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UNIVERSITY OF CALIFORNIA MERCED

BIOCHAR AS A SOIL AMENDMENT: IMPACT ON HYDRAULIC AND PHYSICAL
PROPERTIES OF AN ARABLE LOAMY SAND SOIL

A Thesis submitted in partial satisfaction of the requirements for the degree Master
of Science

in

Environmental Systems

by

Vivian Dominique Lopez

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Gerardo Diaz

2014

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The thesis of Vivian Dominique Lopez is approved, and is acceptable in quality and form for publication on microfilm and electronically:

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University of California, Merced

2014

DEDICATION

To my hard-working and supportive parents who did not have the opportunity to complete their own higher education, but provided me with the resources, love, and support to do it on behalf of them. This one is for you.

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Abstract

Biochar as a soil amendment: Impact on hydraulic and physical properties of an arable loamy sand soil

by

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University of California, Merced, 2014

Biochar is a form of pyrolyzed biomass utilized strictly for human created systems. It has been recognized as a plausible method to address issues related to atmospheric carbon increase and global change, in addition to food insecurity. This research explores the effectiveness of biochar as a soil amendment. This knowledge is necessary because the effects of drought have strengthened, flagging the necessity to develop sustainable methods that will address (1) water shortage and (2) the increasing use of groundwater, which has generated poorly infiltrating, saline-sodic soils. Previous biochar studies have emphasized its increased cation exchange capacity, surface area, and porosity, qualities of which can improve the soil water retention and infiltration rate of soils experiencing drought. Here we investigate the hydraulic and physical impacts of amending an arable loamy sand soil with almond residue biochar of different temperatures, size, and rates. Our biochar was observed to increase in carbon (C) content and stability with temperature of pyrolysis; size was inversely related to C concentration. Additionally, biochar cation exchange capacity and surface area increased with increasing temperature and decreasing size. While these attributes may suggest enhanced aggregate stability and water retention, our findings showed that aggregate stability decreased with biochar addition alone, but increased with wetting/drying cycles; water retention was reduced with increased rates of biochar application, regardless of temperature. Infiltration was observed to increase upon initial application, but reduced with time, regardless of biochar size, temperature, or rate. These findings suggest that almond residue biochar may only be beneficial for retention purposes at low temperature and low application rates, while infiltration increases will likely only be observed for the first few days of application. The results of this study contribute to the growing body of biochar literature, and will be useful in tailoring management practices in improving the infiltration of arable sandy soils if using biochar is of interest.

CHAPTER 1. Introduction

1.1 Overview

California's Central Valley produces almost half of United States'- produced vegetables, fruits and nuts (Tolomeo & Krug 2011). Because of the region's distinct Mediterranean climate, it maintains cool, wet winters and dry summers. However, because the region only receives 5-16 inches of rainfall annually, success of this agricultural hub has been heavily maintained through irrigation (Galloway & Riley 1999). This process largely relies on surface water stored from winter precipitation in the Sierra Nevada and/or groundwater, both sources of which are threatened by a changing climate and source overuse. Recently, a study reported that the severe drought impacting the Central Valley has been linked to anthropogenic influences (Wang et al. 2014). Future model projections of climate in the Central Valley and similar regions anticipate 0.9-5.9°C increases in yearly maximum and minimum average temperatures by the end of the century (Lee et al. 2011; IPCC 2007). Temperature increases will result in a reduced winter, thus bringing an early spring, a shortened crop season, and more rapid evaporation of soil water (Calzadilla et al. 2013; IPCC 2007). While precipitation is speculated to undergo only slight changes (<10%) (IPCC 2007), the increase in temperature is likely to result in an increase in evaporative water loss. Together, temperature and precipitation determine the overall length of the growing season and progression of crop development. These changes will have negative results on agricultural output and serve as cause for concern in a population expected to reach 9.3 billion in 2050 (US Census Bureau).

However, these speculations are no longer just speculations. The current drought has resulted in a shortage of surface water in the Central Valley, resulting in a reduction of at least 6.5 million acre-feet of surface water delivery and agricultural losses valued over \$738 million at minimum in 2014 (Howitt et al. 2014). This extreme condition has been highly linked to human-induced global warming (Swain et al. 2014). In attempts to maintain crop output, Central Valley agricultural practices have shifted from a heavy reliance on surface water use towards groundwater pumping, replacing surface water with 5 million acre-feet of groundwater (Howitt et al. 2014). While groundwater use is not bad in itself, pumping becomes an issue when agricultural consumptive use exceeds the rate at

which the water can be renewed. Not only does it deplete water resources, but it comes with detrimental side effects that include land subsidence and increase in the salinization of irrigated cropland. The latter side effect has become a pressing topic in the Central Valley and is affecting crop growth through the salinization of soils.

Irrigation practices sourcing saline groundwater become detrimental to agricultural soils because they create saline, sodic, or saline-sodic conditions, which describe a high content of salts (Na^+ , Mg^{2+} , Ca^{2+} , etc.), high sodium (Na^+) concentrations or a combination of both, respectively. The presence of any of these conditions directly affects soil physical properties and soil structure (Suarez et al. 2006). The primary properties affected are soil infiltration and hydraulic conductivity, which describe how and at what rate water flows through soils, respectively. In soils containing clay, large sodium (Na^+) ions induce the swelling and dispersion of clay, pushing soil particles away from each other to eventually disrupt soil structure and reduce water drainage. This is because clay has a high cation exchange capacity and has a greater capacity to attract and hold ions, such as Na^+ . Soils prominent in the Central Valley are generally sandy with a low cation exchange capacity, but still contain some clay particles and are still subject to this phenomenon.

To combat a reduction in water drainage, often farmers will add large amounts of soil conditioners, such as gypsum (calcium sulfate). Gypsum functions by replacing soil exchange sites occupied with Na^{2+} with calcium (Ca^{2+}), thus allowing Na^+ to leach from the soil in solution. Local farmers are adding upwards of 1000 pounds/acre foot of gypsum to address reduced drainage; however, this is a short term solution and must be constantly applied to achieve desirable effects (David Doll, personal communication, August 2014). This can result in an excess of Ca^{2+} and possibly reduce the availability of other nutrients such as Mg^{2+} to be available to crops, as Ca^{2+} will dominate the exchange sites and leave other nutrients to leach out in solution (Pavan et al. 1984).

A sustainable solution to enhancing water flow through soils may lie in adding biochar to soils. Biochar is made of carbon-rich matter, typically waste products, burned under low to no oxygen conditions. This product is sustainable, in that it can use excess agricultural (i.e. almond shells), animal (i.e. cow manure), or anthropogenic (i.e. paper waste) residues as feedstock and has been reported to last for hundreds to thousands of years (Lehmann et al. 2009). Moreover, the gaseous by-products can be utilized for energy purposes (Laird 2008). Previous studies have used biochar as a soil amendment to improve soil physical properties (Abel et al. 2013; K. Y. Chan et al. 2007; Novak et al. 2012; Mukherjee & Lal 2013). This has been attributed to biochar's properties, which include having a high porosity to create more pathways for water to pass through and be stored in (Kinney et al. 2012; Barnes et al. 2014); a high cation exchange capacity relative to soils, which can make nutrients more available to plants and promote soil stabilization mechanisms that enhance a soil's ability to store water (Ulyett et al. 2014; Steiner et al. 2009); and having a high carbon concentration that can serve as an energy source for microbes to promote soil stabilization mechanisms through their exudates (Six et al. 2002; Glaser et al. 2002). However, altering soil physical properties for the purpose

of retaining water is not always the pertinent issue at hand. Currently, Central Valley farmers are experiencing saline-sodic soils that have a constrained ability to take up water (David Doll, personal communication, August 2014). While the addition of soil conditioners may serve as a short term solution, their addition in excess may be detrimental to soil health in the long run. Biochar's porous nature, hydrophobicity, and high cation exchange capacity may benefit soil physical properties by increasing hydraulic flow, providing a sustainable solution to Central Valley farmers.

Additionally, the use of almond residue (shells and hulls) biochar, which is used as feedstock in this work, as a soil amendment is sparse in the literature (Alburquerque et al. 2014; Uchimiya et al. 2012), with only one focused on effects on soil properties (Alburquerque et al. 2014). In the 2012/2013 crop year, California produced over 850,000 tonnes of almond kernels, in addition to approximately 0.55 million and 1.4 million tonnes of almond shells and hulls, respectively (Kodad et al. 2008; Offeman et al. 2014; Elleuch et al. 2013; Anon 2013). Currently, both almond by-products are solely used for cow bedding and feed (<http://www.almonds.com/consumers/about-almonds/sustainability>). Therefore, the potential for almond residues to be used as large-scale biomass is possible and has potential to be a sustainable use of agricultural waste.

1.2 Research Objectives

The overall goal of this thesis is to provide to a growing body of knowledge on biochar and its effects on water flow through Central Valley sandy soils. The motivation for this study was the rapidly changing climate and the resulting increasing water shortage in California. Without additional sources of surface water to the hydrologic system, there has been increased use of salinized groundwater for irrigation purposes. An additional underlying goal was to develop useful biochar from readily available agricultural wastes, promoting sustainable efforts. In this study, we investigated the effect of locally-derived almond shell biochar on soil physical and hydraulic properties. Biochar was created at low (350°C) or high (700°C) temperatures, sieved to small (<0.25mm) or large (1-2mm) sizes, and applied at low (10 t/ha) and high (60 t/ha) rates to observe how different biochar additions impact soils. Combinations of these attributes were applied to soils, mixed, incubated for 9 weeks, and analyzed via experimental and modeling methods.

The aim of this thesis was to enhance the understanding of the impact of biochar on soil hydrologic properties, with a focus on using local almond shells for biochar creation and agricultural soils in a semi-arid landscape. The primary objectives guiding this research are as follows:

- To determine if and how biochar application rate, temperature, and/or particle size (biochar characteristics) impact soil structure (aggregation);
- To evaluate if and how biochar characteristics affect water flow through a

loamy sand soil;

- And to examine the quality of char, in terms of physical and chemical properties, with increasing temperature.

To address these research objectives, the thesis was organized traditionally, where chapters represent the stages in the research project. Chapter 2 provides a literature review on the current state of knowledge of biochar. Chapter 3 will elaborate on methods utilized to investigate the aims previously stated. Results of the methods will be discussed in Chapter 4, and Chapter 5 will contain a discussion of the results.

CHAPTER 2. Literature Review

2.1 Introduction

Biochar can be defined as carbonaceous matter burned with little to no exposure to oxygen. It is a form of black carbon, which is the umbrella term for carbon-containing materials that have been thermally and chemically altered (Spokas et al. 2014; Czimczik & Masiello 2007). This term encompasses a continuum of thermally altered materials, from slightly charred biomass to soot. While various forms of black carbon are found as a natural product of forest fires, biochar differs in that it is deliberately created and added to the environment for anthropogenic purposes. It has steadily gained popularity as a subject of scientific study because of its potential for long term carbon sequestration and ability to be beneficial as a soil amendment.

2.2 Methods of Biochar Creation

Biochar is highly variable and its resulting inherent properties are highly dependent on the type of feedstock used, method of creation, temperature and duration of pyrolysis. Methods of production include torrefaction, slow pyrolysis, fast pyrolysis, and gasification. Torrefaction describes a pyrolysis process conducted at low peak temperatures (200-300°C), with a biomass residence time of 10-60 minutes. While this process can produce up to 84% char (mass percent remaining after combustion), the product is typically highly hydrophobic and is enriched in phenols and phenolic compounds that contribute phytotoxic effects (Meyer et al. 2011; Trifonova et al. 2008). Torrefaction is thus less utilized as a method of char production and more so as a pre-treatment process to create biofuels (Sadaka & Negi 2009). The pyrolysis processes typically burn biomass in reduced oxygen conditions, at peak temperatures greater than 400°C (Laird et al. 2009). Yields from this process produce varying ratios of bio-oil, biochar, and syngas. Slow pyrolysis is the most traditional process; it is characterized by slower heating rates (1-20°C/min) and is held at peak temperature for minutes to days (Meyer et al. 2011; Brewer et al. 2009). This form of pyrolysis is ideal for creating char because it is most versatile and economical for the product yield attained (~35%) (Laird et al. 2009; Goyal et al. 2008). Fast pyrolysis creates some char (10-30%), although its primary purpose is to generate bio-oils (50-70%) and gas (15-20%) (Laird et al. 2009). In this method,

fully dried and ground biomass is heated rapidly (300-1000°C/s) to a high peak temperature (>600°C) for a relatively short period of time (Brewer et al. 2009; Goyal et al. 2008). Gasification processes partially oxidize biomass at high temperatures (>800°C) and at atmospheric or elevated pressures (Meyer et al. 2011; Goyal et al. 2008). While gasification takes place in a matter of seconds, it produces only about 10% or less of biomass and around 90% gaseous products (Meyer et al. 2011). Although there are a variety of processes that can be used to create char, each has its own benefits and drawbacks. The process chosen is often a factor of availability of materials and the desired products of interest.

The pyrolysis of biochar has been stipulated to occur in a stepwise-fashion, as noted by Demirbas (2004). The process begins with raw biomass and heat, resulting in some volatile gas and moisture loss, in addition to the presence of unreacted residue. With further heating, the unreacted residue emits a greater content of volatiles, gases, and forms char. The final general step describes further loss of volatiles and gas and the formation of a carbon-rich, less reactive form of char (secondary char). In general, pyrolysis induces a chemical conversion of biomass that contains a reduced content of H and O from loss of water and hydrocarbons, in addition to a higher content of aromatic carbon relative to the feedstock (Baldock & Smernik 2002; Enders et al. 2012). The quality of the char at each of these steps, however, is highly dependent on the temperature, followed by the heating rate (Lua & Guo 2004; Antal & Grønli 2003). The greatest biochar yields have been recognized to occur at low heating rates and temperatures less than 300°C (Shrestha et al. 2010; Demirbas 2004). Increased heating rate has been observed to reduce char yields between 2-10% by weight (Antal & Grønli 2003). This phenomenon is observed because the enhanced heating rate shortens the dehydration step and generates unstable products that produce volatiles (Demirbas 2000; Bridgewater & Peacocke 2000). At longer rates of heating, intermediate products are able to stabilize and generate higher yields. Maximal char yield can thus be achieved by using low temperatures and a low heating rate.

