THE EFFECTS OF BIOCHAR AGE AND CONCENTRATION ON SOIL RETENTION OF
PHOSPHORUS AND INFILTRATION RATE

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By

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ABSTRACT

Changes in land use and land management practices are regarded as one of the main factors in altering the hydrogeological system, causing changes in runoff, surface supply yields, and the quality of receiving water (Tong and Chen, 2002). Phosphorus is a significant contributor to accelerated eutrophication of fresh water and is largely sourced from agricultural runoff (Sharpley et al., 1994). The dominant processes controlling solution composition in agricultural soils are primarily 'chemical' for P (i.e. adsorption/desorption and dissolution/precipitation) (Edwards and Withers, 1998). Biochar has chemical characteristics that have the potential to adsorb P or influence precipitation of P insoluble pools (DeLuca et al., 2009). However, there is limited knowledge about changes in this behavior in soil over time. To determine the effects of biochar on P adsorption and percolation rate, soil columns containing a sandy loam were amended with 0, 1, 2, and 5% (wt/wt) biochar and incubated at field capacity for zero and nine months. Columns were leached with four pore volumes of a 5ppm P solution (Burgoa, 2011). Phosphorus concentration in the leachate was determined using an ICP-AES. Aging of biochar for nine months resulted in an insignificant increase of phosphorus retention in the soil columns. The highest increase in P retention was observed in the columns amended with 1% (wt/wt) biochar at time zero. Potential absorption capacity of biochar and other chemical influences that affect P in the soil environment seem to improve with time. Further aging of biochar would likely result in a significant increase in P adsorption capacity in soil, due to abundant transformations of surface chemistry and encouraged bond formations. Percolation rate was found to significantly increase with increased biochar addition and increased aging time had little effect. Increased concentration of Biochar amendment of soil may help mitigate the negative effects of agricultural land use and water quality of the nearby hydrogeological system.

DISCLAIMER

This project is original work done through Cal Poly, San Luis Obispo, by the author,

Emilie Schneider, under guidance of the advisor, Dr. Burgoa.

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INTRODUCTION AND PURPOSE

The purpose of this senior project laboratory study was to analyze the effects of biochar concentration and incubation time on phosphorus retention in soil and infiltration rate through a prepared soil column and to compare these results to previous research. The beneficial qualities of biochar amended soil have been receiving much attention in scientific research. It is known to have positive effects on soil physical and chemical properties, particularly adsorption and water holding capacity. Properties such as these have great potential for pollution mitigation. Phosphorus is a common fertilizer ingredient used in high amounts in conventional agriculture, the excess of which can be released into the environment, where is has detrimental effects in aqueous systems. If the absorptivity of biochar extends forms of phosphorus found in soils, it may be possible to moderate this problem. The manipulated variables of interest were concentration and aging time of biochar in soil columns maintained at field capacity.

LITERATURE REVIEW

Water Quality: Phosphorus in the Environment

The natural global phosphorus cycle seems to be a one-way flow: mineralization, weathering, erosion, and runoff transfer soluble and particulate phosphorus to the ocean where is eventually sinks into sediments (Smil, 2000). In contrast to rapid global cycles of carbon and nitrogen, natural mobilization and recycling of phosphorus and the P cycle depends on tectonic uplift which exposes primary, inorganic P through denudation over a span of 10^7 to 10^8 years. Low solubility of phosphates and their rapid transformations in to insoluble forms often make this element the growth-limiting nutrient, especially in aquatic ecosystems (Smil, 2000). However, human activities intensify the release of P through increased soil erosion and runoff from fields, recycling crop residues and manures, discharge of industrial and urban wastes, and most significantly, use of inorganic fertilizers (Smil, 2000). Land use changes and anthropogenic emissions contribute to the delivery of river-borne nutrients which can cause enhanced phytoplankton bloom known as eutrophication and even more severe hypoxic events (Turner and Rabalais, 1994). This detrimental process affects fresh and ocean waters and their organisms all over the world.

Since passage of the Clean Water act in 1972, great progress has been made in regulating discharges of pollutants into the waters of the United States and regulating surface water quality. However, as control of pollution from point-sources lacks cost-efficiency, more attention is placed on controlling runoff from agriculture and other nonpoint sources of pollution (Sharpley et al., 1994). The USEPA has identified agricultural runoff as the cause of impairment of 55% of surveyed river length and 58% of surveyed lake area with water quality problems (USEPA

1990). Accelerated eutrophication of surface waters is a major unresolved problem resulting from nutrient inputs stimulating algal blooms. This issue must be addressed because by the time P-related eutrophication of freshwaters is visible, it is often too difficult and too expensive to implement remedial strategies (Sharpley et al., 1994)

Changes in land use and land management practices are regarded as one of the main factors in altering the hydrogeological system, causing changes in runoff, surface supply yields, and the quality of receiving water (Tong and Chen, 2002). Phosphorus is a significant contributor to accelerated eutrophication of fresh water and is largely sourced from agricultural runoff (Sharpley et al., 1994). The dominant processes controlling solution composition in agricultural soils are primarily 'chemical' for P (i.e. adsorption/desorption and dissolution/precipitation) (Edwards and Withers, 1998). Within the soil system, P is generally adsorbed onto Fe and Al oxides (Edelstein and Tonjes, 2012). Biochar has chemical characteristics that have the potential to adsorb P or influence precipitation of P insoluble pools (DeLuca et al., 2009). However, there is limited knowledge about changes in this behavior in soil over time.

What is Biochar?

There is ample evidence linking warming temperatures of Earth to anthropogenic emissions of greenhouses, with climatic consequences such as rise in sea levels, increased desertification, and increased numbers of hurricanes (IPCC, 2001). Renewable energy is an increasingly significant topic of scientific investigation as a carbon-neutral energy source to reduce dependence on fossil fuels (Lehmann, 2007). Carbon-neutral renewable energy sources such as wind and solar energy, hydropower, geothermal energy, and bio-energy help decrease dependency on fossil fuels but cannot reverse climate change. A form of bio-energy that does not

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contribute to CO_2 emissions but may actually draw it from the atmosphere, being carbon-neutral and carbon-negative, is pyrolysis of biomass coupled with land application of the by-product (Lehmann, 2007). The gaseous components and heat released in the exothermic process of "low-temperature" pyrolysis can be captured for energy use. Biochar is the carbon-rich, solid product of thermal decomposition of organic matter under limited supply of oxygen and at relatively low temperatures (<700 °C) (Lehmann and Joseph, 2009). This process often mirrors the production of charcoal, however it distinguishes itself from charcoal and similar materials by the fact that biochar is produced with the intent to be applied to soil as a means of improving productivity carbon storage, or filtration of percolating water (Lehmann and Joseph, 2009).

Biochar can also serve to reduce the negative consequences of removing crop residues from an agricultural field. Removal of crop residues leaves soil unprotected and increases risks of accelerated erosion, depletion of soil organic carbon (SOC), disrupts soil nutrient cycling nutrients, decline of activity and species diversity, and decreases water retention capacity, all of which jeopardize the sustainable use of soil resources (Elsevier, 2008). However, burning crop residues through pyrolysis can produce nutrient-rich by-products (biochars), which upon immediate return to the soil can positively impact soil quality.

Properties of Biochar

Incorporation of biochar into soil is shown to affect the preexisting soil properties in ways attributed to the physical and chemical properties of biochar.

Physical

Unlike the structure of graphite which consists of aromatic rings arranged in perfectly stacked and aligned sheets, biochar is made of irregular arrangements of C containing O and H and, in some cases, minerals depending upon feedstock (Lehmann and Joseph, 2009). Charred biomass consists of recalcitrant aromatic rings as well as more easily degradable aliphatic and oxidized carbon structures (Lehmann, 2007). Biochar exists as particulates and surface oxidation that initiate biotic or abiotic decay are restricted to outer areas of the particle, and maybe initiated rapidly, even after hundreds of years. This leads to overestimation of long-term decay quantified by short-term experiments (Lehmann, 2007).

Key physical features of most biochars are their highly porous structure and large surface area which can provide refugia for beneficial soil micro-organisms, such as mycorrhizae and bacteria, and influences the binding of important nutritive cations and anions (Atkinson et al., 2009). Biochar is often macroporous in nature which reflects cellular structures in the feedstock from which it is produced, which is potentially important for water holding and adsorption of soil (Sohi et al., 2010). When added to soil, biochar appears to divide rapidly into particles of silt size or less due to abrasion, shrink-swell, and other physical weathering processes (Brodowski et al., 2007). Process temperature is the main factor governing surface area, increasing in one study from $120 \text{ m}^2 \text{ g}^{-1}$ at 400 °C to 460 m^2 g-1at 900 °C (Day et al., 2005).Low temperature biochar is stronger than high temperature products with regards to adsorptive properties, but it is more brittle and prone to abrading into finer fractions once incorporated into soil (Sohi et al., 2010).

Chemical

Two properties of biochar make it a valuable addition to soil: (1) its high stability against decay and (2) its superior ability to retain nutrients compared to other soil organic matter

(Lehmann, 2007). It also has environmental benefits that oppose effects of global warming: (1) mitigation of climate change, (2) improvement of physical and chemical properties of soils, and (3) reduction of environmental pollution (Lehmann, 2007). Much research has produced unequivocal proof that biochar is not only more stable than any other amendment to soil and increases nutrient availability beyond a fertilizer effect, but its stability and nutrient retention properties make it more effective than any other organic material in soil (Lehmann and Joseph 2009). Chemical and physical properties such as high charge density and its particulate nature along with specific chemical structure, and high microbial and chemical stability, all contribute to greater nutrient retention and resistance to microbial decay than other organic matter (Atkinson et al., 2010). As a sonsequence of particle surface oxidation of biochar, the adsorption of organic matter and its charge density (CEC per unit surface area) increased (Atkinson et al., 2010). Incorporation of biochar influences soil structure, texture, porosity, particle size distribution, and density.

Biochar is considered to be biologically inert but it may also contain key mineral elements, the quantities of which can be directly related to the levels of these components in the feedstock prior to burning (Baldock and Smernik, 2002; Atkinson et al., 2010). Baldock and Smernik (2002) determined that thermal treatment at temperatures $\geq 200°C$ induce significant variations in chemical composition. Changes in chemical composition, as measured by 13C nuclear magnetic resonance (NMR) indicated that changes with increased pyrolysis temperature included a conversion of O-alkyl C to aryl and O-aryl furan-like structures, which are a more chemically active oxygen-containing carbon ring (Baldock and Smernik, 2002). Research suggests that biochar created at low temperatures may be suitable for controlling the release of

fertilizer nutrients while high temperatures would lead to a material similar to activated carbon (Sohi et al., 2010).

