was done to determine the mass of exchangeable Cu found in both the Crete silt loam and charcoal samples prior to $Cu(C_2H_3O_2)_2$aq treatment. When DI H_2O was added to the Crete silt loam soil sample, 116.4 µmol of Cu was eluted from the soil. When 1 N HCl was added to the soil, no Cu was eluted from the soil. When DI H_2O was added to the charcoal sample, no Cu was eluted from the sample. However, when 1 N HCl was added to the charcoal 10.2 µmol of Cu was eluted from the sample. (See Figure 3)

The second test was done to determine the total mass of exchangeable cations within the Crete silt loam and charcoal samples. For the Crete silt loam sample, 2.01 mmol of 0.2 N $Cu(C_2H_3O_2)_2$aq was added to the soil. A total of 1.45 mmol of Cu were eluted

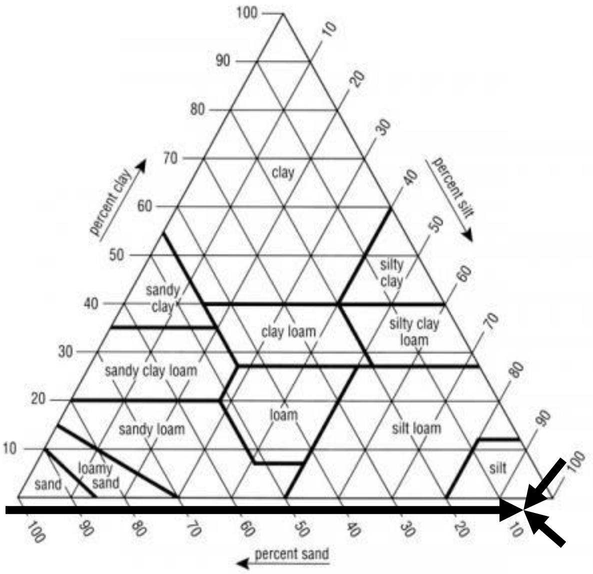

Figure 2. Public domain image of soil texture triangle obtained from the USDA NRCS website. Arrows point to the soil type of the sample.

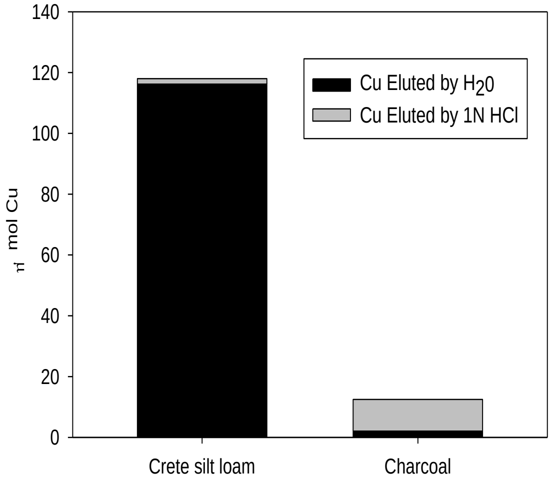

Figure 3. Exchangeable Cu within Crete silt loam and charcoal samples with no $Cu(C_2H_3O_2)_2aq$ addition.

from the soil by DI H_2O. However, only 1.33 mmol of the Cu came from the $Cu(C_2H_3O_2)_2$.aq. At this point, the soil still held onto 0.556 mmol of Cu. Another 0.116 mmol of Cu was eluted from the soil by 1 N HCl. A total of 0.439mmol of Cu was left within the soil. The total CEC of the Crete silt loam sample was 5.82 cmolc$^+$ kg^{-1}. The same amount of Cu was added to the charcoal sample as the soil sample. The DI H_2O eluded 1.57 mmol of Cu from the charcoal. A total of 0.438 mmol of Cu was left in the charcoal. The 1 N HCl displaced 0.0338 mmol of Cu from the sample leaving 0.405 mmol of Cu left within the charcoal. The total CEC of the charcoal sample was 1.69 cmolc$^+$ kg^{-1}. (See Figure 4)

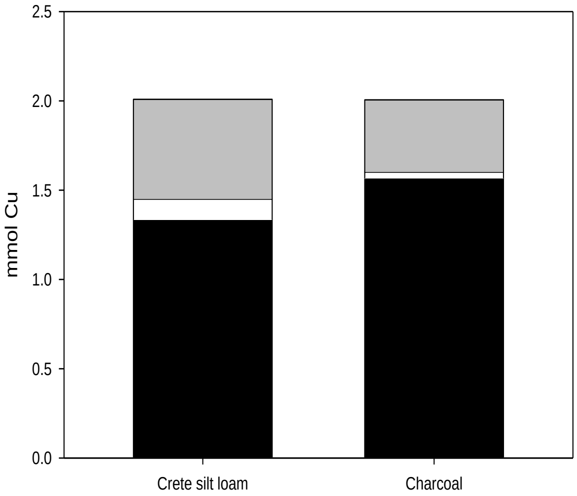

Figure 4. Exchangeable Cu within Crete silt loam and charcoal samples with the addition of 0.2 N $Cu(C_2H_3O_2)_2aq$. The black portion of the graph represents the amount of Cu eluted by H_2O. The white portion of the graph represents the amount of Cu eluted by 1 N HCl. The gray portion of the graph represents the amount of Cu left on the sample.

DISCUSSION

A soil texture analysis is a method used to categorize a soil type. The soil used in my research was determined to consist mostly of silt by the soil texture analysis. This soil type corresponded with the soil classification of Crete silt loam found using the web soil survey (NRCS).

This research looked at the effectiveness of charcoal as an alternative soil amendment that would increase a soil's element retention by increasing its CEC. The results of my study show that charcoal's total CEC is less than the total CEC of Crete silt loam soil. I found no previous studies that determined the individual CEC of soil and charcoal. However, the studies compared the control soil's CEC with charcoal amended soil's CEC. In these studies, the charcoal amended soils had greater CEC's then the control soils. Previous studies have found up to a 40% increase in the CEC of tropical soils after charcoal addition (Uphoff, 2006). Additionally, testing of highly weathered Xanthic Ferralsols in Manaus, Brazil have shown increases in the CEC of soil with the addition of charcoal. The control soil samples had CEC's of 1.61 cmolc$^+$ kg^{-1} whereas the charcoal amended soil samples had CEC's of 1.80 cmolc$^+$ kg^{-1} (Steiner, 2007). In my research, I looked at the difference between the CEC of Crete silt loam soil verse the CEC of charcoal. The reason for my soil sample having a greater CEC then the charcoal sample is probably because my soil type was not highly weathered and already had good nutrient dynamics whereas the control soil in previous studies lacked adequate SOM and good nutrient dynamics caused by intense weathering.

The source of the charcoal in my research was unknown. For future research, it would be beneficial to either purchase charcoal produced by pyrolysis such as EternaGreen^{TM} Biochar or self produce the charcoal either in a covered mound or in a burn barrel. This would allow the source of the charcoal to be known and controlled. Also, an alternative type of soil could be used that lacks good soil dynamics and/or crop production. Sandy or weathered soils may be two alternative soil types that could be tested. Finally to more fully compare the total CEC of charcoal and soil; it may be beneficial to consider adding either organic amendments or mineral fertilizers to the samples prior to testing to gain a greater understanding of the benefits or disadvantages of multiple amendments on soil dynamics. Testing in Brazil on highly weathered Xanthic Ferralsols has shown the CEC of charcoal and mineral fertilized soils to be 1.94 cmolc$^+$ kg^{-1} which is greater than the CEC of the soil when only charcoal was added as an amendment (Steiner, 2007).

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