The temperature that the above steps proceed in is typically dependent on the composition of the biomass used. Cellulose, hemicellulose, and lignin are common components in biomass. Cellulose is an important structural component of cell walls, consisting of β (1 $\rightarrow$ 4) linearly linked D-glucose units; hemicellulose is also present in cell walls, but consists of a large mixture of polysaccharide sugars; lignin is a very complex branched polymer with a high molecular weight, mostly found in the secondary cell walls of woody species. Hemicellulose degrades first from 200-260°C, cellulose loss is between 240-350°C, and lignin loss is observed between 280-500°C (Sjostrom 1993; Downie et al. 2009). Slightly above 50°C, biomass primarily exhibits water loss. A few degrees higher at 250°C, accelerated losses of CO₂ and CO are observed and are observed by further feedstock mass loss (Antal & Grønli 2003). Pyrolysis of char with higher lignin content has been recognized to produce greater char yields (Demirbas 2004; Sun et al. 2012). In addition to lignocellulosic feedstock, there is also a growing interest in using mineral-rich animal manure/litter, sludge, and other forms of waste as a biochar source. Because this

biomass does not contain the same structural components, the progression of its transformation into biochar does not follow the temperature ranges above. Resulting biochar from mineral rich sources tends to contain a higher ash content because of the high content of non-volatile minerals and will thus produce less structured char (Novak et al. 2009).

2.3 Biochar Persistence

Biochar stability has been a trait of interest to investigate because of the steady rise of anthropogenic CO₂ emissions. Because of its stability, biochar has been proposed as a method of carbon storage with the potential to sequester 1.8 Gt of carbon per year if actively adopted as a carbon sequestration strategy (Woolf et al. 2010). Much of biochar's stability is attributed to its highly aromatic nature and associated chemical resistance. Despite this, it is critical to keep in mind that biochar consists of varying degrees of aromatic and aliphatic regions, where aromatic groups are less reactive and aliphatic groups are generally subject to loss (Joseph et al. 2010).

The recalcitrant nature of biochar is a result of thermo-chemical conversion it experiences through the pyrolysis process. Many studies characterize stability through the content through proximate analysis, elemental analysis, and analysis of aromaticity. Proximate analysis provides an indication of fixed matter content after moisture, ash, and volatile matter are removed (ASTM International 2013). It provides an indication, on a mass basis, of the content of thermally stable structures present in a particular char and is primarily for comparative analysis (Joseph et al. 2009). Elemental analysis is also used to describe stability through degree of aromaticity (Spokas 2010). Degree of aromaticity is quantified by ratios of H/C and O/C, where $H/C < 0.6$ and $O/C < 0.4$ are indicative of aromaticity and stability and can correspond to a half-life of 40 up to 100,000 years (Schimmelpfennig & Glaser 2012; Spokas 2010; Mimmo et al. 2014; Zimmerman et al. 2010). Aromaticity is also often described by using ¹³C solid state NMR. Sun and others (2012) reported an increase in the condensation of aromatic groups with increasing temperature of pyrolysis and reduced particle size. Higher temperature chars have generally been reported to have higher degrees of aromaticity with fewer surface functional groups, and are thus speculated to be more structurally stable than lower temperature biochars (Novak et al. 2009; Brewer et al. 2009; McBeath et al. 2014).

Although multiple studies have reported long residence times of biochar, it is important to note that it is still subject to loss by abiotic, biotic, and physical processes. Abiotic processes (chemical oxidation, photo-oxidation) have been observed to cause significant contributions to the degradation of char. In a study comparing abiotic versus biotic oxidation processes, Cheng (2006) found abiotic processes to be more critical in oxidizing biochar surfaces over a short time period (4 months). This oxidation was also correlated with a reduction of aliphatic C that was speculated to have been lost as CO₂ (Cheng et al. 2006). Initial rapid abiotic oxidation may serve as a precursor to microbial mineralization of biochar and may thus reduce the speculated long-term stability of char. Biotic processes have been

also been attributed to biochar loss. Fungi have been noted to enzymatically inhabit, degrade and depolymerize coal and biochar (Laborda et al. 1997; Fakuossa & Hofrichter 1999; Hofrichter & Fritsche 1997; Hockaday et al. 2006). Bacterial response has also been documented, often by reporting effects of biochar addition on microbial respiration in experiments; however, there is no consensus within the scientific community. Several studies have reported an increase (Luo et al. 2011), decrease (Kuz'yakov et al. 2009; Spokas et al. 2009; Liang 2010; Kimetu & Lehmann 2010; Hamer et al. 2004), or no effect (Zackrisson et al. 1996; L Van Zwieten et al. 2010; Steiner et al. 2009) on the mineralization of biochar. It is speculated that any notable increase in biochar mineralization is likely due to microbes using non-pyrolyzed C existing in the biochar (Liang 2010; Lehmann et al. 2011). Physical breakdown of char has also been recently stressed as a method of char loss. Spokas and others (2014) conducted 24 hour laboratory weathering experiments and observed fragmentation of biochar with water and soil exposure. The result was increased loss of fragmented char through soil columns, indicating that char may not remain in soils for long, given the environment it is placed in.

2.4 Properties

The wide selection of feedstock available for use and varying conditions for biochar production has created diverse properties of char. Notable chemical properties include their elevated pH, high cation exchange capacity (CEC) and nutrients. It has been well established that biochar has a high pH and may be useful to increase the pH of acidic soils (Glaser et al. 2002; Gaskin et al. 2008). The high pH of chars is speculated to be a result of greater quantities of hydrolyzed alkali and alkaline salts (Tyron 1948). High CEC is beneficial because it allows useful cations to be bound to biochar surface and available for use by plants. In general, biochar has been observed to enhance CEC (Peng et al. 2011; Cheng et al. 2006; L. Van Zwieten et al. 2010; Steiner et al. 2010). Biochar's enhanced CEC is attributed to a larger surface area and the oxidation of aromatic compounds to reactive carboxylic groups from biotic and abiotic processes (Peng et al. 2011; Cheng et al. 2006; Liang et al. 2006). Previous studies on the CEC of biochar span a wide range, from around 9 cmol/kg (K. Chan et al. 2007) to upwards of 71 mmol/kg (Cheng et al. 2008). Chars made from less structured materials (i.e. manure, waste) tend to have lower cation exchange capacities than those made from agricultural residues (L. Van Zwieten et al. 2010). Additionally, as pyrolysis temperature increases, an increase in CEC is generally observed because of increased surface area (Gaskin et al. 2008). While lower temperatures retain more reactive C=O and C-H groups that have potential to interact with nutrients, these sites must be oxidized to provide CEC benefit (Glaser et al. 2002). Biochar made from poultry litter to wood chips has also been noted to contain significant quantities of Ca, Mg, K, and P that may be made more available to plants, although quantities vary (Jha et al. 2010).

Physical properties associated with char include high surface areas and high porosity. Biochar porosity is a property of interest in biochar studies because it has a large influence on the surface area of char and has the capability to physically

alter soil structure and resulting water flow through soils. Porosity is most affected by desired peak temperature (Lua & Guo 2004) and increases with increasing temperature (Guo & Lua 1998). Higher temperatures cause an increase in the content of volatile material released, thus generating pore spaces within char (Antal & Grønli 2003). Kinney (2012) and others found their most porous biochar to have a porosity of 80% volume. However, there is a limit to increasing porosity by increasing the temperature. Higher pyrolysis temperatures generate greater ash contents and can block pores, thus reducing the porosity (Novak et al. 2009). Surface area is highly affected by porosity and is typically analyzed using Brunauer-Emmett-Teller (BET) surface area analyzer with N₂ adsorption for larger pores (>1.5 nm) or with CO₂ adsorption for smaller pores (<1.5nm) (Mukherjee et al. 2011). Biochar generated from greater ash-containing feedstocks (i.e. manure, waste), have been noted to have lower surface area than those made from more structured, less ashy feedstocks because of ash blocking pore spaces contributing to surface area (Downie et al. 2009; Ronsse et al. 2013). Additionally, higher pyrolysis temperatures have been noted to be associated with higher surface areas because they tend to form more ordered structures and greater presence of micropores (<1 nm), which have been shown to contribute most to surface area (Peng et al. 2011; Keiluweit et al. 2010; Brodowski et al. 2005; Antal & Grønli 2003; Downie et al. 2009; Song & Guo 2012). Reported surface areas of chars are highly variable, ranging anywhere from 0 m²/g for a 500°C cottonseed hull char (Uchimiya et al. 2011) to >400 m²/g in pine xylem char produced at temperatures between 600-700°C (Brown et al. 2006). However, increases in temperature only see increased surface areas to a limit. Jimenez-Cordero and others (2013) saw a peak in surface area at 800°C and a collapse in the surface area at 900°C, attributed to collapse of micropores; similar results were observed elsewhere (Guo & Lua 1998). Surface area, in addition to porosity, can also be visually observed with scanning electron microscope by observing modifications of the original structure (Peng et al. 2011), although it fails to provide much quantitative information.

2.5 Biochar as a Soil Amendment

2.5.1. Terra Preta

The usage of biochar as a soil amendment was inspired by anthropic soils discovered in the Brazilian Amazon now called *Terra Preta*. *Terra Preta*, which is translated as “dark earth” and often labeled as Amazonian Dark Earths (ADE), has been found in the Amazon and has been associated with increased soil productivity in otherwise highly unproductive tropic oxisols (Lehmann & Rondon 2006). These dark, nutrient rich soils were created by pre-Columbian peoples by what is thought to be a subdued “slash and burn” process that ultimately incorporated large contents of char in the soil (Steiner et al. 2004). They have been estimated to be aged from 500 to 8,000 years before present and have long been continuously beneficial to tropic lands despite abandonment by the indigenous population (Lehmann 2006). Beneficial properties include higher soil organic matter (SOM) content, nutrient holding

capacity, nutrient content, elevated pH, and water retention (Glaser et al. 2001; Smith 1980; Sombroek 1966). High contents of aromatic black carbon and organic matter are attributed to enhancing the soil, since there were no other reported differences between *Terra Preta* and nearby soils (Glaser et al. 2001). The persistence and ability to replenish highly weathered soils to grow crops in the tropics for thousands of years inspired a vision of a similar, but intentionally designed material to be utilized as a soil conditioner and carbon storing reservoir.

2.5.2. Chemical Impacts

Biochar has been reported to improve the chemical properties of soils, although its effectiveness is dependent on its inherent properties and the soil it is amended in. Because of its own high pH, biochar addition has consistently increased the pH of acidic soils (Lehmann et al. 2003; Vaccari et al. 2011; Mbagwu 1989). By increasing soil pH closer to neutral, there is an increased availability of nutrients for microbes and plants that will enhance microbial activity and plant growth (Vaccari et al. 2011; Jien & Wang 2013). Using biochar to lime acidic soils also reduces aluminum toxicity, creating a soil environment more suitable for plant growth (Qian et al. 2013). Biochar can also cause an increase in pH that may induce negative effects by inducing micronutrient deficiency and reduced plant growth and addition must thus be taken with caution (Kishimoto & Sugiura 1985; Chan & Xu 2009). It has also enhanced the CEC of soils by providing additional exchange sites and surface area (Atkinson et al. 2010; Glaser et al. 2002). This positive effect is enhanced at higher pyrolysis temperatures and is expected to continue with aging, as oxidation will increase the formation of negative surface sites to attract positive cations (Liang et al. 2006). There have also been reports of higher contents of soil bioavailable macronutrients (N, P, K, Ca, Mg) that are necessary to constantly replenish, especially for agricultural purposes (Jha et al. 2010; J. Major et al. 2010). However, there is evidence that biochar may not significantly enhance nutrient content for plant growth. Van Zwieten and others (2010) compared plant growth in biochar with NPK fertilizer and biochar alone; the char and fertilizer treatment increased growth, whereas the biochar alone had no effect. This indicates that an additional supply of nutrients may be necessary to reap the full benefits of biochar addition.

2.5.3. Physical and hydraulic properties.

Amending soils with biochar has also been reported to alter physical properties of soils. Soil structure is crucial to consider because it impacts major processes such as soil erosion and surface run-off, in addition to plant and microbial proliferation.

Soil physical properties are altered by biochar addition, as it has the capacity to contribute to the already existing soil texture properties by altering porosity, surface area, and aggregate formation. Biochar's light and porous nature is a result of the

pyrolysis process pushing volatile matter out of the original biomass. Its size is also variable, and if undisturbed, varies between 0.6-4.75 mm (Downie et al. 2009). Considering the increased porosity and large size, biochar can reduce the bulk density of soils, thus improving soil aeration, strength, and water flow processes (Downie et al. 2009). The addition of up to 20 g biochar/ kg to an agricultural loamy soil saw an reduction in bulk density relative to the control after a 69 week incubation period (Laird et al. 2010). Surface area of soils has also been reported to improve from biochar addition. The high reported surface areas of char have been observed to improve the surface area of a loamy soil by 18%, which has implications in generating binding sites for nutrients or promoting aggregate formation (Liang et al. 2006; Laird et al. 2010).

The presence and stability of aggregates is important for carbon storage purposes and soil structural purposes. Structurally, aggregates provide enhanced places for air, water, and microbial movement, thus overall benefiting soil quality. The formation of soil aggregates is an important process governed by biological and physico-chemical processes. These processes yield strong micro-aggregates and weaker macro-aggregates ($> 250\mu\text{m}$), where strength is relative to land management procedures (i.e. tilling, irrigation, etc.). Several studies have reported improved aggregate formation with biochar addition, however the mechanism of aggregate formation is still unknown (Glaser et al. 2002; Brodowski et al. 2006; Liang et al. 2006; Ibrahim et al. 2013). It is speculated that the biochar addition provides suitable habitat for biota, stimulating microbe and fungal activity, increasing their exudate production, and providing greater binding agents between particles (Six et al. 2002). It is also plausible that aromatic components, which are predicted to be high in biochar, contribute to stabilization of microaggregates (Brodowski et al. 2006; Tisdall & Oades 1982). Earthworms have also been observed to mix biochar through soil profiles and promote aggregate stabilization (Topoliantz et al. 2006).