Biochar's Impact on Soil Performance

Water Holding Capacity

Biochar incorporation into a soil can have widespread impacts on the intrinsic properties of a soil. Water holding capacity is influenced by both the mineral and organic components of a soil. Higher levels of organic matter are associated with higher water holding capacity and Glaser et al. (2002) water retention to be 18% higher in terra preta than in adjacent soils, a difference believed to be attributed to the higher biochar content and higher levels of organic matter associated with charcoal in these soils. The high stability of biochar due to the extensive structure of aromatic carbons, offers potential to providing long-term modification to soil water holding capacity through its generally macroporous nature (Sohi et al., 2010).

The comparatively rapid division of biochar into silt-size or smaller particles, causes the direct impact on soil texture to be short-lived. It is found that the long-term effect of biochar on available moisture will be positive in sandy soils dominated by larger pores than present in biochar, neutral in medium-textured soils, and potentially detrimental in clay soils (Sohi et al., 2010). Gaskin et al. (2007) determined moisture release curves for a loamy sand field soil to which different amounts of biochar were added. The highest application rate was determined to have a significant effect on volumetric water content, double that of the control soil containing no biochar (Gaskin et al., 2007).

Infiltration of Soil Water

The heterogeneic composition of biochar causes it to exhibit hyrdrophillic, hydrophobic, acidic, and basic properties, all of which contribute to its interaction with the soil solution (Atkinson et al., 2010). In an investigation on the hydraulic properties of Amazonian dark earth, it was found to compare favorably with much "lighter" soils (Atkinson et al., 2010). This was contrary to field observations of the dark earths and led to consideration of the potential of evaluations of the benefits of biochar incorporation to improve mechanical impedance and compaction, to increase infiltration (Atkinson et al., 2010). In some situations, e.g. upland rice growing, biochar applications can improve soil water permeability (Asai et al. 2009). Biochar addition is seen to enhance soil water permeability but this would be more of a challenge in soils with higher clay content (Atkinson et al., 2010). Due to the physical characteristics of biochar, changes in pore size distribution can result within the soil which alters the percolation patterns, residence time, and flow paths of the soil solution (Atkinson et al., 2010). Some authors also suggest that soil water holding capacity is improved with biochar application.. Some authors also suggest that soil water holding capacity is improved with biochar application.. Biochar is particularly porpous and once its hydrophobicity has been overcome, it has potential to oxidize and absorb and retain water (Cheng et al., 2006).

Soil texture may be directly impacted at the macroscale by the addition of biochar because of its particle size distribution and macoporous nature. This would contribute to increased infiltration of the soil water through preferential flow though macropores. However, this effect is short-lived because physically biochar divides rapidly in soil to particles of silt size or less (Brodowski et al., 2007). A study based in Miyako Island, southern Japan, investigated the effect of biohar on nitrate-N concentration in percolating water, change in percolation

through lysimeters was observed for about one year (Chen et al., 2010). Changes in cumulative

percolating water volume showed that the amount of percolating water was reduced by 9% and

12% with bagasse (from a sugar factory) and biosolids (from agricultural sewage) charcoal use,

respectively (Chen et al., 2010). On a broader timescale, biochar is attributed to a decrease in the

percolation rate of soil water, but time and biochar type are factors that likely determine when

this affect is observed as well as its extent.

Nutrient Retention

Many studies have analyzed biochar's effect on nutrient availability and leaching and

have shown that it clearly has an influence on nutrient transformations. The extent of this

influence depends highly on the ion of interest and the properties of biochar obtained from the

feedstock and soil environment. The sources of organic matter used as biochar feedstocks are

shown to alter the availability of key macronutrients such as N and P, and some metal ions such

as Ca and Mg, when incorporated in to the soil (Atkinson et al., 2010). In addition, adsorptive

capacity is shown to increase with increasing pyrolysis temperature (Beaton et al., 1960). Both

increasing and decreasing nutrient uptake and biomass productivity have been reported following

biochar additions to soil and the effect of biochar additions on nutrient availability is not yet

entirely clear (Lehmann et al., 2003). Large proportions of black carbon in an Anthrosol of the

Amazon basin was found to have significantly higher availability of P, Ca, Mn, and Zn than a

nearby Ferrasol, minimal nutrient leaching, and increased plant uptake of P, K, Ca, Zn, and Cu

(Lehmann et al., 2003).

Biochar was shown to increase the cation exchange capacity (Lehmann et al., 2003).

Evidence suggests the cation exchange capacity (CEC) of biochar is consistently higher than that

of the whole soil, clay minerals, or soil organic matter (Sohi et al., 2010). Soil CEC increasesare

due to earboxylate groups on the surfaces of the biochar itselfand to exposed carboxylate groups of organic acids sorbed by the biochar, both of which contribute negative surface charge to biochar particles (Novak et al., 2009). Simultaneously,i ncreases in charge density per unit surface of organic matter develop, which equates with a greater degree of oxidation, or increases in surface area for cation adsorption, or a combination of both (Atkinson et al., 2010). This directly affects the flush of ammonium ions after fertilizer or manure application. The loose associations of ammonium are not necessarily taken up by plants immediately, but have important effects on mitigating losses of nitrate by leaching and subsequently help avoid eutrophication of aquatic and marine environments (Sohi et al., 2010). Biochar has been shown to hold nutrient element in plant available for and also has an affinity for organic compounds and possibly toxic by-products from wastewater treatment processes.

Phosphorus Movement in the Soil and its Relationship to Biochar

The immobilization, mineralization, and redistribution of P in soil depend on physical-chemical properties, such as P sorption by colloidal surfaces as well as mycorrhizal or plant uptake (Stewart and Tiessen, 1987). Phosphorus availability experiences more indirect effects of biochar addition because it cannot be improved simply by organic matter status. Although both the phosphate ions and the biochar surface bear a negative charge, appreciable adsorption can still occur through an interaction capable of overcoming the electrostatic repulsion (Beaton et al., 1960). Analogous adsorption of polyelectrolyte anions by negatively charged clay minerals has been explained in terms of specific hydrogen bonding (Beaton et al., 1960). Counter-ions such as K^+ are nonspecifically adsorbed because of its relatively large size, small charge, and poor geometric fit with the biochar lattice (Beaton et al., 1960).

The process of phosphorus adsorption is thought to be confined almost exclusively to the interaction of $H_2PO_4^-$ ions and the surface (Beaton et al., 1960). Even at equal ionic concentrations, adsorption of phosphorus in the form of $H_2PO_4^-$ should be much greater than that of HPO_4^{2-} or of PO_4^{3-} because of its greater capacity for hydrogen bonding and its smaller electrostatic repulsion effect (Beaton et al., 1960). Adsorptive properties of biochar are attributed to oxide complexes or phenolic acid groups with which it is expected that the protons of $H_2PO_4^-$ with the oxygen of these functional groups. Similarly, the proton of the phenolic groups likely form hydrogen bonds if substantial bond energy with the deprotonated oxygen of $H_2PO_4^-$ (Beaton et al., 1960).

Although other types of bonding may contribute, the postulate of a specific phosphate adsorption comes from experiments in which considerable uptake of phosphate by charcoal was observed even though both the surface and the ion bear negative charges (Beaton et al., 1960). Addition of black charcoal to the previously mentioned Ferralsol and Anthrosol was correlated with increased phosphorus nutrition and plant uptake. Higher crop growth observed in this Anthrosol compared to the Ferralsol was largely an effect of elevated phosphorus and other nutrient availability along with comparatively low nutrient leaching (Lehmann et al., 2003).

Biochar incorporation has been shown, in many studies, to induce soil alkalization (Atkinson et al., 2010). The availability and, subsequently, the adsorption of phosphorus is highly pH dependent. Increases in soil pH are likely to influence P availability, with available forms most common between pH of 4 to 8.5 (Atkinson et al., 2010). The availability of some elements toxic to plant growth, particularly at low pH, such as Al, Cu and Mn, can be reduced by biochar incorporation while the availability of other elements can increase, with biochar induced

increases in soil pH enhancing solubility of phosphorus as well as N, Ca, Mg and Mo (Atkinson et al., 2010).

The increasingly investigated characteristics of biochar uphold a reputation for it to help ameliorate problems of poorly fertile soils. Agricultural soils in the southeastern U.S. Coastal Plain Additions were investigated to determine if biochar could contribute to improving fertility of this sandy, acidic soil (Novak et al., 2009). A biochar incubation experiment similar to the focus of this report, was done by Noval et al. (2009) in Norfolk Ap soil. An increasing level of biochar was correlated with decrease in concentrations of multivalend cations in the leachate. Phosphorus concentration in leachate was also found to decrease with increasing biochar application (Novak et al., 2009). The decrease was attributed to a combination of reactions such as retention o-PO_4^{3-} through ligand exchange reactions involving oxygen-containing functional groups on the biochar surface, adsorption of o-PO_4^{3-} by Fe and Al oxides and hydroxides, and by adsorption and precipitation by Ca, Mg-phosphates (Bohn et al., 1979).

MATERIALS AND METHODS

Material: Soil and Biochar

The amending material is a high-carbon biochar derived from the pyrolysis of wood waste and provided by Alterna Energy, Inc. Metal content of the biochar was determined by the Alterna Energy Labs (Appendix A). The feedstock was a mix of spruce, pine, and fir which was pyrolized at 420 °C using the Van Aardt process (van Aardt et al., 2010). The soil used in this experiemtn was Wasco Series Sandy Loam soil, a Coarse-loamy, mixed, superactive, nonacid, thermic Typic Torriorthent (Appendix B).

Background

Biochar and Soil Classification: Cations

The soil and biochar were analyzed for Ca, Mg, Na, and K content with the Ammonium Acetate Extraction Analysis method using SpectrAA for Atomic Absorption Spectroscopy (AAS) (SSSA, 1996). The extraction procedure used 4.0 g of soil and biochar in 25.0 mL of 1M ammonium acetate solution added to a centrifuge tube. Tubes were shaken for 30 minutes with a mechanical shaker and centrifuged for 10 minutes at 3000 rpm using n Eppendorf Centrifuge 5810R, 15 amps. Tubes were decanted and filtered with No. 1 Watman filter paper into 100 mL volumetric flasks. This procedure was repeated once more and the volumetric flasks were brought to volume using 1 M ammonium acetate. Flasks were sealed and mixed well. The procedure was performed in duplicate, obtaining two extracts for each material. Soil and biochar extracts were analyzed in duplicate. A calibration curve was created before measuring each cation using the flame method of the AAS. Due to high concentration, Ca, K, and Na were diluted by a factor of 20 in order to fit the curve.

Biochar and Soil Classification: pH

The pH of the soil and biochar was determined by DI water and 0.01 M $CaCl_2$ methods with 1:2 soil:solution and biochar:solution ratios. Measurements were taken using a Fisher Scientific AB15 pH Meter (SSSA, 1996).

Batch Study: P Retention of Biochar and Wasco Series Sandy Loam

Phosphorus solutions of 0, 5, 10, 20, and 100 ppm P were prepared using 1000 ppm P Perkin Elmer Pure stock solution in a 0.001 M KCl matrix. Standards of 0, 5, 10, 20, and 100 ppm were made using 1000 ppm P Perkin Elmer Pure stock solution in a 0.001 M KCl matrix in 100 mL volumetric flasks. To obtain a background of the effects of the biochar and Wasco Series sandy loam individually on phosphorus retention, centrifuge tubes were prepared with 4g biochar or soil and 20 mL of 0, 5, 10, 20, and 100 ppm P solution and shaken on an automatic shaker for 30 minutes, 1 day, or 7 days. Each treatment was prepared in triplicate. After shaking for the specified time, the tube contents were filtered with plastic long-stem funnels and Whatman No. 1 filter paper into clean Fisherbrand centrifuge tubes. To remove fine particles from the biochar leachate and organic coloration in the soil filtrate, a second filtration was performed using Environmental Express 20 mL syringe filters with 0.45µm PVDF disk filters into scintillation vials. Samples were stored in refrigeration between steps. The extracted solutions were analyzed on the ICP-AEP spectroscopy and the standards were used for calibration of the analysis.

Column Study: Leachate Collection

Cores made from PVC pipe measuring seven inches in length and four inches in diameter were enclosed by netting on one side. Based on a soil bulk density of 1.2 g/cm^3 and the column volume, the columns were each filled with 942 g soil plus the weight of the assigned biochar concentration (Table 1).

Table 1. Weights of the columns containing dry soil and assigned biochar concentration.

Biochar Added (%wt/wt)	Dry Column Weight (g)
0%	942
1%	951
2%	961
5%	989

Experiment setup and actual weights are displayed in Table 2. Wasco Series Coarse sandy loam amended with concentrations of 0, 1, 2, and 5% (wt/wt) of biochar (Appendix A).

The columns were incubated at field capacity for 0 and 9 months in a 75°F room. Triplicate analysis was done for each combination of biochar concentration and incubation time. Starting weights of the amended, field-capacity-wet cores were recorded before the addition of phosphorus solution (Table 2). Each core was leached with four pore volumes of a known total volume of 5 ppm phosphorus-P in 0.001 M KCl solution. Volumes were determined by calculating the difference in weight between the soil at field capacity and dry soil and corresponded amount of solution collected after each application, within 5%. Polyethylene bottles were placed on top of a top-loading balance with a funnel in the mouth. The scale was used to monitor approximate volume of leachate collected with time. Two polyethylene bottles were filled per pore volume. Cumulative volume was recorded with time, which was used to calculate the corresponding infiltration rates of the different treatments. The percent recovery of each solution was recorded based on the ending column weights and total volume collected.

Table 2. Treatments of soil cores with corresponding soil weights (g), pore volumes of P solution (mL), and beginning core weights (g).

Core #	Soil Wt (g)	% Biochar Added	Months	mL P Soln Added per 4 Pore Vols.	Beginning Core Wt (g)
1	1191.2	0	0	260	1479.52
2	1192.9	0	0	260	1473.02
3	1192.7	0	0	260	1466.93
12	1193	0	9	260	1421.98
13	1195	0	9	260	1419.44
14	1193.5	0	9	260	1417.1
19	1203.3	1	0	270	1508.42
20	1201.9	1	0	270	1503.97
21	1203	1	0	270	1506.41
29	1202.1	1	9	270	1451.36
30	1205.1	1	9	270	1448.53
31	1203.4	1	9	270	1453.2
37	1212.3	2	0	290	1534.88
38	1214.5	2	0	290	1539.6
39	1211.3	2	0	290	1531.71
47	1212.2	2	9	290	1491.3
48	1211	2	9	290	1488.92
49	1213	2	9	290	1486.76
55	1238.7	5	0	350	1609.95
56	1243.6	5	0	350	1618.93
57	1239.8	5	0	350	1608.81
65	1239.5	5	9	350	1589.4
66	1238.8	5	9	350	1578.64
67	1242.6	5	9	350	1595.67

The columns had previously been used for research exploring the effects of biochar on nitrate retention and likely had residual nitrate remaining (Burgoa, 2011). For this previous project, the soil cores were subjected to a similar method of adding nitrate solution of known concentration to the core and allowing it to infiltrate through the soil. The leachate was collected in a polyethylene bottles in a similar manner. It was analyzed on a Thermo Orion Model 90-02 double junction nitrate-specific reference electrode to determine the concentration remaining in the leachate and adsorbed to the soil cores containing the different treatments of biochar concentration and aging time (SSSA, 1996).

Infiltration Rate Determination

As previously mentioned, the polyethylene collection bottles were placed on top loading balances below the cores. To each soil core, four pore volumes of P solution of known concentration were added and allowed to infiltrate through the column throughout the duration of leachate collection, and collected in the polyethylene bottles. Time zero was recorded as soon as the first pore volume of solution was added to the top of the column. The elapsed time was recorded when each bottle reached weights of approximately 40g, 80g, 120g, and 180g . At approximately 180g, the filled collection bottle was quickly replaced with an empty bottle, the starting weight and time were recorded for the new bottle, and a new pore volume of solution was added for every two bottles filled. Using the weights of the empty bottles initially and the cumulative weight of the bottle throughout the duration of leachate collection, the infiltration rate for each column over time was determined. The mean flow rate for each treatment was calculated and compared to other treatments.

ICP Method for Determining P Concentration

Phosphorus concentration of leachate was determined using the ICP-AEP and P retention was calculated using the actual concentration of the 5ppm P solution which was determine the same way (SSSA, 1996).

Spectrophotometric Analysis for Determining P Concentration: Trial and Error

Total plant available phosphorus was originally analyzed using extraction and analysis procedure by Dr. Chip Appel that used antimony potassium tartrate and molybdate colorizing reagents (Appel, 2012). Extracted solutions were to be read on an Ocean Optics USB4000-USB-ISS-UV/VIS Spectrophotometer. Triplicates of 5 g of biochar or soil and 25 mL of 0.01 M $CaCl_2$

shaken in Falcron tubes for 30 minutes then filtered through a Whatman No. 1 filter into a clean

45-mL flip-top container. Initially, deionized water and activated carbon was used for extraction

of P, however excessive coloring and dispersion of small particulates within the extracted

solution would have caused high interference with the spectrophotometer. It was decided to use a

low concentration of $CaCl_2$ as the extracting solution to reduce dispersion and coloration of the

extract. Standards of 0, 0.25, 0.5, 1.0, 2.5, and 5.0 ppm were made using 1000 ppm P Perkin

Elmer Pure stock solution in deionized water in 100 mL volumetric flasks. The

spectrophotometer was calibrated and used according to the user's manual. Standards were read

at 420 nm wavelength and a calibration curve was created. This method did not create a usable

curve (R^2 ~0.95-0.99) likely because of the low sensitivity and selectivity of the

spectrophotometric method of analysis and high risk of P contamination in the multi-reagent

colorization preparation of samples. It was decided to use the ICP, a highly sensitive and

selective method of chemical analysis.

Statistical Analysis

Statistical analysis was performed using Minitab Statistical Software, version 16, Minitab

Inc., 2012. Analysis of variance tests were done on the resulting data on the P concentrations

resulting from the background analysis, the P concentration of the leachate collected from the

columns of difference biochar concentrations and aging times, and on the infiltration rates.

Multiple-comparison ANOVA and multiple regression statistical tests allowed for comparisons

between the different treatments for each analysis to determine significant if differences were

produced from the individual or interaction of treatments at a 95% confidence interval.

RESULTS AND DISCUSSION

Background

Biochar and Soil Characterization: Cations

Analysis of cation content of the soil and biochar used for this project with the atomic absorption spectrometer revealed the presence of Ca, Mg, K, and N in both. A more complete analysis of the elemental composition of biochar was done by Alterna Biocarbon (Appendix A). In the soil, calcium was in the highest concentration of about 85 ppm, followed by average of 30 ppm Na, average of 24 ppm K, and average of 5 ppm Mg (Table 3). The biochar contained lower levels than soil in all nutrients except potassium which had an average concentration of 46 ppm. Calcium averaged 36 ppm, 29 ppm Na, and 2 ppm Mg in the biochar. The replicates of this analysis yielded percent error within an acceptable range except for the measured K and somewhat Na in soil. Soil is a highly heterogeneous material and the high error could be due to sampling, variation between soil samples, operator, or instrument error.

Table 3. Background analysis of extractable cations in bare soil and biochar.

Cation (AAS)	Ca (mg/L)	Mg (mg/L)	K (mg/L)	Na (mg/L)
S1†	84.86	4.62	34.13	30.84
S2‡	85.08	4.51	14.76	28.27
B1†	35.6	2.27	45.06	28.89
B2‡	36.14	2.29	46.41	29.65
%Error*, S	0.26	2.31	56.75	8.33
%Error*, B	1.49	1.16	2.90	2.58

†S1: Soil sample, replicate 1; B1: Biochar sample, replicate 1.
‡S2: Soil sample, replicate 2; B2: Biochar sample, replicate 2.
*%Error= [(Rep 2- Rep 1)/Rep 2] x100%

This analysis is important because it shows that biochar contains an inherent amount of cations within the predominantly carbon structure. The quantities of key mineral element within biochar can be directly related to the levels of these components in the feedstock prior to burning

(Atkinson et al., 2009). These cations are also naturally attracted to the cation exchange sites in the soil. The soil contains more extractable Ca and Mg than biochar with 85 ppm Ca and 5 ppm Mg, compared to 36 ppm Ca and 2 ppm K in biochar. Biochar contains 45 ppm Mg compared to 15-34 ppm K in the soil. Sodium is present in relatively the same amount, 30 ppm, in both materials. Analysis of the total metal content of biochar was done by Alterna Energy Inc. (Appendix B). Calcium was found in the highest concentration of all metals in biochar at 12,800 ppm. Considering the other three cations, K was the next highest of 5370 ppm, then Mg with 842 ppm, then Na as the lowest with 57 ppm. The relative pattern of total metal content differs from the analysis of extractable cations in that K was extracted in the highest amount, followed by Ca, Na, then Mg. The relatively high concentration of K may be related to its low tendency to be adsorbed to the biochar surface due to its low charge density and poor geometric fit with the biochar lattice, which results in comparatively easy extraction (Beaton et al., 1960).