Biochar's usage to improve soils, especially those with limited structure and low water holding capacity, emerged from studies reporting biochar's high porosity (Liang et al. 2006) and surface area (Kishimoto & Sugiura 1985; Van Zwieten et al. 2009; Herath et al. 2013), both properties of which are highly dependent on production methods, especially temperature of pyrolysis. As previously mentioned, an increase in temperature has been reported to increase the porosity of biochar (Guo & Lua 1998). An increase in porosity creates additional capillary soil pores, thus creating additional pathways for water movement and potential water storage while reducing bulk density. A surface area increase is generally attributed to a larger proportion of biochar micropores, which can further promote water adsorption (Vartapetian & Voloshchuk 1995). Enhanced water adsorption can also be attributed to hydrophilic functional groups on the biochar surface, such as carboxy, hydroxyl, and methoxy groups that form over time, since biochar is typically initially hydrophobic (Abel et al. 2013; Cheng et al. 2006; Baccile & et al. 2009). Increased temperature of biomass pyrolysis thus has the potential to provide water-storing conditions. A study by Novak and others (2009) observed 6.7 to 15.9% increases in water retention by adding various chars to a loamy sand, with the greatest increases

attributed to higher temperature char (500°C). Conversely, no effects on water retention were observed in a similar study where pecan biochar was added to a loamy sand at 44 t/ha (Busscher et al. 2010). These two opposing studies elucidate the heterogeneity of different biochars and their effects in different soil types.

Biochar has also had effects on infiltration, which is the ability of water to penetrate a soil surface. Often, infiltration is quantified by determining saturated hydraulic conductivity (K_{sat}). The effects of biochar on infiltration vary in the literature. K_{sat} has been observed to increase (Asai et al. 2009; Herath et al. 2013; Lei & Zhang 2013; Oguntunde et al. 2008), decrease (Barnes et al. 2014; Uzoma et al. 2011; Deveraux et al. 2012), or have no detectable effect (Laird et al. 2010; Hardie et al. 2013). Herath and colleagues (2013) reported increases in the K_{sat} of a corn stover char amended silt loam soil (10-11.3 t/ha), while 20 t/ha black locust char reduced the K_{sat} of a sandy soil in a study by Uzoma and others (2011). The heterogeneity in these studies is a function of the soil texture that biochar is added to; the expectation is that biochar will reduce drainage in sandy soils, whereas increased drainage will occur in clayey soils (Atkinson et al. 2010; Major et al. 2010). This effect is not always achieved, however, pointing to the importance of also considering biochar physical properties and rate (Barnes et al. 2014).

CHAPTER 3. Methods

3.1 Soil Sampling

Soil was sampled from the top 30 cm of a young Winter Forage Crop (barley/oat mix) field located on Migliazzo & Sons Dairy Farm in Atwater, CA (Lat: 37.55779, Long: -120.548670). The site has a Mediterranean climate with an average of 15 inches of rainfall annually and an average annual temperature of 61°F (16.9°C) (<http://websoilsurvey.nrcs.usda.gov/>). The soil is classified as Atwater Loamy Sand (AgA) according to the United States Department of Agriculture (USDA) Web Soil Survey. The loamy sand texture was confirmed by conducting soil particle analysis by the hydrometer method (Bouyoucos 1962) and consists of approximately 80% sand, 14% silt, and 7% clay. Moist soil was passed through a 4 mm (No. 5) sieve to remove any rocks and any other forms of large matter. Soil was not air-dried for the experiment in order to best preserve natural microbial community. Soil was stored in a 4°C refrigerator and used within 2 months of collection.

3.2 Soil Physical and Chemical Analyses

3.2.1. Soil Bulk Density

Soil bulk density is a measure of solids and pores in a soil for a given volume. It can serve as an indicator of compaction in a soil and reflects functionality of soil structure for water flow and aeration. A subsample of field moist soil was packed into a soil core to determine bulk density. Packing method was consistent and added approximately 30g of soil for every packing segment; after each addition, the soil was tapped down three times to achieve a suitable density. Soil was settled by tapping the outside of the soil core cylinder. Following packing, a flat spatula was used to level soil. The core was dried in an oven at 105°C for 24 hours and weighed. Bulk density was calculated by

$$\rho_B = \frac{m_{dry}}{V_{core}}$$

where m_{dry} is mass of dry soil and V_{core} is volume of the cylinder. The resulting bulk density was

$1.33 \pm 0.01 \text{ g/cm}^3$.

3.2.2. Soil Water Content

Approximately 25 g of field moist soil was placed onto an aluminum tin to determine initial soil water content. The sample was then placed into a 105°C oven for 24 hours. Soil gravimetric water content was determined by

$$\theta_g = \frac{m_w}{m_t}$$

where m_w is mass of water and m_t is total mass added. Soil volumetric water content was determined by

$$\theta_v = \frac{m_w}{m_t} * \frac{\rho_B}{\rho_w}$$

where ρ_B is soil bulk density and ρ_w is the density of water (1 g/cm^3). The resulting gravimetric and volumetric water content was 0.20 and 0.26 ± 0.01 , respectively.

3.2.3. pH

Although bulk soil was not dried, a subset of field moist soil was air-dried for 48 hours for pH measurements. Soil pH was measured using a 1:2 (w/v) ratio in both de-ionized (DI) water and a 0.01M CaCl_2 solution. Using CaCl_2 as a solvent is often advantageous because of its reproducibility, similarity to natural soil electrolyte solution, reduces the variability of salt content in soils and ensures soils stay in a flocculated condition (Kalra & Maynard 1991). Samples were allowed to mix and equilibrate for 30 minutes in a Techne TSRT9D Roller Mixer (Bibby Scientific Limited, Staffordshire, UK). A Fischer Scientific™ Accumet™ Basic pH Meter (Thermo Fischer Scientific, Waltham, MA) was used for measurement. Measurements were conducted in duplicate.

3.2.4. Carbon and Nitrogen Contents and Isotopic Composition

Carbon and nitrogen concentration and isotopic composition of soil was determined using a Costech ECS 4010 CHNS-O Elemental Analyzer (Valencia, CA) coupled with a DELTA V Plus Isotope Ratio Mass Spectrometer (Thermo Fischer Scientific, Inc., Waltham, MA). Samples were pulverized using a mortar and pestle and dried for 24 hours at 105°C to sufficiently remove any moisture prior to analysis. Approximately 5 mg of sample was rolled into a 4x6 mm tin capsule (Costech Analytical Technologies Inc., Valencia, CA). Measurements of carbon and nitrogen were run in triplicate. The elemental analyzer was calibrated using high-purity acetanilide standard (Costech Analytical Technologies Inc., Valencia, CA) and a well-studied sediment sample from the Kings River Experimental Watershed in the Southern Sierra Critical Zone Observatory (CZO).

The stable isotope ratios analyzed were $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$. The ratios were calculated using the following equation:

$$\delta(\text{‰}) = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000$$

R corresponds to the elemental ratio (heavy/light), where $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ equate to $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively. The standards used were Vienna Pee Dee Belemnite (VPDB) and N_2 gas for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively.

The methods described here were also used to determine the C and N contents and stable isotope compositions for the biochar amended soil.

3.3 Biochar Production

3.3.1. Slow Pyrolysis

Raw almond hulls and shells were provided by University of California's Cooperative Extension in Merced County. Residues were sieved to remove particles smaller than 2mm (No. 10 mesh) to avoid charring powdery-particulate matter.

For pyrolysis, almond residue biomass was placed in 250 mL heat-resistant Inconel® crucibles (Metal Technology, Inc., Albany, OR). This procedure was adapted from Keiluweit (2010). Approximately 60 g of dried almond hull and shell pieces were placed in the crucible, filling approximately 90% of the space and leaving a centimeter of space at the top. The form-fitting Inconel® crucible lids created an oxygen-limited environment for pyrolysis of biomass.

Following weighing and filling the crucibles, almond residues were pyrolyzed under low oxygen conditions in a large Thermo Scientific™ Thermolyne™ tabletop muffle furnace (Thermo Scientific, Waltham, MA). Filled crucibles were placed in the muffle furnace. The heating rate of the furnace was approximately 9°C/min. Samples were allowed to reach peak temperature (350°C or 700°C) and remain at the respective temperature for an hour. The pyrolysis temperatures used in this study were chosen to be on both ends of the pyrolysis spectrum. After pyrolyzing for an hour at peak temperature, the furnace was shut off. The crucibles were then removed from the furnace after an hour, cooled in a desiccator for another hour, and weighed once cooled. Following weighing, char residues were placed in airtight bags and stored in the dark until further use.

3.3.2. Sieving

Prior to use in experiments, the char was lightly crushed to two different sizes (<250 μm or 1-2 mm) with a ceramic mortar and pestle and sieved. For the 1-2 mm sized char, residues remaining between a 1 mm (No. 18) and 2 mm (No. 10) sieve were collected and stored in a separate airtight bag. For the <250mm char, residues

passing through a 0.250 mm (No. 60) sieve were collected and stored in another airtight bag. The mortar and pestle was cleaned after crushing each biochar temperature sample to avoid any contamination. After being placed in their respective airtight bags, both subsamples of char were stored in the dark until further use.

3.4 Biochar Physical and Chemical Analysis

3.4.1. Proximate Analysis

Both forms of char were subjected to proximate analysis according to a procedure adopted from the American Society for Testing and Materials (ASTM) D1762-84 (ASTM International 2013). The procedure was used to determine moisture, volatile matter, and ash contents and was conducted in duplicate. The char sample was ground with a ceramic mortar and pestle instead of a ball mill to avoid any matter loss by heat generated from a ball mill. Only particles greater than 150 μm (No. 100 sieve) were used to avoid any particles being swept away by volatile gases in the furnace. Additionally, only particles smaller than 850 μm (No. 20 sieve) were used. Approximately 1 gram of each char was placed in Fisherbrand® high-form porcelain crucibles (Thermo Fisher Scientific Inc., Waltham, MA). Moisture loss was determined by placing the uncovered samples in a pre-heated muffle furnace at 105°C for 2 hours. Following cooling and weighing, samples were heated in a covered crucible at 950°C for 6 minutes to determine the amount of mass lost from volatile matter (VM). To determine the content of ash remaining, the sample subsequently subjected to 750°C burning, uncovered, for 6 hours. Fixed C was determined by subtracting 100 from the sum of moisture, VM, and ash remaining.

3.4.2. pH

Biochar pH measurements were taken in a 1:10 (w/v) ratio with DI water and a 0.01M CaCl_2 solution. Similar to methods conducted for soil pH, biochar was shaken and equilibrated for 30 minutes prior to measurement with a pH meter. Measurements were conducted in duplicate.

3.4.3. Carbon and Nitrogen Contents and Isotopic Composition

Carbon and nitrogen concentration and isotopic composition of biochar was determined using the same instrumentation as described previously for soils (See Section 3.2.4). Biochar was ground using a mortar and pestle and also dried at 105°C for 24 hours. The primary difference was that 0.5 and 3 mg of each biochar sample was measured out to better detect the carbon and nitrogen contents, respectively. Biochar was expected to have high carbon contents but low nitrogen contents; thus, 0.5 mg would be sufficient for detecting the carbon content, whereas the 3 mg would be more suitable to detect nitrogen content.

The stable isotope ratios analyzed were $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^2\text{H}$, otherwise denoted as

δD . The ratios were calculated using the following equation found in Section 3.2.4, with the addition of the hydrogen (H) stable isotope, $^2H/^1H$, which also equates to δD . As previously mentioned, the standards used were Vienna Pee Dee Belemnite (VPDB), N_2 gas, and Vienna Standard Mean Ocean Water (SMOW) for $\delta^{13}C$, $\delta^{15}N$, and δD , respectively.

3.4.4. Biochar Surface Functionality

Biochar surface functionality was determined using a Bruker Fourier Transform Infrared spectroscopy (FTIR) equipped with diffuse reflection (DRIFTS) accessory (Bruker Biosciences Corp., Billerica, MA). All biochar samples were ground to powder consistency using a mortar and pestle and dried at $60^\circ C$ for 24 hours. Biochar was not diluted with KBr because signal was lost with any ratio of dilution. Samples were scanned in mid-IR range from 4000 to 400 cm^{-1} at 20 Hz for 32 scans. The spectral resolution was 4 cm^{-1} . A baseline correction was carried out for each spectra using the OPUS Spectroscopy Software associated with the Bruker FTIR instrument.

3.4.5. Effective Cation Exchange Capacity

Effective cation exchange capacity (ECEC) was measured using the summation method. This method is not a direct method of a material's CEC, but is an estimate based on the summation of exchangeable Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and exchangeable acidity. Biochar and soil were leached with ammonium acetate (NH_4OAc) to extract base cations from exchange sites. The concentration of base cations in the leachate was then measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) by the Sierra Nevada Research Institute (SNRI) Environmental Analytical Laboratory (EAL) at UC Merced.

3.4.6. Surface Area

To analyze the specific surface area of the char, a Micromeritics Tri-Star 3000 (Micromeritics Instrument Co., Norcross, GA) gas adsorption analyzer was utilized. Prior to use, biochar samples were dried at $105^\circ C$ for 24 hours to ensure samples were thoroughly dry. Approximately 1 mg of fine char ($<250\text{ }\mu m$) and 1 g of coarse char ($1\text{-}2\text{ mm}$) were massed out into instrument-specific glass vials. The samples were then degassed with ultra-high purity N_2 at $105^\circ C$ for 30 minutes at a Micromeritics FlowPrep station (Micromeritics Instrument Co., Norcross, GA). The instrument functions by purging the vials with helium, releasing known contents of N_2 into the sample vial, and detecting changes pressure from the amount of N_2 adsorbed onto the sample surface layer. Throughout the whole process, the sample is immersed in liquid Nitrogen to maintain a constant temperature of 77.2 K . The data is sent to the software program, and then used to generate a Brunauer, Emmett, and Teller (BET) isotherm and calculate surface area via the BET equation.

3.4.7. Elemental Composition

Biochar samples were analyzed for C and N contents using a Costech ECS 4010 CHNS-O Elemental Analyzer (Valencia, CA) coupled with a DELTA V Plus Isotope Ratio Mass Spectrometer (Thermo Fischer Scientific, Inc., Waltham, MA), as was conducted for soils. In addition to those measurements, oxygen (O) and hydrogen (H) composition was analyzed using the same elemental analyzer but with a CO flow through to separate the elements. For O and H composition, pieces were ground using a mortar and pestle; approximately 2-4 mg of ground char was weighed into 3x5 mm silver capsules (Costech Analytical Technologies Inc., Valencia, CA). The elemental analyzer was calibrated using stearic acid and benzoic acid standards (Costech Analytical Technologies Inc., Valencia, CA).

3.5 Soil and Biochar Mixtures

3.5.1. Mixtures

Two sets of soil-biochar mixtures were created because two sets of water flow experiments were conducted. Temperature of biochar pyrolysis (350°C, 700°C), biochar particle size (<250µm, 1-2mm), and biochar application rate (10 t/ha, 60 t/ha), were the variables of interest amongst the two experiments. The first experiment, which will be referred to as the “Pressure Cell Experiment” from this point on, solely had soil-biochar mixtures that differed by pyrolysis temperature and application rate. This set of experiments was limited by the amount of pressure cells, and thus have only one biochar particle size (1-2mm). The second experiment, further referred to as the “Infiltration Experiment,” had manipulations of temperature, particle size, and application rate. Both sets include a set of controls without biochar. Additionally, all treatments were conducted in triplicate.