As previously mentioned, the method of which P is adsorbed to biochar is through attractions of the protons of $H_2PO_4^-$ to the oxide complexes within the structure of biochar and between the protons of phenolic acid groups to the unprotonated oxygen of $H_2PO_4^-$ (Beaton et al., 1960). The positively charged cations from biochar and soil may contribute to interference with the adsorptive processes between biochar and the soil, or may be assimilated in to the increased CEC of the soil as a result of biochar addition (Atkinson et al., 2009).

Biochar and Soil Characterization: pH

The two methods used for measuring pH of soil and biochar produced slightly different results. The calcium-chloride method consistently produced lower pH readings than the readings done with deionized water (Table 4). Between methods soil pH averaged 7.2 in $CaCl_2$ and 8.0 in

DI water. Biochar averaged 7.4 in $CaCl_2$ and 8.02 in DI water. Biochar consistently yielded a

higher pH reading than the soil.

Table 4. Background analysis of pH bare soil and biochar using two different methods.

pH	$CaCl_2$	DI Water
S1	7.20	7.91
S2	7.27	8.07
B1	7.38	8.02
B2	7.41	8.03
% Error†, S	0.96	1.98
% Error†, B	0.40	0.12

†%Error= [(Rep 2- Rep 1)/Rep 2] x100%

The discrepancies between the two methods of pH measurement are due to the $CaCl_2$

encouraging flocculation of finer particles in solution, allowing for a more steady reading and

likely a more accurate reading of the medium. However, the DI water method may produce pH

readings closer to those exhibited in the soil system Ca and Cl ions are not present in high

enough concentrations in the soil solution. To test for a significant difference between the means

of both materials for each pH method, statistical analysis was done on the differences between

the means of both materials using a paired T-test (Table 5).

Table 5. Statistical analysis of the difference between mean pH values of soil and biochar for
each method of measurement.

Statistical Result	DI Water Method	$CaCl_2$ Method
95% CI for mean difference (pH)	(-0.9880, 0.9180)	(-0.4141, 0.0941)
P-Values for T-test of mean difference=0 (vs. not 0)	0.722	0.079

The high p-values that resulted from the paired T-tests indicate that with 95% confidence, there

is no evidence for a significant difference between the mean pH of soil and biochar for both

methods of pH measurement.

Batch Study: P Retention of Bare Biochar and Wasco Series Sandy Loam

Phosphorus retention is displayed as the P concentration measured in the filtrate solutions because in some treatments, especially with biochar, the resulting concentration was greater than that of the stock solution added. Results such as this are significant because it is indicative of an inherent P content of the biochar extracted over a period of one week. For the purpose of a successful statistical analysis, these values were used because they were all positive integers. Negative integers were produced in the calculations of P retained because in some cases, the P concentration in filtrate exceeded that of the stock solution added. The results were statistically analyzed with Minitab Statistical Software using two-factor ANOVA and multiple comparisons ANOVA. Table 6 shows the variables which contributed to the results of the batch study and which were used as factors for statistical analysis of the mean P retention. Tables 7 and 8 show the ANOVA results of the effect on the interaction between treatment factors of P concentration and time and the factors alone on mean P retention of soil and biochar.

Table 6. Variables used in statistical analyses of mean P retention.

Factor†	Type	Levels	Values
Treatment (P, ppm)	Fixed	5	0,5, 10, 20, 100
Time (Days_	Fixed	3	0, 1, 7

†These factors were the same for both soil and biochar batch study.

Table 7. Analysis of variance for mean P retention by soil as predicted by P solution added, days of shaking, and an interaction between the two variables

Source	DF	SeqSS	AdjSS	AdjMS	F	P
Treatment (P, ppm)	4	62601.1	62601.1	15650.3	21102.56	0.000
Time (Days)	2	194.9	194.9	97.4	131.39	0.000
Treatment*Time	8	393.0	393.0	49.1	66.24	0.000
Error	30	22.2	22.2	0.7		

Table 8. Analysis of variance for mean P retention by biochar as predicted by P solution added, days of shaking, and an interaction between the two variables.

Source	DF	SeqSS	AdjSS	AdjMS	F	P
Treatment (P, ppm)	4	50298.3	50298.3	12574.6	122791.20	0.000
Time (Days)	2	194.9	194.9	97.4	131.39	0.000
Treatment*Time	8	123.9	123.9	15.5	151.24	0.000
Error	30	3.1	3.1	3.1		

Different concentrations of P solution were used for the background study, so it is expected that this is a statistically significant influencing factor on P concentration. The interaction between P added and shaking time on the filtrate concentration. Statistical analysis on mean P concentration in filtrate solutions for both soil and biochar yielded p-values=0 for the interactions. There is very strong evidence that the interaction between P concentrations added and shaking time is significant.

Tables 9 and 10 display the treatment combinations and the corresponding mean P concentration in the filtrate and the numbers which do not share the same letter, are statistically different. Within the soil filtrate results, the 5, 10, 25, and 100 ppm P treatments produced results in which the 7 day shaking time was significantly different than 0 days (Table 9).

Table 9. Statistical analysis of the mean P concentration of the soil filtrate from the different background treatments.

Time (Days)	Ppm P Added	Mean ppm P in filtrate	Grouping							
0	104.1	93.6	A							
1	104.1	91.783		B						
7	104.1	82.815			C					
0	22.2	17.293				D				
1	22.2	15.717					E			
7	22.2	12.44						F		
0	11.4	8.08							G	
1	11.4	7.433							G	
7	11.4	5.593								H
0	5.7	4.37								I
1	5.7	3.720								I J
7	5.7	2.863								J
0	0.125	0.923								K
1	0.125	0.836								K
7	0.125	0.860								K

Table 9 shows that the soil particles have the potential to adsorb more P with increased exposure time. Differences in mean P concentration of filtrate reflects the significant influence of factors of this batch study and their interaction depicted in Table 8.

Biochar exhibited significant differences in mean filtrate concentration between the 0 day and 7 days shaking time for the 25 and 100 ppm solutions (Table 10). Differences between mean filtrate concentration reflect the significant interaction between time and concentration depicted in table 6. It is also important to note that the filtrate for the 0 ppm treatment for soil was greater than the solution added, which shows that soil has an inherent P concentration which is readily released. With biochar, the 0, 5, and 10 ppm treatments resulted in a greater concentration of P in the filtrate than was added. This also shows that biochar contains phosphorus within its chemical makeup, which is also released into solution. This is an important observation for the later analysis of the soil core leachate.

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Table 10. Statistical analysis of the mean P concentration of the biochar filtrate from the different background treatments.

Time (Days)	Ppm P Added	Mean ppm P in filtrate	Grouping						
0	104.1	111.84	A						
1	104.1	104.48		B					
7	104.1	92.79			C				
0	22.2	23.31				D			
1	22.2	22.05				D			
7	22.2	19.35					E		
0	11.4	12.47						F	
1	11.4	12.35						F	
7	11.4	10.57						F G	
1	5.7	8.07							G H
0	5.7	7.68							H
7	5.7	7.01							H
7	0.125	3.46							I
1	0.125	3.38							I
0	0.125	2.77							I

Compared to biochar, the soil resulted in more significant differences in mean P concentration between the different shaking times within each added solution concentration.

Interaction plots graphically display this interaction and except for the 0 ppm P solution, a decrease in filtrate concentration in observed with increased shaking time, showing that both biochar and soil contain adsorptive properties (Figures 1 and 2). Grouping information using the Tukey method showed differences in filtrate concentration between days, within each solution added (Table 9 and Table 10).
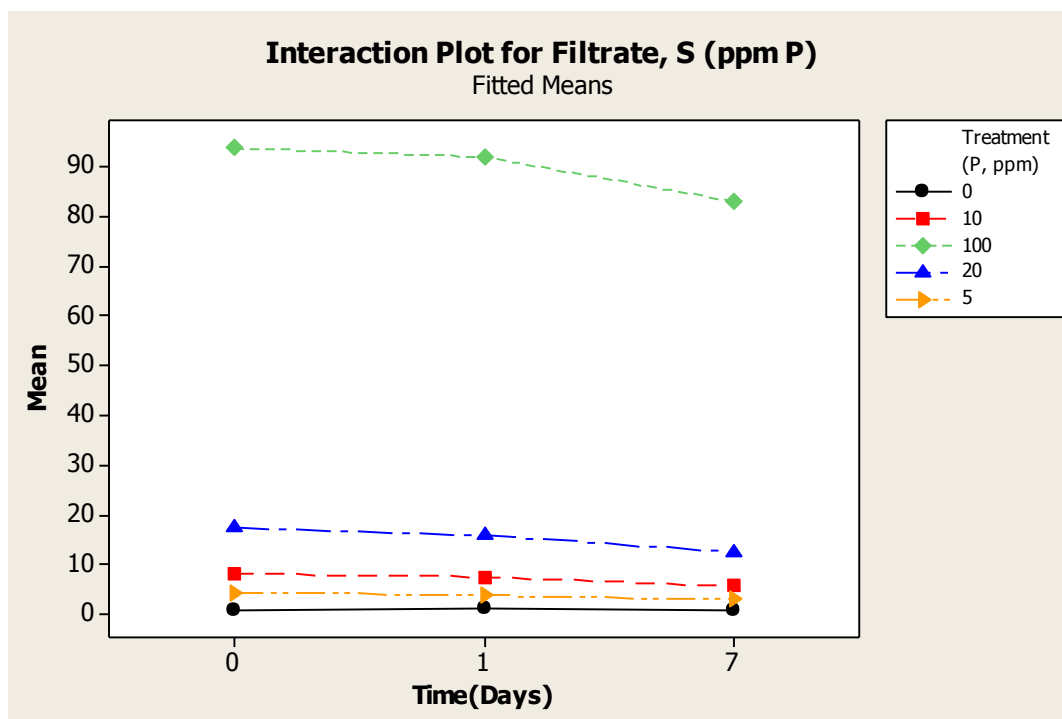
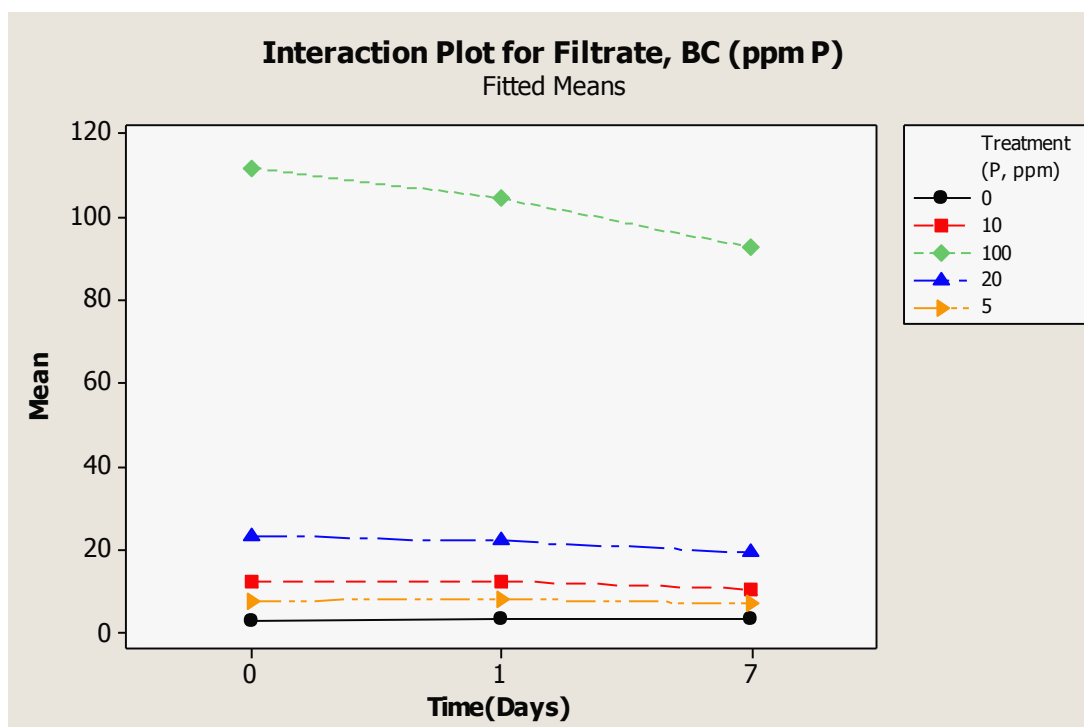Figure 1. Interaction plot between treatment and time for soil filtrate.