Biochar application rates were calculated by assuming a 0.3 m incorporation depth and a bulk density of 1.33 g/cm³. The addition of biochar varied per experiment because the container volumes used were different. Treatments for both the pressure cell and infiltration experiments can be observed in Table 3-1 and Table 3-2.

Table 3-1 Tempe Cell Experiment Treatments

Temperature	Particle Size (mm)	Application Rate (t/ha)	Char Added (g)
350 °C	1-2	10	0.24
	1-2	60	1.43
700 °C	1-2	10	0.24
	1-2	60	1.43

Table 3-2 Infiltration Experiment Treatments

Temperature	Particle size (mm)	Application Rate (t/ha)	Char Added (g)
350 °C	<250, 1-2	10	0.26
	<250, 1-2	60	1.59
700 °C	<250, 1-2	10	0.26
	<250, 1-2	60	1.59

Soil was separated into batches per treatment, where the mass was equivalent to filling the respective core/container for either the pressure cell or infiltration experiment. Mass of soil to fill each respective core/container was determined prior to starting the packing process for the experiments and was based on the packing procedure noted above for bulk density. The calculated amount of biochar per treatment was added to these batches and gently shaken in closed containers for 1 minute. To avoid aggregation, the batches were also gently hand mixed for 30 seconds.

3.5.2. Carbon Dioxide Measurements

The incubation period for both sets of experiments was approximately 64 days. Samples from both sets of experiments were placed in containers, covered with plastic wrap and incubated at 20°C in the dark. Prior to incubation, samples were drained to field capacity typical of sandy soils (1 meter head or 0.01 bar) (Richards & Weaver 1943). Samples were weighed and sprayed weekly with DI water to maintain constant moisture content across the incubation period. Carbon Dioxide (CO₂) gas samples were taken throughout the incubation period for both sets of experiments to observe changes in CO₂ flux with each treatment over time, where flux served as a proxy for microbial activity. Gas samples were taken on day 1, 5, 8, 13, 15, 20, 27, 48, 55, 63 for the Pressure Cell Experiment and day 1, 8, 22, 36, 50, 64 for the Infiltration Experiment. The discrepancy of sampling in both experiments was due to the nature of the Pressure Cell Experiment, which required a period of hydraulic experimentation in between the incubation period (further discussed in the next section). Prior to the sampling date, the respective jars were capped for 24 hours. Approximately 12 ml of headspace was pulled from lids equipped with septa and injected into previously evacuated vials. Carbon dioxide concentration was measured using a Shimadzu gas chromatograph with a thermal conductivity detector (Shimadzu GC-2014, Columbia, MD).

Additional subsamples were pulled from the last three samples of the Infiltration Experiment (day 36, 50, 64) to isotopically characterize the CO₂ being respired. A Thermo Scientific GasBench II (Thermo Scientific, Waltham, MA) was used to

conduct this analysis. Carbon dioxide isotope composition results were compared to the isotopic composition of Carbon from both the biochar and soil. A sample's CO₂ ratio was considered to be a product of greater respiration from biochar or soil (carbon sources) depending on the gaseous isotopic proximity to either source.

3.6 Soil and Biochar Mixtures: Hydraulic Experiments

3.6.1. Tempe Cell Experiment.

Four different treatments with three replicates were used in this experiment; biochar size was consistent at 1-2mm, while biochar temperature (350°C, 700°C) and application rate (10 t/ha, 60 t/ha) were manipulated. Tempe Cells with a high flow ½ bar ceramic plate were utilized for this portion of the experiment (Soilmoisture Equipment Corp., Santa Barbara, CA). The Tempe Cell included top and base caps, a brass soil core, and a 0.5 cm ceramic plate, which had a known hydraulic conductivity of 3.11E-05 cm/sec. The core had a 5.5 cm diameter and a height of 3 cm. Brass soil cores in the Tempe Cell were packed according to the procedure used for determining soil bulk density as previously discussed. Keeping this method consistent across the experiment provides consistency to the cores and ensures that bulk density is approximately 1.33 g/cm³.

3.6.1.1. Saturated Hydraulic Conductivity (K_{sat})

Following packing, Tempe Cells were saturated in de-aired water overnight. After saturation, hydraulic conductivity of each sample was measured. Tempe Cells were connected to Tygon tubing to monitor the inflow and outflow of water. A consistent water head level was marked in centimeters on a tube filled with de-aired water; this represented the inflow of water. The tubing connected to the top of the Tempe Cell was also marked in 1 centimeter intervals. Two sets of time points were then recorded for every centimeter of water flowing in and out of the saturated cell. The inflow and outflow time points were used as input into the model that will be discussed in the modeling section. The set-up is depicted in Figure 3-1.

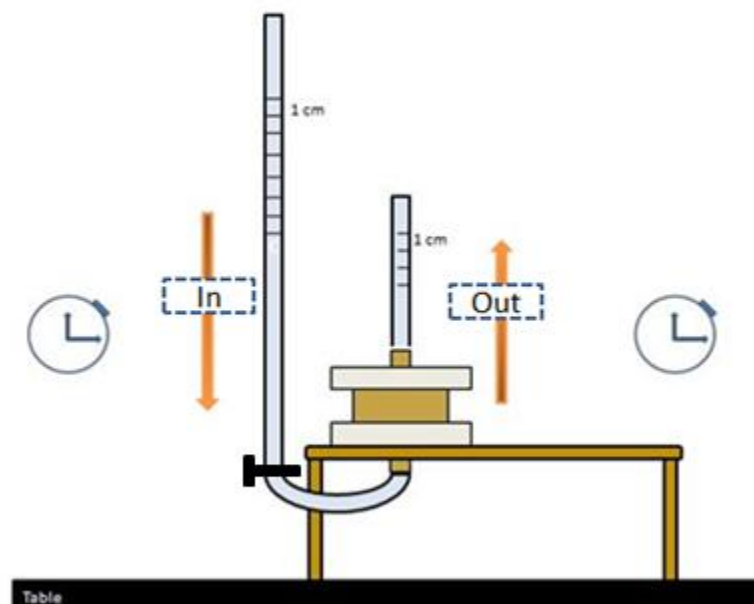


Figure 3-1 Set up of the Tempe Cell experiment. A Tempe Pressure Cell was attached to plastic rods and tubing. Time points were collected every time the water meniscus passed a centimeter mark. Time points were collected from both ends (in and out).

3.6.1.2. Water Retention Curve

In addition to the determination of K_{sat} , a soil water retention curve (WRC) was generated using the Tempe Pressure Cells. A WRC represents the non-linear relationship between water content and soil water potential in unsaturated soils. This relationship is characteristic for various soil classifications and can provide an idea of how soil water properties will change with biochar addition. Following K_{sat} tests, the saturated Tempe Cells were subjected to a range of pressures for three weeks. The Tempe Cells were left at 22cm, 60cm, 101cm, 142cm, 195cm, 234cm, and 422 cm of head for 2-3 days, depending on the time it took for the pressure level to equilibrate. Because the ceramic plates within the Tempe Cell were 0.5 bar (~500 cm head) plates, we used a maximum pressure head of ~0.4 bar (422 cm head) to avoid damaging the ceramic plate. After each equilibration period, the Tempe Cells were weighed to determine the amount of water lost. From these points, a WRC was formulated. This process was conducted prior, during, and after the 64 day incubation period to observe if there were any noticeable changes with time.

3.6.2. Infiltration Experiment.

A Mini Disk Portable Tension Infiltrometer from Decagon Devices, Inc. (Pullman, WA) was used for this portion of the experiment. The infiltrometer was filled with water in the water reservoir tube (95 mL) and the suction regulation tube. The stainless steel disc controlling water flow has a diameter of 4.5cm. While potential suction values range from 0.5 to 7 cm of suction, this experiment utilized 2 cm of suction as suggested for most soils in the Minidisk Infiltrometer User Manual (Decagon Devices Inc 2014) . White cups with a perforated bottom were used as the soil cores. They had a diameter of 5.8 cm and a height of 3 cm. To prevent soil loss through the perforations, a filter was placed on the bottom. The cups were packed similarly to the Tempe Cells; however, the amount of soil and biochar added was adjusted accordingly for the change in volume.

After packing, the cups were set to dry in residual heat from an oven previously heated to 50°C. This was conducted to ensure moisture loss, without compromising the loss of microbial activity. Following drying, an infiltrometer was connected to a calibrated data logger that would record changes in water level from the infiltrometer at every second. Once connected, the infiltrometer was placed as level as possible on the surface of a soil-char packed cup and water flow through the soil began as a result of contact. The infiltrometer was removed from the soil when the logger began to show a steady, flat-lining volume change, indicating that water was either slowly infiltrating the system or not at all. The resulting time and cumulative infiltration data was input into a Microsoft Excel Macro Workbook provided by Decagon Devices, Inc. (www.decagon.com/macro). The set-up of the infiltration experiment can be seen in Figure 3-2.

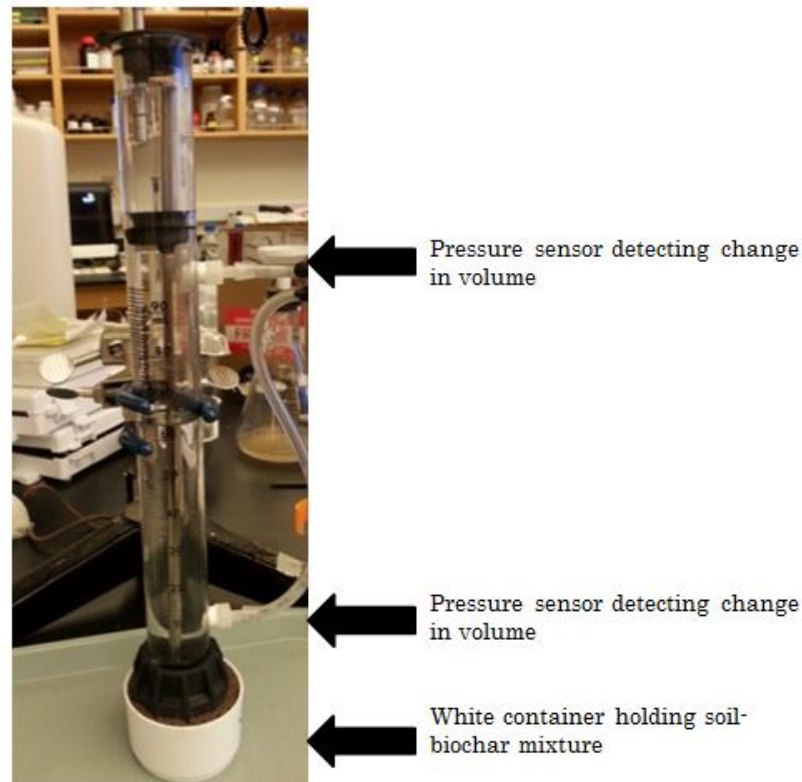


Figure 3-2 Set-up of the Infiltration Experiment.

3.7 Determination of Saturated Hydraulic Properties

3.7.1. Modeling with HYDRUS 1D

HYDRUS 1D is a program with the capability of simulating water flow through soil in 1 dimension. We utilized the inverse modeling capabilities of HYDRUS 1D and entered Tempe Pressure Cell data to estimate water flow parameters through each biochar amended soil treatment. To do this, HYDRUS 1D solves for the Richards equation and the specified hydraulic model, which was the van Genuchten retention function in this study (van Genuchten 1980a).

The Richard's equation can be used to model water movement in saturated and unsaturated soils (Šimůnek et al. 2009). It neglects air in liquid flow and flow from thermal gradients. The equation is as follows:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[K \left(\frac{\partial}{\partial x} + \cos \alpha \right) \right] - S,$$

where h is the pressure head, θ is the volumetric water content (v/v), t (seconds), x is the spatial coordinate, S is the sink term (v/v/t), α is 0 for vertical flow, and K is unsaturated hydraulic conductivity function that equates to:

$$K(h, x) = K_s(x)K_r(h, x),$$

where K_r is relative hydraulic conductivity and K_s is saturated hydraulic conductivity.

As previously mentioned, the Van Genuchten retention function was utilized to evaluate estimate soil hydraulic parameters and fit experimental data via inverse modeling. The function is as follows:

$$S_e(h) = \frac{1}{\left(1 + (\alpha|h|)^n\right)^{(1-1/n)}},$$

where h is the pressure head (cm), α is a parameter related to the inverse of air entry suction, n is a parameter related to the pore-size distribution of the soil, and S_e is a dimensionless value for effective saturation that equates to:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r},$$

where θ is the volumetric water content (v/v), θ_r is the residual water content (v/v), and θ_s is the saturated water content (v/v).

3.7.1.1. Tempe Cell Model –A saturated system

The model was based on input from the Tempe Cell experiment, the setup of which can be observed in Figure 3-1. The model duration varied with each experiment. There were two layers, a 3 cm soil layer and a 0.5 cm porous ceramic disc layer. The upper and lower boundaries of the model were best defined by variable pressure head, which was experimentally measured as inflow and outflow pressure head values. Because the system was saturated, K_{sat} was the only water flow parameter for the soil layer that could be fitted by HYDRUS 1D's inverse functionality. No parameters were fitted for the porous ceramic disc layer because it had a factory-known K_{sat} of 3.11E-05 cm/s. The primary data input for the inverse solution was the cumulative flow of water entering the cell at a given time.

To determine Van Genuchten parameters to our water retention curves, we used Microsoft Excel's Solver functionality to reduce the sum of squared errors between the model and experimental volumetric water content data. Volumetric water content at field capacity (θ_{fc}) was used as a proxy to determine if and how rate and temperature affected the water retention curve. Field capacity is the upper limit of water storage, describing water content after excess water has drained. For sandy soils, this occurs around 100 cm head (0.1 bar).