Figure 2. Interaction plot between treatment and time for biochar filtrate.

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The interaction plots show the differences of the effect of time on mean P concentration within each initial treatment concentration. A difference in slopes between the plotted lines signifies an interaction between treatment and time on the mean results. The 100 ppm P solution is the treatment that had the most significant interaction with shaking time and 20 ppm shows a slight interaction as well. In both interaction plots, an increase in treatment concentration relates to a more prominent interaction with shaking time on the mean P concentration in the filtrates (Figures 1 and 2). An increase in P concentration is expected to exhibit a greater interaction with time because an increase in P concentration with the same amount of soil and biochar material allows for relatively more interactions capable of overcoming the electrostatic repulsion between negative charges of the particle surface and the $H_2PO_4^-$ ions (Beaton et al., 1960).

A correlation between the concentration of P added and P retained is expected and is represented by strongly correlated quadratic relationships in soil and biochar (Figures 3 and 4). The graphs display average P sorption ($\mu g/g$) by the soil and biochar alone. In both biochar and soil, the relationships seem to differ between shaking times. The exponential component of each quadratic equation within the soil and biochar plots is negative which shows that increasing P addition has a decreasingly positive effect on sorption. A maximum sorption by the two materials for each shaking times is reached between 20 and 100 $\mu g/mL$. The increase in sorption before this point is likely due to the increased exposure time allowing for the interaction between the $H_2PO_4^-$ and the charged soil particles and oxide complexes and phenolic groups of the biochar structure but because a constant weight of both materials is used, it is possible that sorption was ultimately limited by number of sorption sites (Beaton et al., 1960).

Average P Sorption of Soil for Different Concentrations of P and Different Shaking Times

$y = -0.0145x^2 + 2.493x + 4.3788$
$R^2 = 0.9936$

$y = -0.0167x^2 + 2.3209x + 0.2413$
$R^2 = 0.9995$

$y = -0.0119x^2 + 1.7583x + 0.031$
$R^2 = 0.9989$

P Sorption (μg P/g soil)

P in Solution (μg/mL)

◆ 0 Day (μgP/g)

■ 1 Day (μgP/g)

▲ 7 Days (μgP/g)
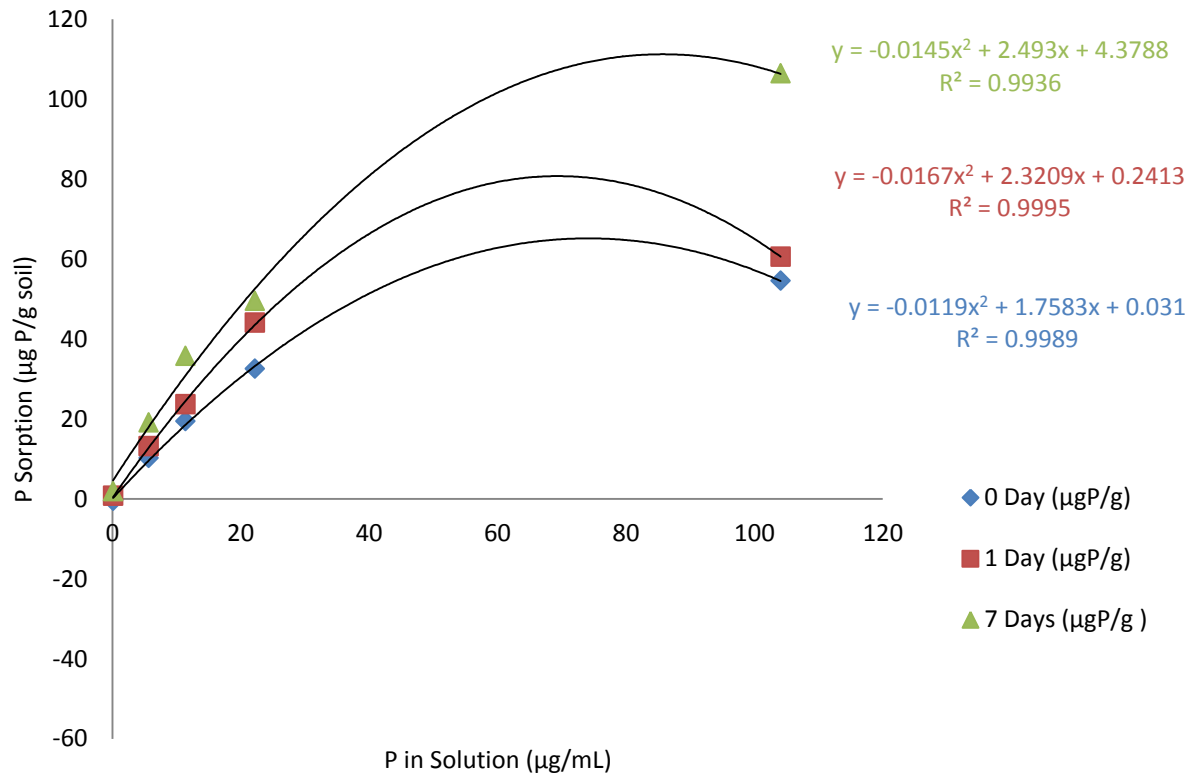
Figure 3. Background study on the average P sorption on of soil alone with different P concentrations added, shaken for different times.

Figure 4. Background study on the average P sorption of biochar alone with different P concentrations added, shaken for different times.

The background analysis allowed us to evaluate the sorption potential for both soil and biochar as individual media. Analysis of the P sorption was also useful in determining the amount of inherent phosphorus in both materials that might be released upon initiation of the experiment. The stock solution labeled "0 µg/mL P" was determined to actually contain 0.125 ppm P, likely from contamination of glassware. Although there was some P in the "0 µg/mL P" stock solution, the P concentration in the filtrate was subtracted from this initial value so the sorption values are accurate reflections of the behavior of both materials.

Tables 11 and 12 show the average values of P retention used to create Figures 3 and 4. Biochar shows a significant amount of desorption of phosphorus. Shaking times of 0 and 1 day showed only desorption overall and shaking time of 7 days exhibited sorption. Desorption is likely a reflection of some of the inherent P content of biochar being extracted by agitation in a solution. Release of P, Ca, and Mg from biochar into solution was exhibited during potentiometric titrations in a study by Sibler et al. and were attributed to rapid element-detachment reactions, followed by zero-order reactions which persisted as long as the system was far from equilibrium (2010). Alterna Energy, Inc. reported a total concentration of 190 ppm P, which was likely involved in such reaction.

Table 11. Average P retention of soil for different concentrations of P and different shaking times.

P added (µg/mL)	0 Day (µgP/g)	1 Day (µgP/g)	7 Days (µgP/g)
0.12	-0.51	0.78	1.89
5.70	10.20	13.15	19.13
11.43	19.44	23.64	35.73
22.23	32.59	44.04	49.55
104.10	54.53	60.58	106.40

Table 12. Average P retention of biochar for different concentrations of P and different shaking times.

P added (µg/mL)	0 Day (µgP/g)	1 Day (µgP/g)	7 Days (µgP/g)
0.12	-13.21	-14.31	-12.67
5.70	-7.27	-10.75	-3.75
11.43	-3.81	-2.64	9.81
22.23	-19.08	3.52	30.09
104.10	-37.25	-5.82	51.50

The interaction between treatment and shaking time shows an increase in absorptive potential of the biochar and soil particles with increased exposure time to phosphorus solution. The greatest differences between 0 days and 7 days of shaking were seen in the 100 ppm P

treatment for biochar and soil. Greater P adsorption exhibited with increase in shaking time is likely cause by the increase in interaction between $H_2PO_4^-$ and the particle surfaces of soil and biochar. Increased exposure by agitation for a longer duration enhances the capability of overcoming the electrostatic repulsion between the negative surfaces and the anion (Beaton et al., 1960). In addition, agitation in solution may be encouraging exposure of new sorption

Column Study Results: Leachate Collection

Infiltration Rate

Statistical analysis was done on mean flow rates of the different treatments using Two-Factor ANOVA and multiple comparisons ANOVA testing the individual factors, interaction, and differences between treatments (Table 14 and Table 15). With p-value=0, there is very strong evidence that mean infiltration rate is associated with treatment. Grouping information using the Tukey method showed which resulting mean differences of rate between the treatments were statistically significant. Numerical assignments to treatment combinations are depicted in Table 13. Given the confidence interval, we are 95% confident that the treatments found to result in mean infiltration rate that were not statistically different were treatments 5, 6, and 7. Treatments that resulted in mean rates statistically different from each other are also depicted in Table 15.

Table 13. Numerical assignments to the different treatment combinations.

Treatment	Time (months)	% Biochar
1	0	0
2	0	1
3	0	2
4	0	5
5	9	0
6	9	1
7	9	2
8	9	5

Table 14. Analysis of variance for mean infiltration rate (mL/sec) as predicted by months, % biochar added, and an interaction between the two variables.

Source	DF	SeqSS	AdjSS	AdjMS	F	P
Months	1	1904.97	1904.97	1904.97	1571.29	0.000
% Biochar	3	563.93	563.93	187.98	155.05	0.000
Months*Biochar	3	274.12	274.12	91.37	75.37	0.000
Error	88	106.69	106.69	1.21		
Total	95	2849.61				

Table 15. Statistical analysis of the mean infiltration rate (mL/sec) of the different treatments of %biochar (wt/wt) amendment and incubation time of soil columns.

Treatment #	Time (Months)	% Biochar	Mean (mL/sec)	Grouping†
4	0	5	15.419	A
3	0	2	11.203	B
2	0	1	7.010	C
1	0	0	4.718	D
8	9	5	2.138	E
7	9	2	0.307	F
6	9	1	0.183	F
5	9	0	0.086	F

†Means that do not share a letter are significantly different.

The two-factor ANOVA results indicate which factors are significant predictors of the infiltration rate of phosphorus solution through the soil columns throughout the duration of the experiment (Table 14). After accounting for %biochar, there is very strong evidence that time is a significant predictor of mean infiltration rate (p-value = 0) and after accounting for months, there is significant evidence that %biochar is a significant predictor of mean flow rate (p-value = 0). However, the results of the test of the interaction between the predictors is statistically significant (p-value = 0), and this result is of more importance. That is, changes in infiltration rate associated with %biochar added to soil appears to vary with aging time. A boxplot displays the median and spread of rates for each treatment (Figure 5).
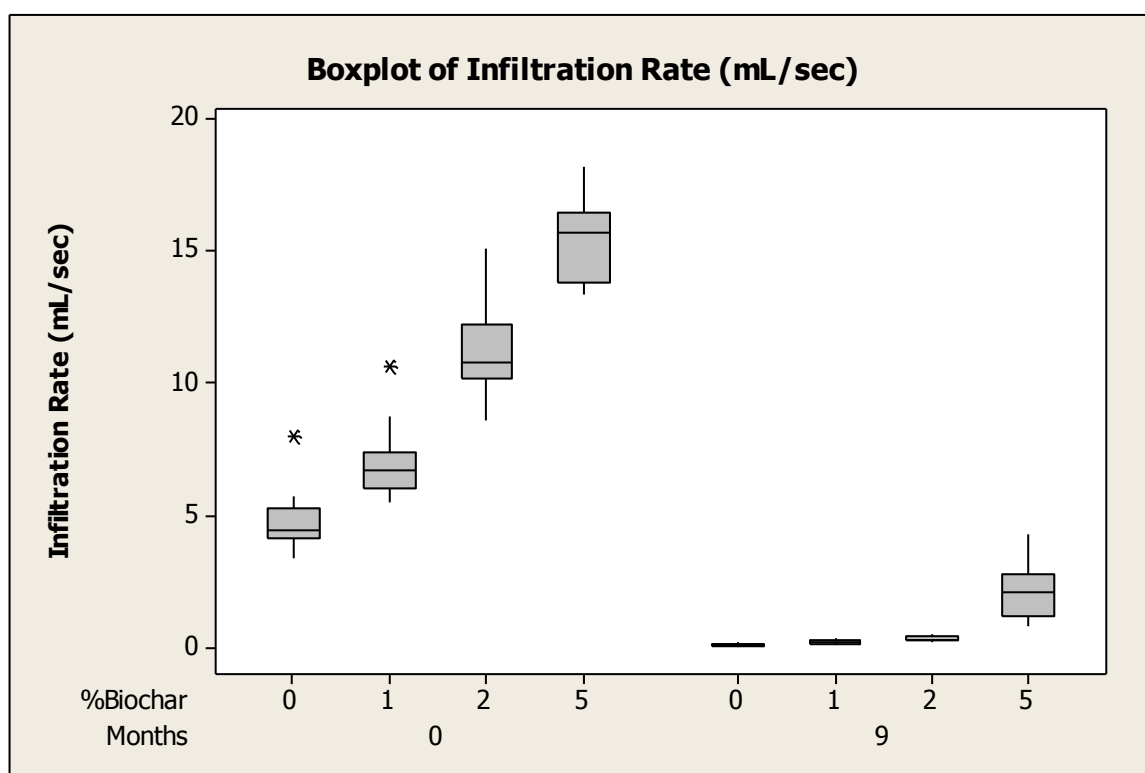
Figure5. Boxplot of infiltration rates for soil columns containing different concentrations of biochar and incubated for 0 or 9 months.

Multiple regression analysis was also done on calculated infiltration rates of the different treatments to produce an equation quantifying the relationship between the two predictors. A regression equation was produced using Minitab Statistical software modeling a relationship between quantitative predictors of months and % biochar and rate (mL/sec) (Table 16a).

Rate (mL/sec) = 7.03 - 0.990 Months + 1.28 %Biochar; R-Sq = 86.2%

Table 16a. Multiple regression analysis of mean flow rate. Rate (mL/sec) = 7.03 - 0.990 Months + 1.28 %Biochar.

Predictor	Coef	SE Coef	T	P
Constant	7.03	0.37	18.88	0.000
Months	-0.99	0.05	-21.22	0.000
% Biochar	1.28	0.11	11.42	0.000
S= 2.06, R-Sq= 86.2%, R-Sq (adj) = 85.9%				

Table 16b. Analysis of variance for the multiple regression analysis of mean infiltration rate.

Source	DF	SS	MS	F	P
Regression	2	2456.4	1228.2	290.44	0.000
Residual Error	93	393.3	4.2		
Total	95	2849.7			

Evaluating the overall F test of this analysis (F=290.44; p-value=0), we have very strong evidence that either months or %biochar are significant predictors of infiltration rate because of the large value of the F statistic (Table 16b). The regression for months resulted in a p-value (months) = 0 and t=-21.22. The small p-value and small t-test statistic give strong evidence that months is a significant predictor of infiltration rate and for columns of the same %biochar, an increase in time by 9 months is associated with a decrease in infiltration rate by 8.91 mL/sec (-0.990 x 9 months). The regression for biochar resulted in p-value = 0 and t-value = 18.88. There is very strong evidence that %biochar is a significant predictor of flow rate and for columns that experienced the same aging time, an increase in 1% biochar is associated with an increase in infiltration rate by 1.28 mL/sec. This relationship indicates that infiltration rate is increased by increased addition of biochar.

The observed results can likely be attributed to the effect on the texture at the macroscale, correlated with the particle size distribution of biochar. Upon addition biochar can initially contribute to an increase in infiltration rate because of the increase in macropores and encouragement of preferential flow (Sohi et al., 2010). Eventually, biochar physically breaks down in the soil into silt-size or smaller particles, although the time scale of this project was likely not enough time for such mechanical breakdown. The recalcitrance and macroporous nature of biochar eventually lends a significant contribution to the water holding capacity (WHC) of a soil (Sohi et al., 2010). This trend is obvious with an increased exposure time to soil, but the time span of this study may have been too short of a time period to observe the physical

breakdown, relative to the timescale of which biochar can have significant effects on soil

properties. With an increased incubation period a positive trend between biochar concentration

and WHC as well as time and WHC. It is suggested that that in the longer term the effect of

biochar on available moisture will be positive in sandy soils ordinarily dominated by much larger

pores than present in biochar, rather neutral in medium-textured soils, and potentially detrimental

to moisture retention in clay soils (Sohi et al., 2010).

Summary of the treatments for each core and the results of infiltration rate and P

retention analysis (results to follow) are displayed in Table 17.

Table 17. Summary of the treatments for each core and the results of infiltration rate and P retention analysis.

Core #	Soil Wt (g)	% Biochar Added	Months	Vol P Solution Added Per 4 Pore Volumes	Beginning Core Wt (g)	Ending Core Wt (g)	Solution Retained (mL)	% Solution Retained	µg P/g soil Retained
1	1191.2	0	0	260	1479.52	1497.64	18.12	1.74	0.99
2	1192.9	0	0	260	1473.02	1495.76	22.74	2.19	0.97
3	1192.7	0	0	260	1466.93	1471.07	4.14	0.40	0.79
12	1193	0	9	260	1421.98	1424.08	2.1	0.20	0.71
13	1195	0	9	260	1419.44	1419.27	-0.17	-0.02	0.87
14	1193.5	0	9	260	1417.1	1416.81	-0.29	-0.03	0.96
19	1203.3	1	0	270	1508.42	1527.49	19.07	1.77	1.16
20	1201.9	1	0	270	1503.97	1515.85	11.88	1.10	0.89
21	1203	1	0	270	1506.41	1555.67	49.26	4.56	0.99
29	1202.1	1	9	270	1451.36	1452.7	1.34	0.12	0.99
30	1205.1	1	9	270	1448.53	1453.65	5.12	0.47	1.07
31	1203.4	1	9	270	1453.2	1456.88	3.68	0.34	0.84
37	1212.3	2	0	290	1534.88	1537.08	2.2	0.19	0.76
38	1214.5	2	0	290	1539.6	1541.32	1.72	0.15	0.84
39	1211.3	2	0	290	1531.71	1535.26	3.55	0.31	0.82
47	1212.2	2	9	290	1491.3	1493.17	1.87	0.16	0.77
48	1211	2	9	290	1488.92	1491.6	2.68	0.23	0.7
49	1213	2	9	290	1486.76	1488.93	2.17	0.19	0.81
55	1238.7	5	0	350	1609.95	1611.92	1.97	0.14	0.77
56	1243.6	5	0	350	1618.93	1618.51	-0.42	-0.03	0.77
57	1239.8	5	0	350	1608.81	1610.59	1.78	0.13	0.67
65	1239.5	5	9	350	1589.4	1588.83	-0.57	-0.04	0.5
66	1238.8	5	9	350	1578.64	1580.03	1.39	0.10	0.75
67	1242.6	5	9	350	1595.67	1591.8	-3.87	-0.28	0.91

ICP Method for Determining P Concentration

Statistical analysis was done using a two-factor ANOVA to test for an interaction between %biochar and time and also an ANOVA with multiple comparisons to determine which treatments had a statistically significant different effect on phosphorus retention. Using 95% confidence, the resulting p-value=0 which meant the test revealed that there is strong evidence that treatment is associated with micrograms of phosphorus retained. Grouping information using the Tukey method showed that resulting mean differences of P retained between the treatments were not statistically significant. Given the confidence interval, we are 95% confident that the treatments found to result in mean P retained that were not statistically different from each other.