3.7.2. Cumulative Infiltration using a Mini Disk Infiltrometer

3.7.2.1. Infiltration Experiment – An unsaturated system

The Microsoft Excel Workbook provided by Decagon Devices, Inc. used a function describing cumulative infiltration, I

$$I = C_1 t + C_2 \sqrt{t}$$

where t is time, C_1 and C_2 are parameters relating the hydraulic conductivity and soil sorptivity, respectively. To calculate the hydraulic conductivity, k :

$$k = \frac{C_1}{A}$$

C_1 describes the slope of the curve describing cumulative infiltration against the square root of time and A is a parameter determined by the following functions:

For $n \geq 1.9$,

$$A = \frac{11.65(n^{0.1} - 1)\exp[2.92(n - 1.9)\alpha h_o]}{(\alpha r_o)^{0.91}}$$

For $n < 1.9$,

$$A = \frac{11.65(n^{0.1} - 1)\exp[7.5(n - 1.9)\alpha h_o]}{(\alpha r_o)^{0.91}}$$

where n and α (cm^{-1}) are parameters describing the van Genuchten water retention curve (1980b), h_o (cm^{-1}) is the suction applied at the soil surface, and r_o is the radius of the infiltrometer disk (Decagon Devices Inc 2014). Hydraulic conductivity was determined using these functions using a 2.2 cm disk and -2 suction.

3.8 Analysis of Incubated Soil-Char Mixtures

3.8.1. Water Drop Penetration Time

Water Drop Penetration Time (WDPT) is a simple test directed at determining the degree of soil water repellency (hydrophobicity) by placing a drop or drops of water on a soil surface and observing the time required for penetration. Hydrophobic soils have the potential to reduce plant growth, most notably by reducing infiltration of water into soils and/or enhancing leaching of nutrients (Doerr et al. 2000). WDPT was measured using a procedure adapted from (Leelamanie et al. 2008). Tempe Cells and Infiltration cups were air dried for 72 hours prior to conducting the test. After water contents were recorded to be similar (<0.15), one drop of de-ionized water was placed on a flat soil surface of the sample. A pipette set at $50 \pm 1\mu\text{L}$ (equivalent to a drop) was hoisted 1 cm above the sample using a clamp attached to a ring stand. Once the drop was placed, a stopwatch was started and stopped once the water drop fully penetrated the surface. If any WDPT was greater than 3600 seconds, it was labeled as 3600 seconds.

Table 3-3 Water Drop Penetration (WDPT) times and their corresponding class and degree of repellency (Leelamanie et al. 2008; King 1981; Bisdom et al. 1993; Chenu et al. 2000).

Class	WDPT(s)	Repellency Category
0	≤ 1 s	Non-repellent
1	1 - 60 s	Slightly Repellent
2	60 - 600 s	Strongly Repellent
3	600 - 3600 s	Severely Repellent
4	>3600 s	Extremely Repellent

3.8.2. Water Stable Aggregates

After incubation and hydraulic experiments, the biochar-soil mixtures were subjected to a water stable aggregate stability test. Water stable aggregate stability was measured using a modified wet sieving procedure adapted from Nimmo and Perkins (2002). However, rather than pre-wetting the soils by capillary rise under atmospheric conditions, we used a modified wetting technique adapted from Sun et al. (2014). The new technique wets the soils slowly within a vacuum chamber, hereby de-airing the water and soils simultaneously (Sun et al. 2014). Other than its low cost and acclaimed reproducibility, this method's advantage is that it reduces entrapped air within aggregates and the resulting disruptive forces caused by water flow (Sun et al. 2014; Kemper & Rosenau 1986). Approximately 4 grams of 1-2 mm aggregates from the dry biochar-soil mixture were massed out onto aluminum trays

for the wetting technique. Aluminum trays were placed in a pressure plate extractor (Soilmoisture Equipment Corp., Santa Barbara, CA) that was connected to a vacuum and a DI water source. Once the samples were in the pressure plate apparatus, a clear sheet of plexiglass was used instead of the original lid to allow a clear observation of the process. After turning on the water source, the air pressure was reduced within the apparatus, evacuating air from both soil and water. After visual confirmation of soil saturation within 2-4 minutes, the water source and vacuum were shut off and the soil within the aluminum trays was immediately transferred to 0.25 mm mesh wet sieving apparatus sieves (Eijkelkamp Agrisearch Equipment, Giesbeek, Netherlands). The apparatus moved the sieves 1.3 cm in a vertical motion for 3 minutes at a rate of 35 cycles per minute. Sieving was conducted in sieve cans filled with DI water, followed by a separate set of sieve cans filled with a dispersing agent that varied with the pH of the given sample. Soils with a pH greater than 7 require 0.2% sodium hexametaphosphate solution, while soils with a pH less than 7 use 0.2% NaOH dispersing solution (Kemper & Rosenau 1986). Samples remaining in cans with DI water are left in an oven 105°C overnight and weighed (M1). Any sample remaining on the sieve is then subjected to their respective dispersing agent until only sand particles remain on the sieve (Kemper & Rosenau 1986). This set of cans is also left in an oven at 105°C overnight and weighed (M2). The stable aggregate fraction, %S, is equal to:

$$\% S = \frac{M_2}{M_1 + M_2} * 100\%$$

Where M_1 is the mass remaining in cans after water dispersing and M_2 is the sample mass remaining in cans after exposure to the dispersing agent.

It is important to note is that our aggregates were air-dried prior to conducting this procedure. Kaiser and others (2014) have elucidated that air drying may provide over-estimations of aggregate stability, as air-drying can create or strengthen existing organo-mineral interactions.

3.9 Statistical Analysis

Where applicable, differences in means were analyzed by ANOVA using R statistical software (r-project.org). Significant differences were accepted at $p < 0.05$. If significance was found, Tukey's HSD (honest significant difference) test was conducted to clarify significance across biochar pyrolysis temperatures within treatment groups (i.e. no incubation or post incubation experiments -Tempe Cell, or Infiltrometer).

CHAPTER 4. Results

4.1.1. Proximate Analysis and pH

Table 4-1 Basic chemical properties of biochar, including pH and proximate analysis. All measurements were conducted in duplicate, with the exception of percent yield of char and mass remaining. Mass remaining is the average of 10 pyrolysis runs and percent yield is the overall yield of char generated from all 10 runs.

	Temp (°C)	Mass Remaining (g)	Yield (wt.%)	pH (CaCl ₂)	pH (DI)	Proximate Analysis (wt. %)			
						Moisture	Volatile Matter	Ash	Fixed C
Charred Almond Residue	350	21.78 (0.41)	32.66	9.77 (0.03)	10.82 (0.02)	3.42 (0.12)	31.51 (0.06)	8.69 (0.13)	56.38 (0.31)
	700	14.22 (0.22)	17.76	12.42 (0.02)	12.07 (0.01)	6.42 (0.08)	6.35 (0.06)	10.33 (0.14)	76.91 (0.27)
Raw Almond Residues	N/A	N/A	N/A	4.78 (0.01)	5.10 (0.02)	7.38 (0.05)	73.30 (0.11)	4.90 (0.02)	14.41 (0.19)

Biochars produced at different charring temperatures generate different properties as noted by Table 4-1. After an hour of pyrolysis at peak temperatures, the amount of original almond residue biomass recovered decreased from 32.65% to 17.75% as temperature increased. Moisture content, ash, and fixed C increased with 700°C pyrolysis, whereas volatile matter content was higher in the 350°C char. Additionally, the starting pH of the almond residues was slightly acidic at pH 4.78 as noted in Table 4-1. Upon charring, there was an increased basicity in pH that also increased as temperature increased.

4.1.2. Ultimate Analysis of Biochar

The ultimate analysis of biochar before and after incubation was analyzed. The 'Post Incubation Experiment' includes both experimental types, the Tempe Cell used for water retention and the Infiltrometer. Because the fine particles (<250um) were

of similar size to clay particles in the Infiltrometer experiment, they were unable to be efficiently separated from the post incubation mixtures and are not included in the ultimate analysis.

Before any incubation or experimentation, carbon concentration in coarse char is notably greater than in fine char as observed in Table 4-2. Additionally, char generated at 700°C has slightly greater carbon concentration than char at 350°C. In coarse char carbon concentration, there is a reduction in carbon concentration of the char after being incubated for 9 weeks. Before incubation, 350°C char has a carbon weight percent of $75.14 \pm 3.64\%$ and drops to $49.06 \pm 7.65\%$ and $63.52 \pm 2.81\%$ in the Tempe Cell and Infiltration experiment, respectively. Similar trends are observed for 700°C char. This information is visualized in Figure 4-1.

Less clear trends are observed for char's weight percentage of N, which is presented in Table 4-2 and Figure 4-2. With the exception of 700°C char after Infiltration, %N generally increased with increasing temperature although it was only significant for char picked from the Tempe Cell experiment. Before incubation, 350°C fine has the greatest %N, while 350°C coarse char has the lowest at $0.67 \pm 0.01\%$. Un-incubated chars did not significantly change N concentration with increasing temperature, but did have greater N concentration with pyrolysis in general.

Before incubation, the carbon-nitrogen (C:N) ratio had no significant effects across pyrolysis temperature (Figure 4-3). Additionally, C:N ratios of low temperature char were not significantly different before and after incubation. The C:N ratio of high temperature char significantly increased following the Infiltration experiment (~249), but was significantly reduced in the Tempe Cell experiment, having a C:N ratio of approximately 71. This decline is likely affected by the low %C and high %N of 700°C char relative to the other treatments (see Figure 4-1 and Figure 4-2).

Hydrogen content was greatest in the almond residues, followed by 350°C char, regardless whether it was coarse or fine. The 700°C char had the lowest %H at $1.19 \pm 0.00\%$ and $1.07 \pm 0.03\%$ for coarse and fine char, respectively. As temperature increase, hydrogen content depleted.

Oxygen content was also reduced as pyrolysis temperature increased. Almond residues had the greatest %O, while 700°C char had the lowest %O at $6.52 \pm 0.42\%$ and $9.21 \pm 0.34\%$ for coarse and fine, respectively.

Following incubation, hydrogen contents in char were greatest in 350°C coarse char. In both the Tempe Cell and Infiltration experiment, 700°C coarse char experienced a reduction in hydrogen relative to their 350°C counterparts. Oxygen content experienced a similar trend, where less pyrolyzed char contained more oxygen.

H:C and O:C ratios were observed to decline with higher pyrolysis temperature. These trends are better emphasized in the Van Krevelen diagram below (Figure 4-7). The higher ratios present from after the experiment suggest that the char is slightly less stable, as O:C and H:C ratios closer to 0 are comparable to carbonized

graphite.

Table 4-2 Ultimate analysis of char before incubation and after incubation.

Post Incubation Experiment	Material	Temp (°C)	Size	Ultimate Analysis (Wt. %)					Atomic Ratio	
				C	N	H	O	C/N	H/C	O/C
No Incubation	Almond Residues	N/A	N/A	47.18 (3.64)	0.38 (0.01)	5.80 (0.07)	29.68 (2.60)	146.76 (4.23)	1.48 (0.03)	0.56 (0.21)
	Biochar	350	Coarse	75.14 (3.64)	0.67 (0.01)	4.08 (0.01)	18.67 (0.24)	130.14 (5.38)	0.65 (0.11)	0.19 (0.11)
	Biochar	700	Coarse	85.40 (2.17)	0.89 (0.22)	1.19 (0.00)	6.52 (0.42)	163.63 (42.05)	0.17 (0.06)	0.05 (0.07)
	Biochar	350	Fine	60.46 (0.40)	1.14 (0.07)	4.21 (0.01)	18.79 (0.21)	72.49 (17.96)	0.83 (0.01)	0.27 (0.01)
	Biochar	700	Fine	63.17 (0.93)	0.80 (0.01)	1.07 (0.03)	9.21 (0.34)	92.11 (2.84)	0.20 (0.05)	0.11 (0.07)
Tempe Cell	Biochar	350	Coarse	45.94 (12.87)	0.30 (0.07)	3.73 (0.10)	17.76 (0.35)	173.24 (32.22)	0.90 (0.39)	0.27 (0.39)
	Biochar	700	Coarse	50.27 (14.93)	1.21 (0.34)	1.12 (0.03)	5.9 (0.29)	71.09 (41.71)	0.27 (0.43)	0.09 (0.45)
Infiltration	Biochar	350	Coarse	63.44 (3.76)	1.54 (0.05)	3.83 (0.07)	17.6 (0.22)	122.30 (50.20)	0.72 (0.12)	0.21 (0.12)
	Biochar	700	Coarse	79.04 (0.90)	0.37 (0.03)	1.24 (0.25)	9.1 (1.13)	249.89 (14.49)	0.19 (0.65)	0.09 (0.39)

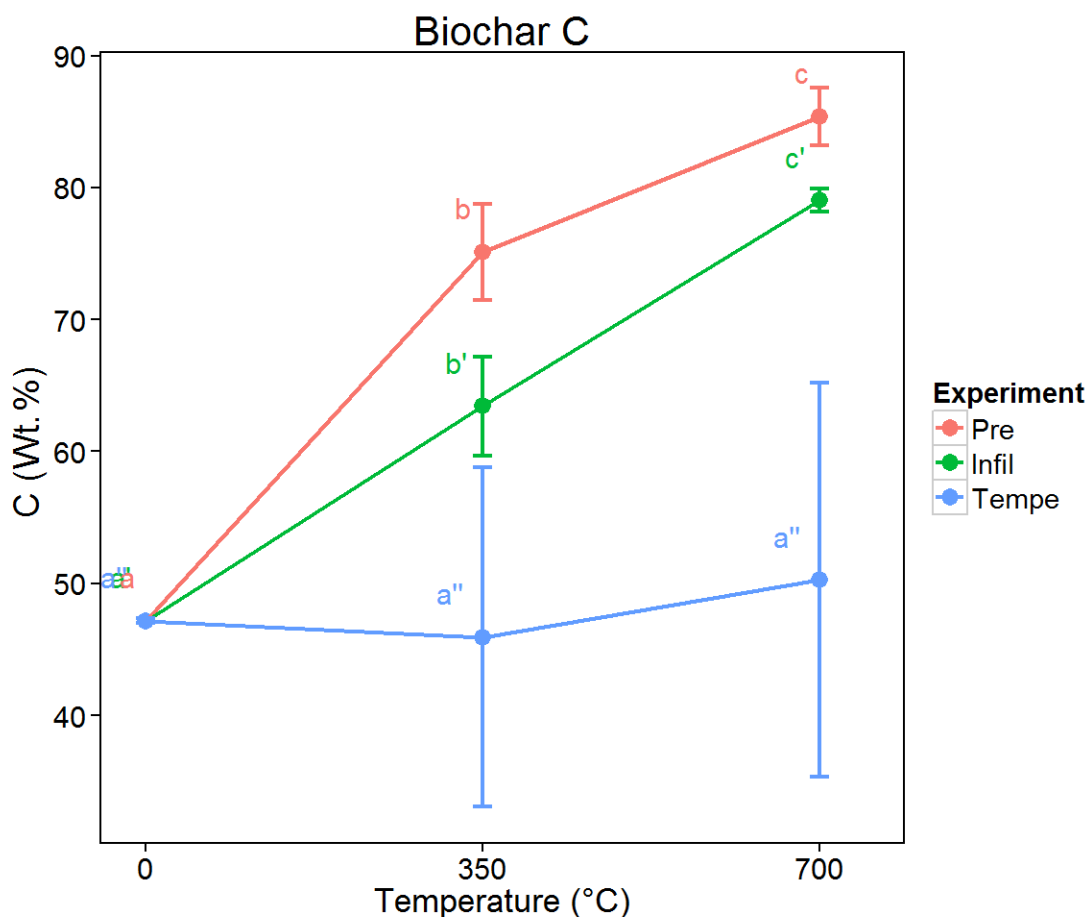


Figure 4-1 - C content of biochar across increasing pyrolysis temperature and before and after incubation. Lines represent the hydraulic experiment conducted, where "Pre" represents biochar that was not incubated. A temperature of 0°C represents bulk raw almond residue biochar. Means are presented with standard error bars (n = 3). Different letters denote significantly different means ($p < 0.05$) at each temperature after Tukey's HSD test. Values were compared across experiment, and are differentiated by "a", "a'" and "a''" for "Pre", "Infil", and "Tempe", respectively.

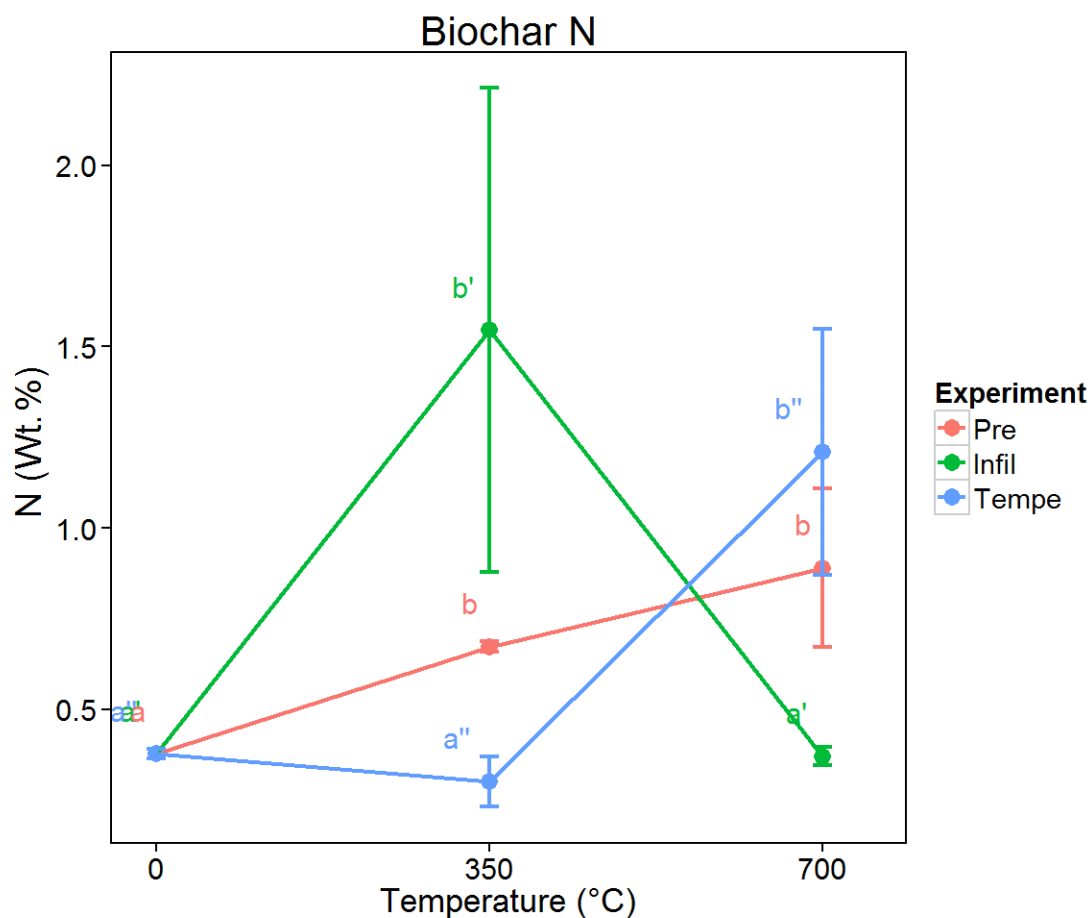


Figure 4-2 - N content of biochar across increasing pyrolysis temperature and before and after incubation. Lines represent the hydraulic experiment conducted, where "Pre" represents biochar that was not incubated. A temperature of 0°C represents bulk raw almond residue biochar. Means are presented with standard error bars (n = 3). Different letters denote significantly different means (p<0.05) at each temperature after Tukey's HSD test. Values were compared across experiment, and are differentiated by "a", "a'" and "a''" for "Pre", "Infil", and "Tempe", respectively.

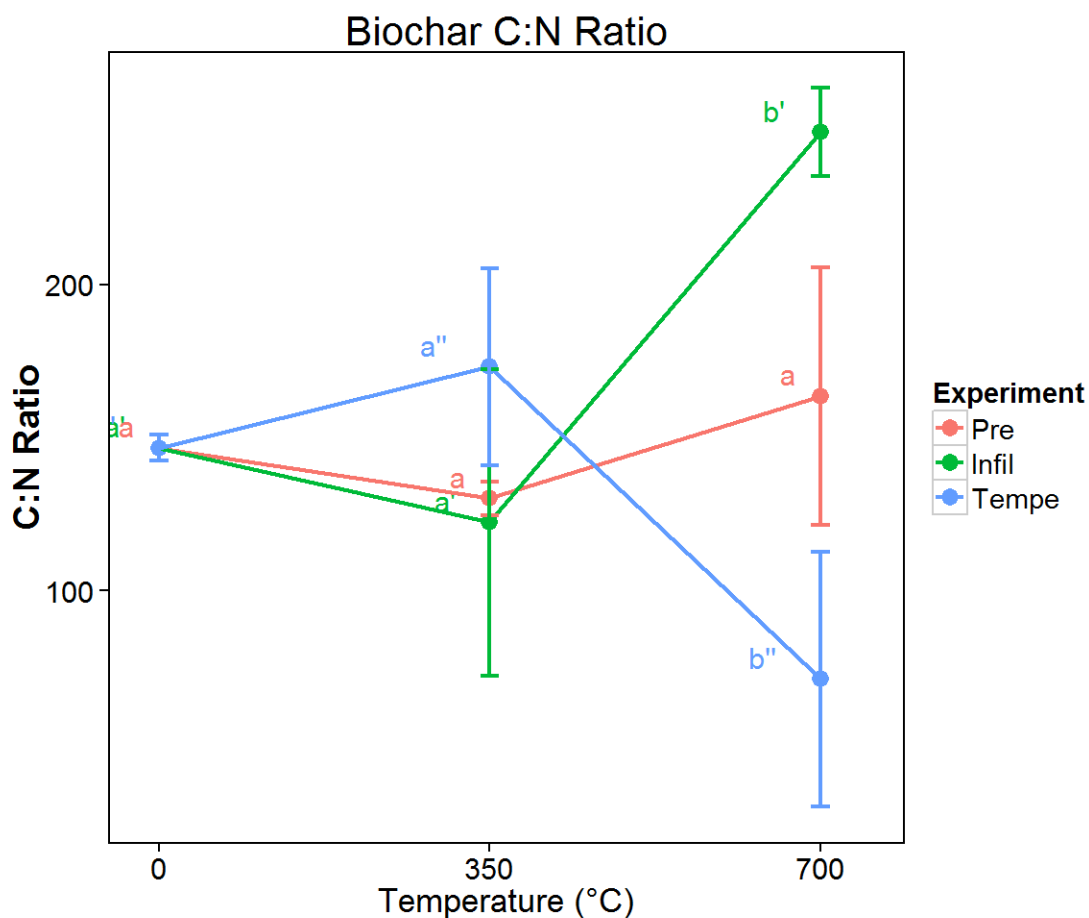


Figure 4-3 - Biochar C:N ratio across increasing pyrolysis temperature. Lines represent the hydraulic experiment conducted, where "Pre" represents biochar that was not incubated. A temperature of 0°C represents bulk raw almond residue biochar. Means are presented with standard error bars (n = 3). Different letters denote significantly different means ($p < 0.05$) at each temperature after Tukey's HSD test. Values were compared across experiment, and are differentiated by "a", "a'" and "a'" for "Pre", "Infil", and "Tempe", respectively.

4.1.2.1. $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and $\delta^2\text{H}$ Ratios

The $\delta^{13}\text{C}$ stable isotope ratio of coarse biochar before and after incubation can be observed in Figure 4-4. The $\delta^{13}\text{C}$ of the original almond residue feedstock was depleted, averaging about -27.6‰ , which is typical of C3 vegetation (-25‰ to -32‰). As the residue was pyrolyzed, the isotopic ratio slightly increased then declined; however, no significant differences were observed with an increase in pyrolysis temperature. After undergoing the incubation process, char pieces were picked from samples and analyzed for their isotopic ratio. After the incubation experiment, 350°C char became enriched at $-25.51 \pm 0.66\text{‰}$, while 700°C char became depleted to $-26.83 \pm 0.63\text{‰}$. Similar to 350°C char from the Tempe Cell experiment, 350°C char from the Infiltration experiment became enriched ($-26.80 \pm 0.48\text{‰}$). However, no significant change was observed in the Infiltration experiment for 700°C char relative to lower temperature char.

Biochar $\delta^{15}\text{N}$ stable isotope ratio presented different trends. The uncharred almond residue ratio was $-1.29 \pm 0.24\text{‰}$. All 700°C chars, incubated or not, were most enriched relative to the uncharred matter. The greatest enrichment was observed after the 700°C chars were incubated, where char had a ratio of $5.65 \pm 0.91\text{‰}$ and $6.50 \pm 0.88\text{‰}$ after being subjected to the Infiltration and Tempe Cell experiment, respectively. Without incubation, 700°C chars had a ratio of $0.20 \pm 0.22\text{‰}$. Low temperature char extracted from the Tempe Cell experiment was not significantly different from the unincubated char; however, 350°C char was significantly enriched from the Infiltration experiment.

Biochar $\delta^2\text{H}$ changes across pyrolysis temperature and treatment (incubated/unincubated) are shown in Figure 4-6. All biochars, regardless of pyrolysis temperature and treatment demonstrated a similar trend. The trend shows a general depletion (loss of the heavy H isotope) with low temperature char, but reverses and becomes enriched in the heavy H isotope at a high pyrolysis temperature. There was at least a $>96\text{‰}$ enrichment of $\delta^{15}\text{N}$ as temperature of pyrolysis increased.

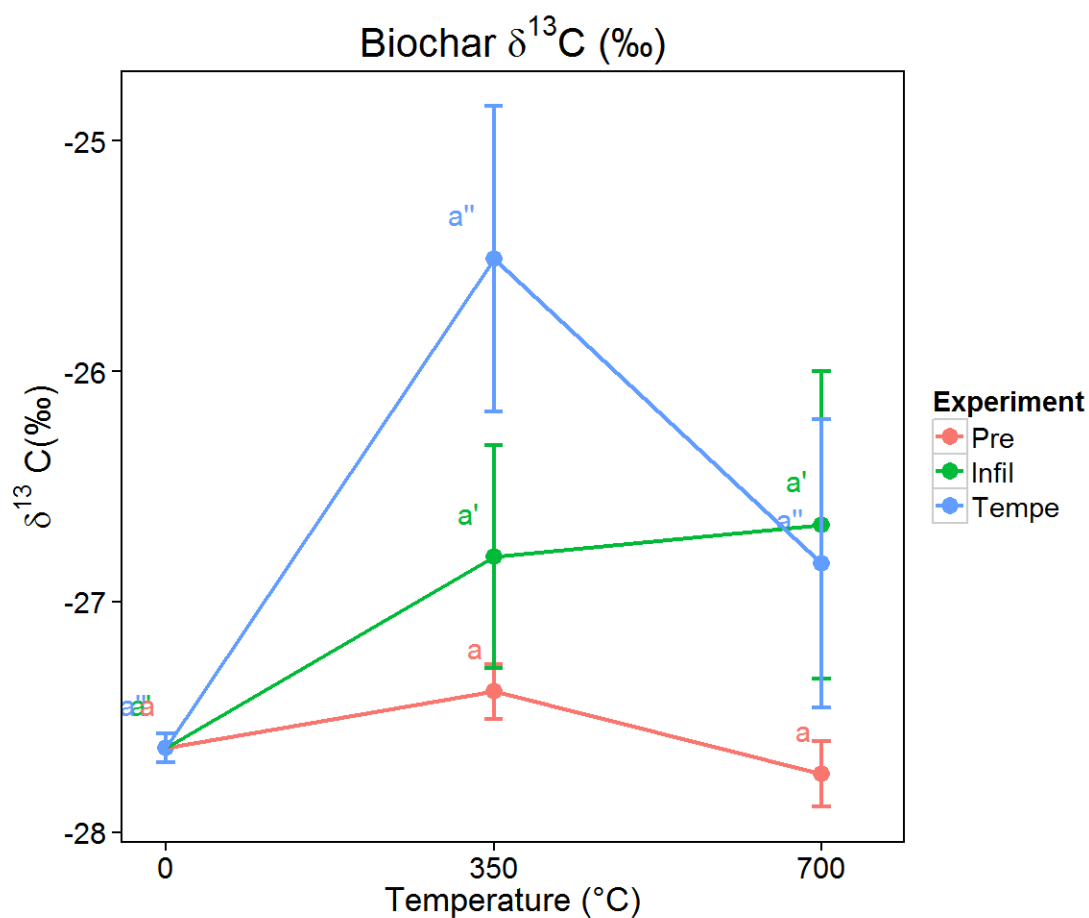


Figure 4-4 - Biochar C stable isotope ratio across increasing pyrolysis temperature of coarse char. A temperature of 0°C represents bulk uncharred almond residue. Lines represent the hydraulic experiment conducted, where "Pre" represents biochar that was not incubated. Means are presented with standard error bars (n = 3). Different letters denote significantly different means ($p < 0.05$) at each temperature after Tukey's HSD test. Values were compared across experiment, and are differentiated by "a", "a'" and "a'" for "Pre", "Infil", and "Tempe", respectively.