In addition to the statistical analysis of the effect of treatment combinations, each factor and the interaction of the two were evaluated using Minitab. The results of the two-factor ANOVA show that there is no significant interaction on phosphorus retention between the predictors of time and %biochar (p-value = 0.98) under the conditions of this study (Table 15). Within a 95% confidence interval, time is also not a significant individual predictor (p-value = 0.36) of mean phosphorus retention. However, %biochar is a significant predictor (p-value = 0) of mean phosphorus retention under the experimental conditions. Average P retention (µg P/g soil) of the different % biochar additions for the two incubation times are displayed in Figure 6. Boxplots display the median phosphorus sorption (µg P/g soil) for different % biochar within 0 months and 9 months incubation periods and the spread of the results (Figure 7). Interval plots display the mean P retention within the spread of the data (Figure 8).

Table 18. Analysis of Variance for mean micrograms P retained/ g soil, as predicted by months, % biochar added, and an interaction between the two variables.

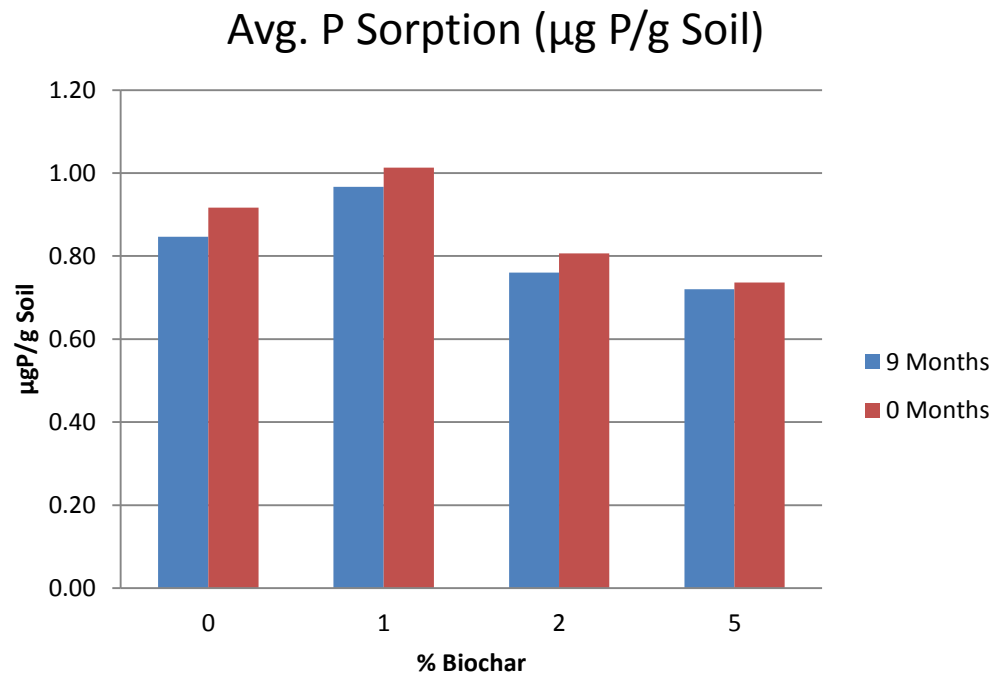| Source	DF	SeqSS	AdjSS	AdjMS	F	P
Months	1	0.01	0.01	0.01	0.87	0.364
% Biochar	3	0.24	0.24	0.08	5.72	0.007
Months*Biochar	3	0.002	0.002	0.0007	0.05	0.984
Error	16	0.22	0.22	0.01		
Total	23	0.48				

Figure 6. Average P sorption (µgP/g soil) compared between different treatments of biochar concentrations and incubation times.
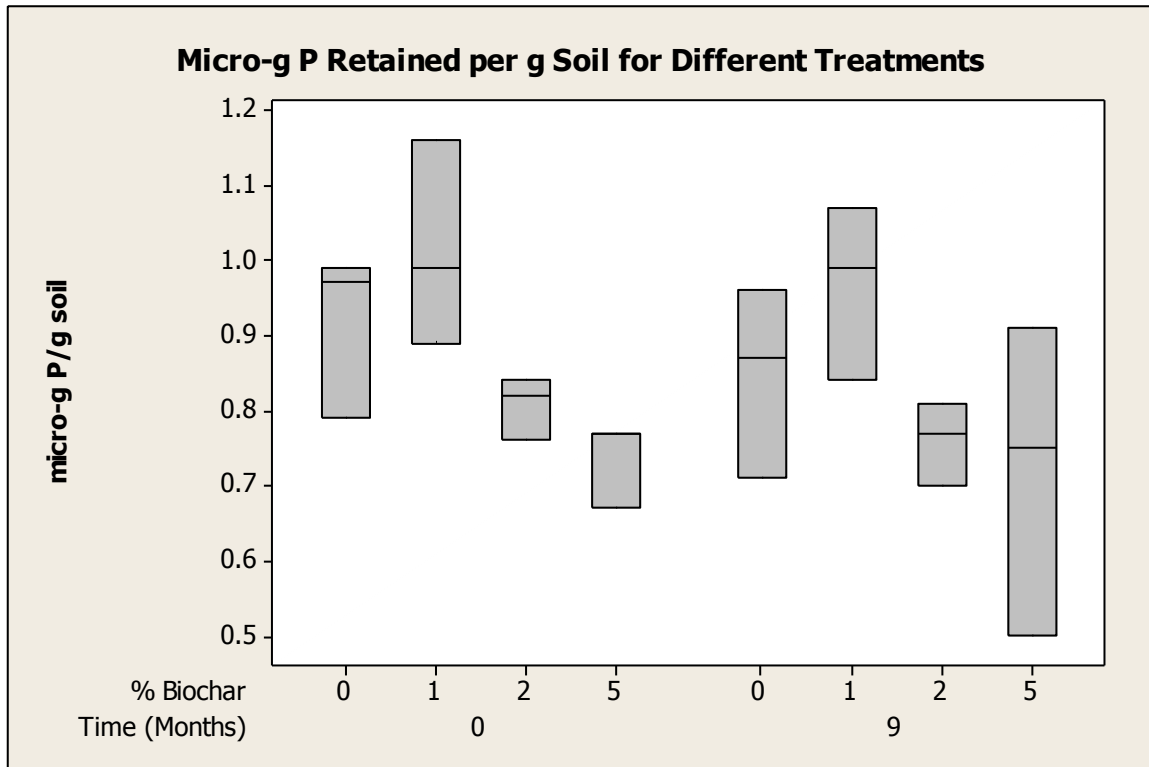
Figure 7. Boxplot displaying median value and spread of the resulting values of P retention (µg) for each treatment.
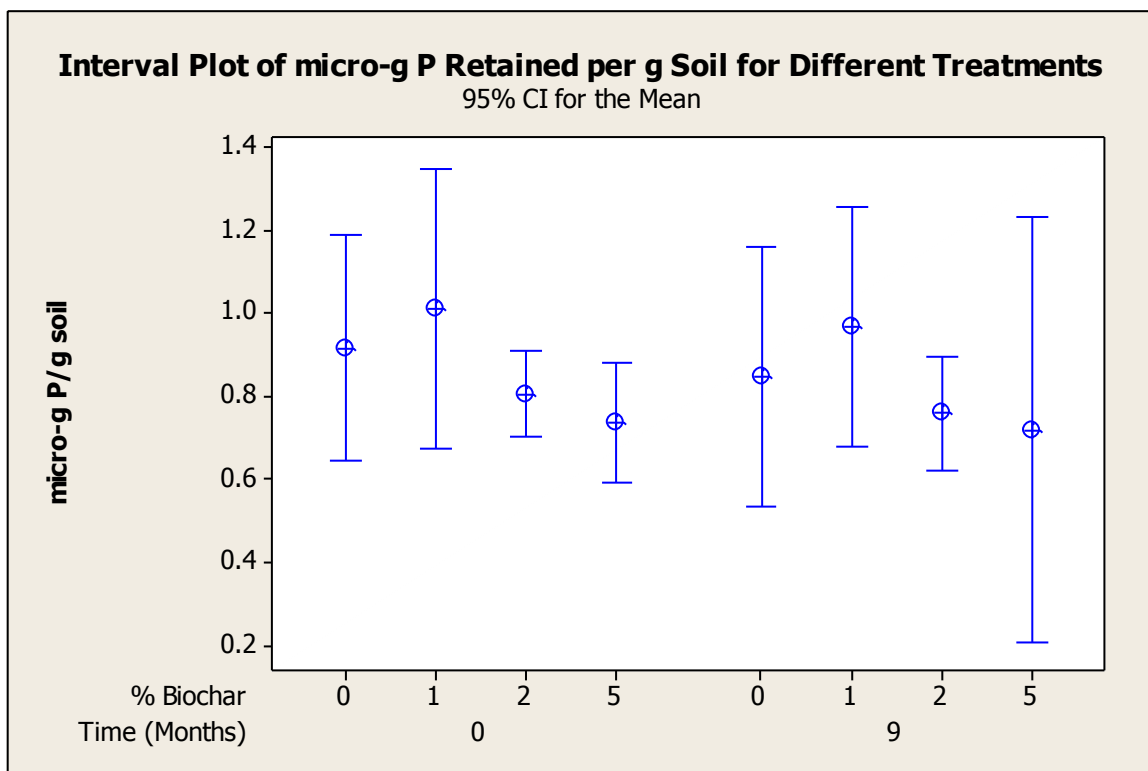

Figure 8. Interval plot displaying mean value and spread of the resulting values of P retention (µg) for each treatment.

The greatest mean retention of P was exhibited by treatment 2 (0 months, 1%) and the lowest by treatment 8 (9 months, 5%). Increased phosphorus retention was seen in the order of treatment 2(0 months, 1%), 6(9 months, 1%), 1(0 months, 0%), 5 (9 months, 0%), 3 (0 months, 2%), 7 (9 months, 2%), 4 (0 months, 5%), and 8 (9 months, 5%). This showed a negative relationship between biochar concentration and P retention nut the statistical grouping output by Minitab shows no significant difference between zero and nine months of aging time or between the biochar concentrations. Both factors of time alone and the interaction between time and % biochar were not statistically significant predictors in mean µg P adsorption/g soil with p=0.364 and p=0.964, respectively. Biochar concentration was found to be the only statistically significant predictor of adsorbed µg P /g soil with p=0.007.

Although the adsorption of P is not statistically different throughout the different treatments, the adsorption observed is likely attributed to the chemical and physical properties of biochar. The adsorptive properties of biochar are attributed to the surface-oxide complexes or phenolic end groups on aromatic framework. Hydrogen bonding takes place between the protons of $H_2PO_4^-$ and oxygens of the oxide complexes and the protons of the phenolic groups form a high bond with the oxides in a bond of high binding energy (Beaton et al., 1960). Phosphorus adsorption characteristics on activated charcoal were investigated in an experiment conducted by Beaton et al. (1960). Graphite and graphite-like materials have a lamellar structure which makes multilayer adsorption a possibility in capillaries, along with previously mentioned adsorption happening simultaneously. Phosphorus adsorption is found to be endothermic since it increases with temperature. This would cause the effects of biochar addition to soil to vary throughout climates and temperature regimes. Much of the energy expended in these adsorptions may be used in the removal or partial removal of the hydration shell from the $H_2PO_4^-$ on and/or to

remove water molecules from the surface of the carbon oxide layer (Beaton et al., 1960). Further investigation on phosphorus adsorption with biochar amendment should investigate these differences.

The only factor which had a statistically significant effect on P retention was the biochar concentration ($p=0.007$). This is likely because of the immediate increase in availability of adsorption sites with an increase in amount of biochar added. Biochar's known recalcitrance in soil may be preventing significant chemical changes to the structure of biochar or chemical interactions between biochar and phosphorus to overcome electrostatic repulsions, accounting for the insignificant difference in P retention over the span of nine months of aging time (Beaton et al., 1960).

CONCLUSION

This study revealed some of biochar's ability to affect different soil characteristics. From the analysis of variance results, we can conclude with confidence that % wt/wt biochar and the aging time of biochar interact to have a significant effect on water retention, thus affecting percolation through soil. Increased aging time exhibits a negative relationship with infiltration rate which shows biochar's increased affect in water holding capacity the longer it is in the soil. However, an increased concentration of biochar in soil exhibits a positive relationship with infiltration rate within both time periods, with an increasing amount of biochar added corresponding to an increase in infiltration rate, and thus lower water holding capacity.

In addition, phosphorus retention does seem to be affected by biochar concentration. We were able to conclude with 95% confidence that biochar concentration affects phosphorus retention (μg P/g soil). However, within the time scale of the study, we were not able to conclude a statistically significant relationship between aging time and phosphorus retention.

With an increase in concentration in soil, biochar corresponds with an increase in infiltration rate and with an increase in aging time, the infiltration rate significantly decreases but the trend with concentration is preserved. However, the time span of this study revealed no significant difference of retention between 0 and 9 months of aging.

Biochar material has been shown to weather and further develop its CEC and improve nutrient retention over time. Different soil types and climates undoubtedly have different influences on the extent of biochar's effect on soil properties and the rate at which these develop into a significant factor affecting the soil environment. To increase the knowledge and

predictability of the benefits and uses of biochar, further research on this topic is needed within varying factors and larger time scales.

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APPENDIX A

METAL CONTENT OF ALTERNA ENERGY, INC. BIOCHAR

Metal	Concentration (ppm)
Aluminum	793
Antimony	<0.5
Arsenic	<0.2
Barium	41.5
Cadmium	0.8
Calcium	12,800
Chromium	2.09
Cobalt	1.1
Copper	207
Iron	3610
Lead	2.6
Lithium	2
Magnesium	842
Manganese	63.4
Mercury	0.003
Molybdenum	0.3
Nickel	2.7
Phosphorus	190
Potassium	5370
Selenium	<0.2
Silicon	2980
Sodium	57.3
Strontium	64
Tellurium	<0.4
Thallium	0.6
Titaniu,	9.16
Vanadiam	<0.2
Zinc	103

APPENDIX B

WASCO SERIES OFFICIAL SOIL DESCRIPTION

The Wasco series consists of very deep, well drained soils on recent alluvial fans and flood plains. These soils formed in mixed alluvium derived mainly from igneous and/or sedimentary rock sources. Slope is 0 to 5 percent slopes. The mean annual precipitation is about 6 inches and the mean annual temperature is about 64 degrees F.

TAXONOMIC CLASS: Coarse-loamy, mixed, superactive, nonacid, thermic Typic Torriorthents

TYPICAL PEDON: Wasco sandy loam, cultivated. (Colors are for dry soil unless otherwise stated.)

Ap1--0 to 9 inches; brown (10YR 5/3) sandy loam, dark gray (10YR 4/1) moist; massive; slightly hard, very friable, nonsticky and nonplastic; few very fine roots; many very fine interstitial pores; slightly acid (pH 6.4); abrupt smooth boundary.

Ap2--9 to 15 inches; yellowish brown (10YR 5/4) sandy loam, dark grayish brown (10YR 4/2) moist; massive; slightly hard, very friable, nonsticky and nonplastic; few very fine roots; few very fine tubular and many very fine interstitial pores; neutral (pH 6.6); abrupt smooth boundary. (Combined thickness of the A horizon ranges from 9 to 40 inches)

C1--15 to 32 inches; brown (10YR 5/3) sandy loam, dark gray (10YR 4/1) moist; massive; slightly hard, very friable, nonsticky and nonplastic; few very fine roots; common very fine tubular and many very fine interstitial pores; neutral (pH 7.2); abrupt smooth boundary. (14 to 21 inches thick)

C2--32 to 65 inches; pale brown (10YR 6/3) sandy loam, brown (10YR 4/3) moist; massive; slightly hard, very friable, nonsticky and nonplastic; few very fine roots; common very fine tubular and many very fine interstitial pores; slightly effervescent, carbonates disseminated; moderately alkaline (pH 8.2).

TYPE LOCATION: Kern County, California; about 3.5 miles southeast of the community of Wasco; approximately 300 feet east and 2,550 feet south of the northwest corner of section 32, T. 27 S., R. 25 E., MDB&M; Latitude 35 degrees, 32 minutes, 11 seconds north and Longitude 119 degrees, 18 minutes, 41 seconds west; USGS Wasco Topographic Quadrangle, NAD 27.

RANGE IN CHARACTERISTICS: The soil between the depths of 8 and 24 inches is dry in all parts from mid-April until mid-January and is continuously moist in some parts for 60 to 90 consecutive days in the winter. Mean annual soil temperature is 62 degrees to 67 degrees F. The soil temperature is never below 47 degrees F. in the San

Joaquin Valley. Some pedons have disseminated carbonates at depths below 16 to 40 inches. Rock fragment content is 0 to 15 percent. Rock fragments are less than 0.5 inch in diameter. Organic matter is less than 1 percent in the upper part of the profile and decreases regularly with increasing depth. Organic matter content is less than 0.2 percent below 49 inches depth.

The A horizon has color of 10YR 5/2, 5/3, 5/4, 6/2, 6/3, 6/4; 2.5Y 5/2 or 6/2. Moist color is 10YR 3/3, 4/2, 4/3, 5/2; 2.5Y 4/2 or 5/2. Texture is sandy loam or fine sandy loam. Reaction is slightly acid to moderately alkaline.

The C horizon has color of 10YR 5/3, 5/4, 6/3, 6/4, 7/2; 2.5Y 5/2, 5/4, 6/2, 7/2 or 7/4. Moist color is 10YR 3/3, 4/2, 4/3, 5/3; 2.5Y 4/2, 4/4, 5/2, 5/4 or 6/2. Texture is coarse sandy loam, sandy loam or fine sandy loam. Some pedons have thick stratification below a depth of 40 inches with texture of loamy sand to silt loam. Distinct thin stratification is not present. Reaction is neutral to moderately alkaline.

COMPETING SERIES: These are the Cantua and Uxo series. Cantua soils (MLRA 15), on uplands, are 40 to 60 inches deep to a paralithic contact of soft, calcareous sandstone. Uxo soils (MLRA 30), on alluvial fans and fan aprons, are moist for 10 to 20 days cumulative between July and October following convection storms, have gravel content in the A horizon of 40 to 75 percent and have Btk horizons.

GEOGRAPHIC SETTING: Wasco soils are on recent alluvial fans and flood plains. Slope is 0 to 5 percent. These soils formed in mixed alluvium derived dominantly from igneous and/or sedimentary rock sources. Elevation is 225 to 1,000 feet in the southern part of San Joaquin Valley and cool phases occur at elevations as high as 3,700 feet in the Mojave Desert. The climate is arid to semiarid with hot, dry summers and cool, somewhat moist winters. Mean annual precipitation is 4 to 7 inches. Mean January temperature is 44 degrees to 47 degrees F.; mean July temperature is 80 degrees to 85 degrees F.; mean annual temperature is 59 degrees to 62 degrees F. in the Mojave Desert and 62 degrees to 65 degrees F. in the San Joaquin Valley. Frost-free season is 250 to 300 days in the San Joaquin Valley and 210 to 250 days in the Mojave Desert.

GEOGRAPHICALLY ASSOCIATED SOILS: These are the Milham and Panoche series. Milham soils, on fan remnants, alluvial fans, plains and low terraces, have an argillic horizon that has a fine-loamy particle-size control section. Panoche soils, on alluvial fans and plains, have a fine-loamy particle-size control section.

DRAINAGE AND PERMEABILITY: Well drained; negligible or very low runoff; moderately rapid permeability.

USE AND VEGETATION: Used for growing field, forage and row crops. Some areas are used for livestock grazing, wildlife habitat, recreation and homesites. Native vegetation is Atriplex spp., annual grasses and forbs.

DISTRIBUTION AND EXTENT: Mainly in the southern part of the San Joaquin Valley and to a lessor extent in the Mojave Desert. The series is of large extent. MLRA 17, 30.

MLRA SOIL SURVEY REGIONAL OFFICE (MO) RESPONSIBLE: Davis, California

SERIES ESTABLISHED: San Bernardino County, California, Mojave River Area, 1978.

REMARKS: The Wasco soils were formerly mapped as Hesperia series. Hesperia soils are now recognized as having a torric bordering on a xeric moisture regime. The cool phases at the higher elevations and shorter FFS should be a new series with near mesic soil temperature.

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