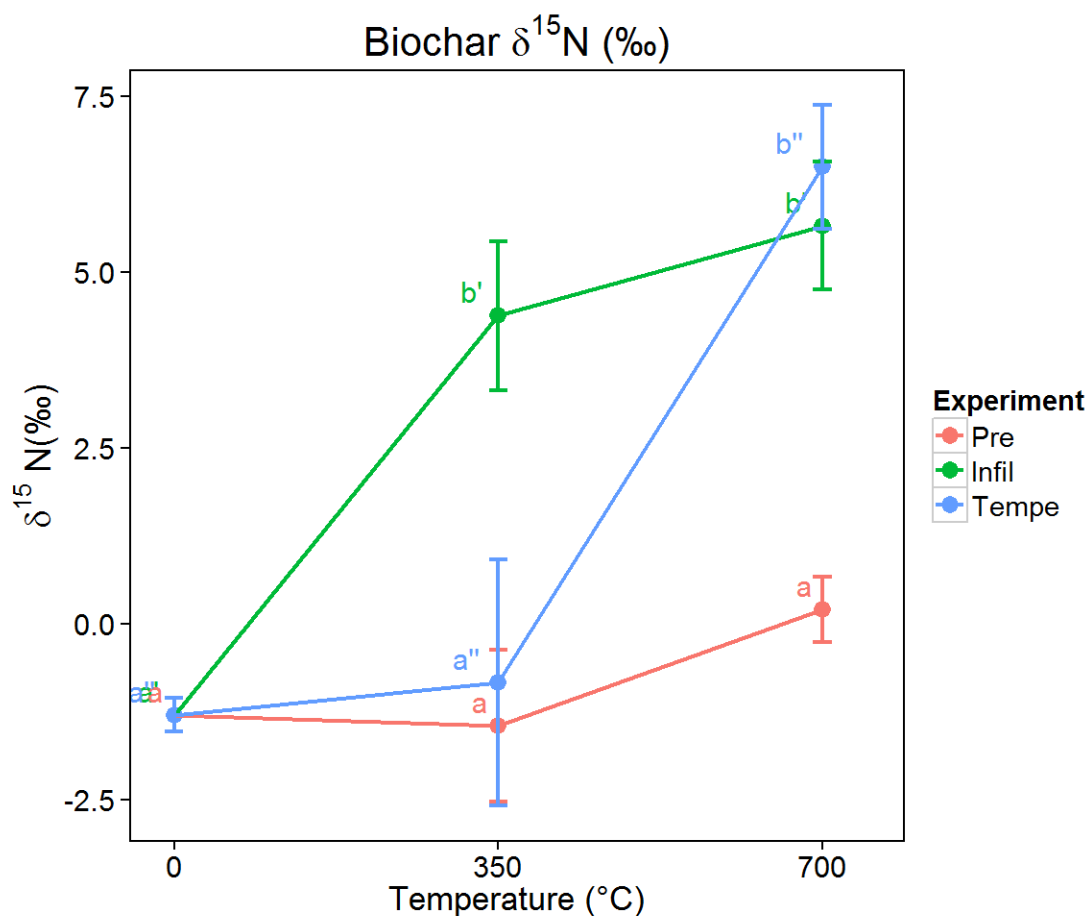


Figure 4-5 – Biochar N stable isotope ratio across increasing temperature and from different hydraulic experiments. A temperature of 0°C represents bulk uncharred almond residue. Lines represent the hydraulic experiment conducted, where "Pre" represents biochar that was not incubated. Means are presented with standard error bars ($n = 3$). Different letters denote significantly different means ($p < 0.05$) at each temperature after Tukey's HSD test. Values were compared across experiment, and are differentiated by "a", "a'" and "a'" for "Pre", "Infil", and "Tempe", respectively.

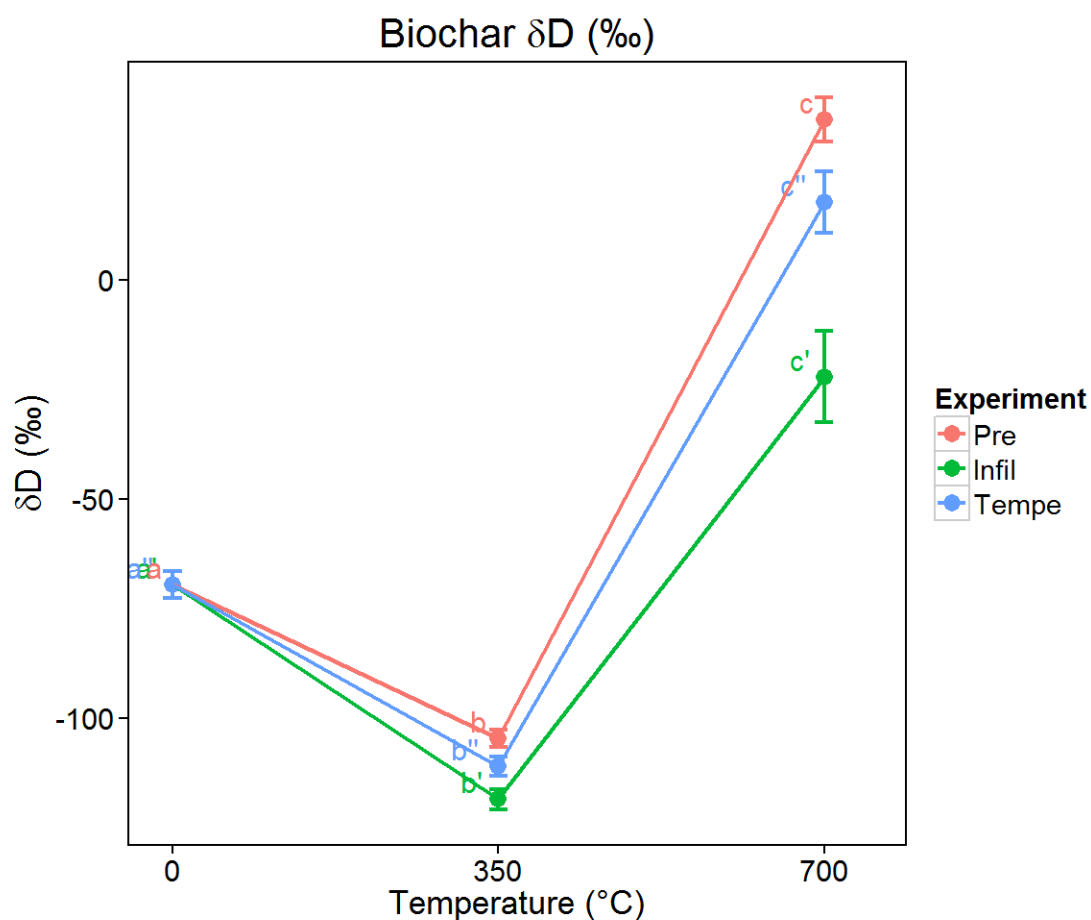


Figure 4-6 - Biochar H stable isotope ratio across increasing temperature and from different hydraulic experiments. A temperature of 0°C represents bulk uncharred almond residue. Lines represent the hydraulic experiment conducted, where "Pre" represents biochar that was not incubated. Means are presented with standard error bars (n = 3). Values were compared across experiment, and are differentiated by "a", "a'" and "a'" for "Pre", "Infil", and "Tempe", respectively.

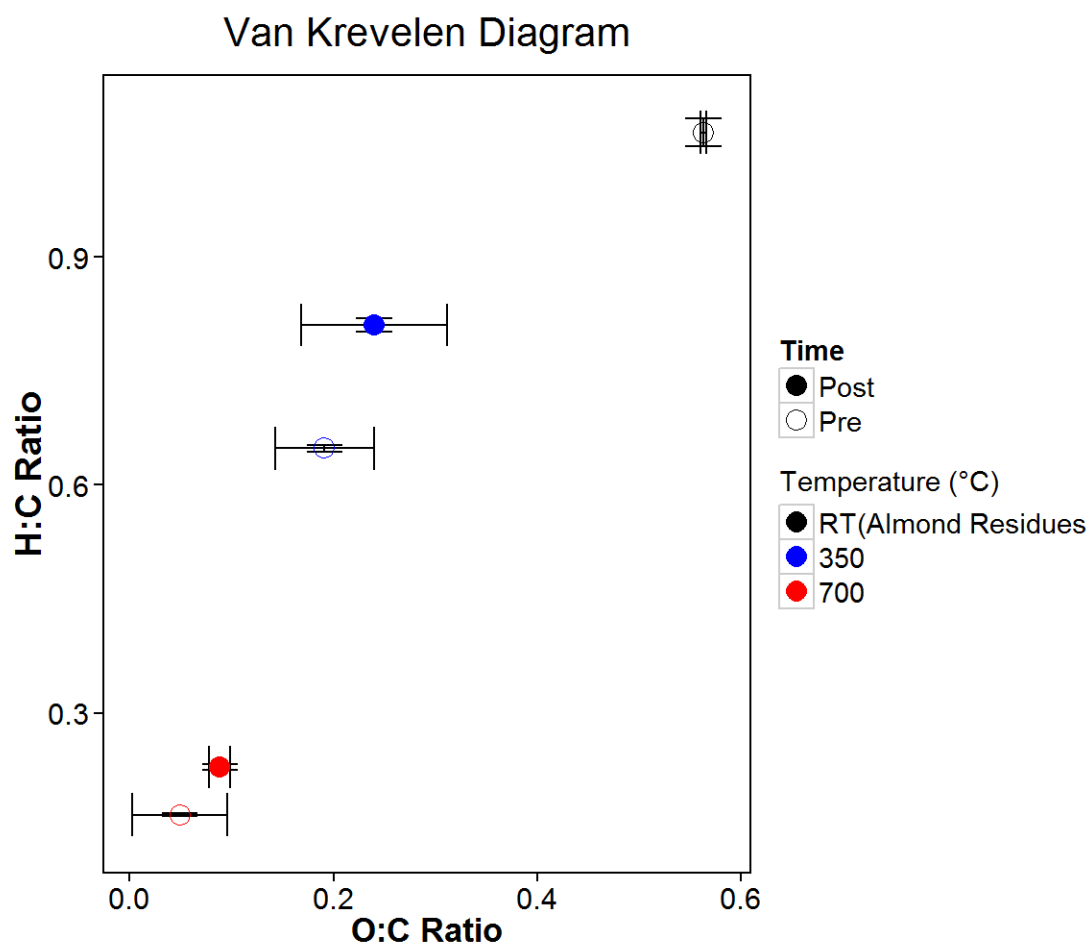


Figure 4-7 Van Krevelen diagram for char pieces before incubation and after. After incubation encompasses both hydraulic experiments (Tempe Cell and Infiltration). Original uncharred almond residues are in black. Standard error bars and means (n=3) are shown.

4.1.3. FTIR spectroscopy

The DRIFT-FTIR spectra of the almond residue biomass and the produced almond residue biochar at 350°C and 700°C are shown below in Figure 4-8. Peak assignments are shown in Table 4-3. Biochar created at 350°C shows similar peaks of the original biomass, although they appear to be less resolved. Most functional groups are lost as the original biomass feedstock is highly thermally transformed at 700°C. There is clear loss of the broad peak from 3500-3200 cm^{-1} as temperature of pyrolysis increases. This region is associated with O-H bonds in water and likely describes an increase in water loss. Aliphatic groups, noted by a peak around 2934 cm^{-1} , also disappear as pyrolysis temperature increases. Pyrolysis also gradually removed C=C (1600 cm^{-1} , 1440 cm^{-1}), phenol-OH (1375 cm^{-1}), and C-O-C (1270-1250 cm^{-1}) peaks describing lignin functional groups, indicating that lignin was lost during the pyrolysis process. Additional losses include the presence of C-H bends found in alkenes (1000-650 cm^{-1}), while a significant gain in the C-H bending of alkynes was observed at 700°C.

Table 4-3 FTIR Peak Band Assignments

Wavenumber (cm^{-1})	Functionality Assignment
3500-3200 ^a	O-H stretching associated with H-bonded hydroxyl groups in water
2935 ^a	Asymmetric C-H stretching from aliphatic CH_x groups
1740-1700 ^a	C=O stretch primarily carboxyl; also aldehydes, ketones, esters
1600 ^a	C=C stretching from aromatic groups
1510 ^a	C-C stretching from aromatic skeletal vibrations
1440 ^a	C=C stretching from lignin-associated aromatic C bonded to an unsaturated group; aliphatic $-\text{CH}_2$ deformations from lignin and carbohydrates
1375 ^a	Phenolic OH in plane bending, associated with lignin units
1270-1250 ^a	Ester C-O-C groups, aryl ethers; phenolic C-O from lignin units
1000-650 ^b	C-H stretching of alkenes
700-610 ^b	$\text{C}\equiv\text{C-H}$, C-H bending of alkynes

^a(Keiluweit et al. 2010)

^b(Tomasi 1994)

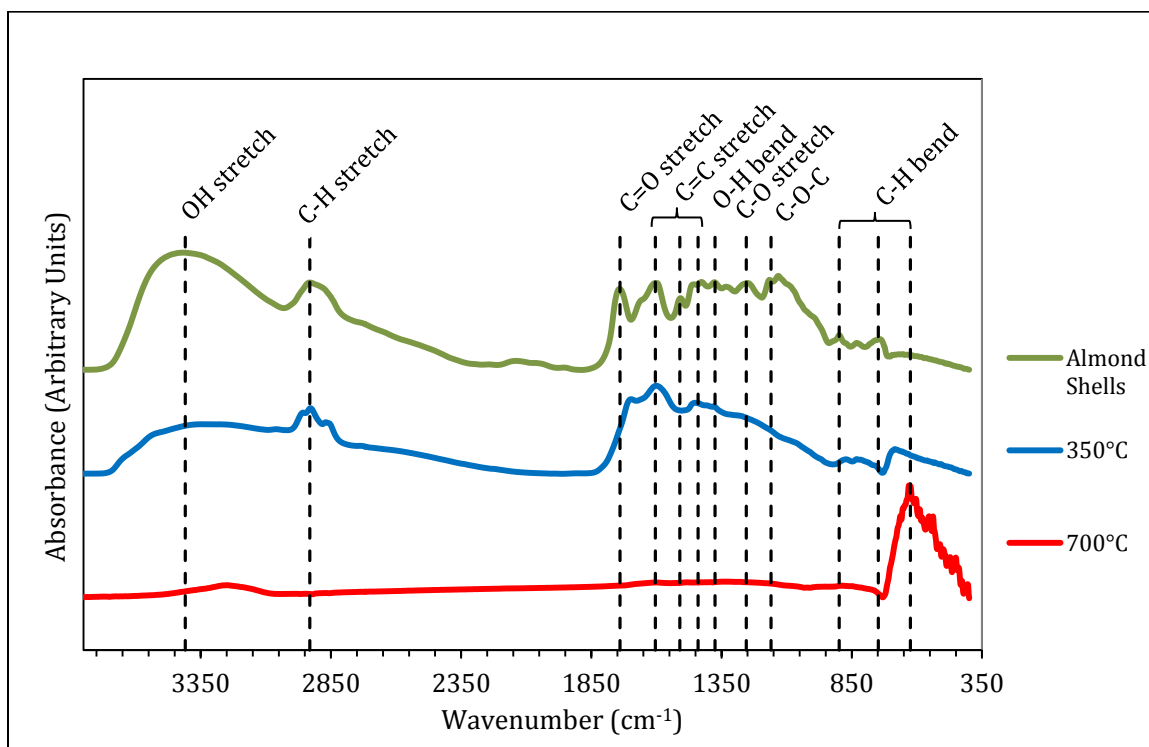


Figure 4-8 FTIR spectra of raw almond residue and resulting biochar at 350°C and 700°C. Peaks were identified according to the wavenumbers and associated functionalities found in Table 4-3.

4.1.4. Effective Cation Exchange Capacity

Effective cation exchange capacity encompasses a summation of exchangeable base cations (Ca^{2+} , K^+ , Mg^{2+} , Na^+) and is shown for biochar in Table 4-4. The lowest ECEC was observed for the un-amended soil at 13.98 ± 0.05 cmol/kg. All biochar had an ECEC at least 3 times greater than that of soil. ECEC varied within biochar, but was observed to increase with increasing temperature and decreasing size. The greatest ECEC was observed in 700°C fine char at 97.57 ± 0.38 cmol/kg.

Table 4-4 Effective cation exchange capacity (ECEC) and electrical conductivity (EC) of soil and biochar in cmol/kg and dS/m, respectively.

Material	Temperature ($^\circ\text{C}$)	Size	Al cmol kg^{-1}	Ca cmol kg^{-1}	K cmol kg^{-1}	Mg cmol kg^{-1}	Na cmol kg^{-1}	CEC cmol kg^{-1}	EC (dS/m)
Soil	N/A	N/A	<0.01	7.59 (0.07)	2.37 (0.08)	3.17 (0.01)	0.75 (0.01)	13.98 (0.05)	2.00
Biochar	350	Coarse	0.01	2.37 (0.03)	38.82 (2.92)	1.37 (0.00)	0.49 (0.01)	43.12 (2.96)	2.02
Biochar	350	Fine	0.02	10.12 (0.13)	61.05 (2.62)	3.26 (0.00)	0.59 (0.00)	75.13 (2.76)	2.05
Biochar	700	Coarse	0.01	1.16 (0.02)	51.18 (0.58)	1.93 (0.00)	0.64 (0.01)	53.67 (0.60)	2.07
Biochar	700	Fine	0.01	6.04 (0.10)	88.84 (0.11)	1.56 (0.16)	0.99 (0.00)	97.57 (0.38)	2.17

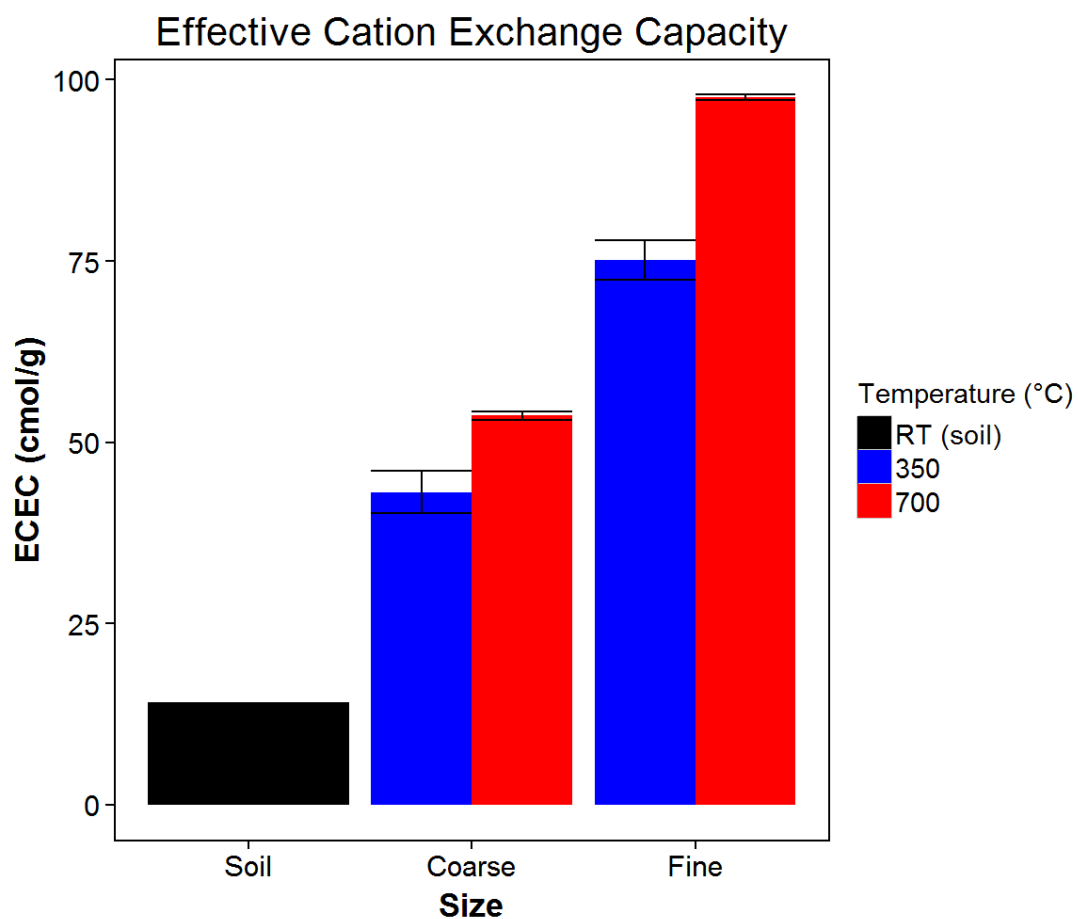


Figure 4-9 Effective cation exchange capacity (ECEC) of biochar and soil at different temperatures and textures. ECEC of soil is included for comparison. Error bars represent the standard error between measurement replicates, where $n = 2$.

4.1.5. BET-N₂ Surface Area

Specific surface area is shown in Figure 4-10. Low temperature coarse char (350°C) was 0.05 ± 0.00 m²/g and increased with smaller size and higher temperature, where 350°C fine and 700°C fine char had surface areas of 1.06 ± 0.05 m²/g and 15.02 ± 0.40 m²/g, respectively. Fine char 700°C had a recorded surface area 14 times greater than 350°C coarse char. Coarse char pyrolyzed at 700°C is not reported because it was unable to be measured by the surface area analyzer. Surface area was significantly correlated with both temperature (ANOVA, $F = 1572.93$, $p < 0.001$) and size (ANOVA, $F = 11.21$, $p < 0.05$). Both coarse and fine 350°C char had surface areas less than the surface area of soil (3.14 ± 0.13 m²/g).

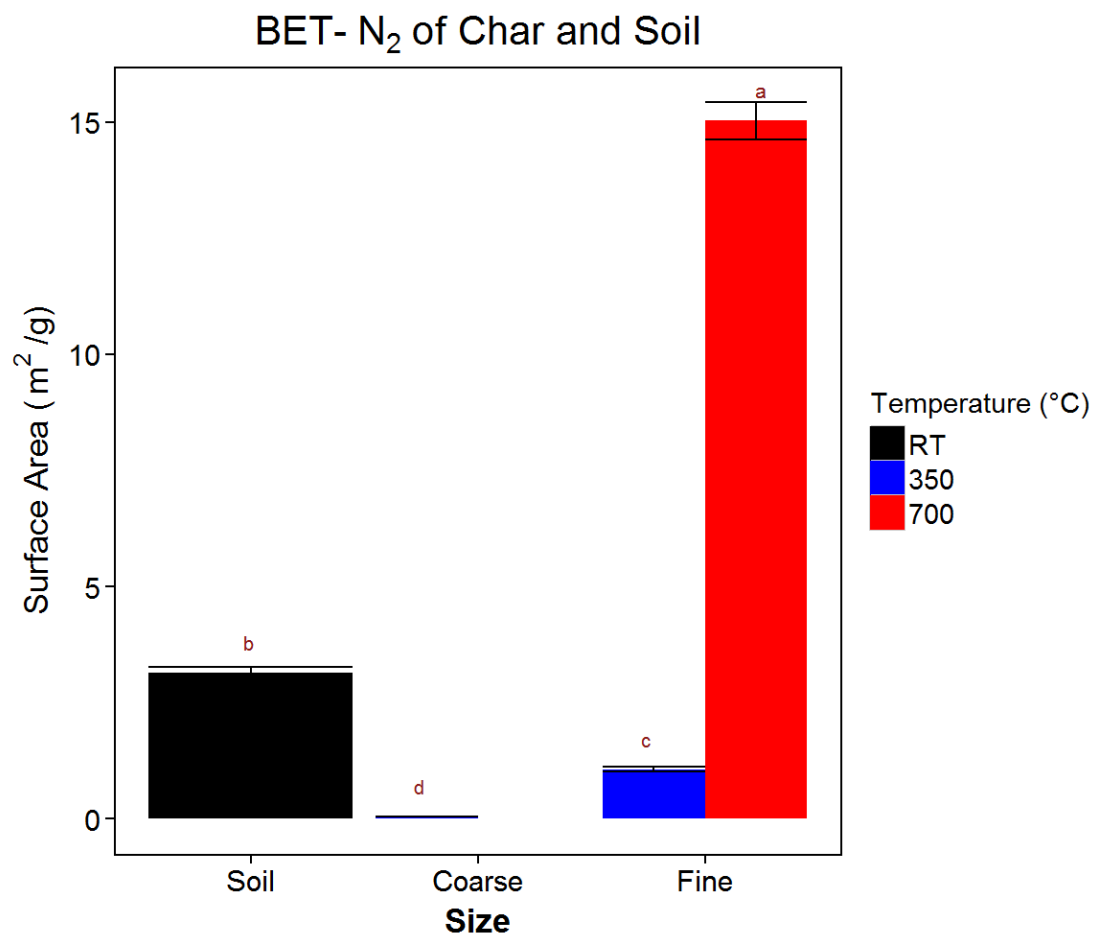


Figure 4-10 Specific surface area as determined by BET-N₂. Varied letters represent significant differences among means after conducting a Tukey's Honest Significant Difference test (n=3, p<0.05). Coarse char at 700°C was unable to be read by the BET-N₂ analyzer and has thus been omitted.

4.2 Soil Chemical Properties

4.2.1. Un-amended Soil

Properties of the collected un-amended arable soil are shown below in Table 4-5. The soil pH ranged whether de-ionized water or a 0.01M CaCl₂ solution was used, indicating that the soil may be slightly basic. Soil ECEC was 13.98±0.05 cmol/kg, with Ca²⁺ contributing most to its content of basic ions. The soil had a C weight percent of 1.32±0.01 and consisted of 0.13% N by weight.

Figure 4-10 shows soil surface area compared to that of both fine and course biochar at high and low temperatures. Soil surface area was greater than fine and course char at low temperatures, but 1/5 that of fine biochar at 700°C.

Table 4-5 Soil chemical properties

pH (DI)	pH (CaCl ₂)	Al cmol kg ⁻¹	Ca cmol kg ⁻¹	K cmol kg ⁻¹	Mg cmol kg ⁻¹	Na cmol kg ⁻¹	ECEC cmol kg ⁻¹	EC (dS/cm)	C (Wt.%)	N (Wt.%)
9.39 (0.01)	7.49 (0.07)	<0.01	7.89 (0.07)	2.37 (0.08)	3.17 (0.01)	0.86 (0.01)	13.98 (0.05)	2.00 (0.03)	1.32 (0.01)	0.13 (0.00)

4.2.2. Amended Soils

Amended soils consist of the soil-biochar mixtures that varied by pyrolysis temperature (350°C or 700°C), size (coarse or fine), and rate of application (10 t/ha or 60 t/ha). Tempe Cell experiment mixtures vary with temperature and application rate but size was held constant. Infiltration experiment mixtures vary with temperature, size, and rate of application.

4.2.2.1. Carbon and Nitrogen Contents

The C and N contents of biochar amended soils differed across increasing rates, temperature, and pre incubation versus post incubation (Infiltration and Tempe Cell). At low rate of application, C content peaked for 350°C char amended soils at 2.01 and 2.31 %C, for post-Tempe and Infiltration incubation. C content of mixtures amended with 700°C char had about 30% less %C than soils amended with 350°C char and were not significantly different from the %C of the control (as shown by a temperature of 0°C). The unincubated soil mixture had greater %C with 700°C char addition, possibly suggesting that the post incubated soil-char mixtures may have lost C from microbial activity. At a higher rate of application, a complete opposite trend was observed. Incubated soils increased in C content as high temperature biochar was added, while the unincubated mixture saw a sharp decline when amended with 700°C char. The increased C content of high temperature biochar amended soils may reflect the greater addition of high C containing char (see Table 4-2).

Changes in N concentration of soil biochar mixtures can be seen in Figure 4-12. The unincubated mixtures saw a slight increase in N concentration with biochar addition, although the temperature of the char had no significant difference. The %N in the Infiltration experiment (green) was on average higher than the %N of the Tempe Cell soil-char mixtures regardless of char temperature or rate of char addition. These results may suggest that biochar does not add significant amounts of N to soil.

The C:N ratios of the soil-biochar mixtures can be seen in Figure 4-13. Relative to the C:N ratios of the biochar alone where all had a ratio >70, C:N ratios of the soil-char mixtures were significantly lower and no mixtures exceeded a C:N ratio of 21.1 (pre-incubation 350°C soil-char mixture). With the exception of soil amended with 700°C char at 10 t/ha, all C:N ratios of incubated mixtures were observed to increase with biochar addition, suggesting that biochar added some C to the soil. This trend is validated by the increasing C concentration of soils amended with 60 t/ha of 700°C char in Figure 4-11, but has no bearing at 10 t/ha at either temperature.

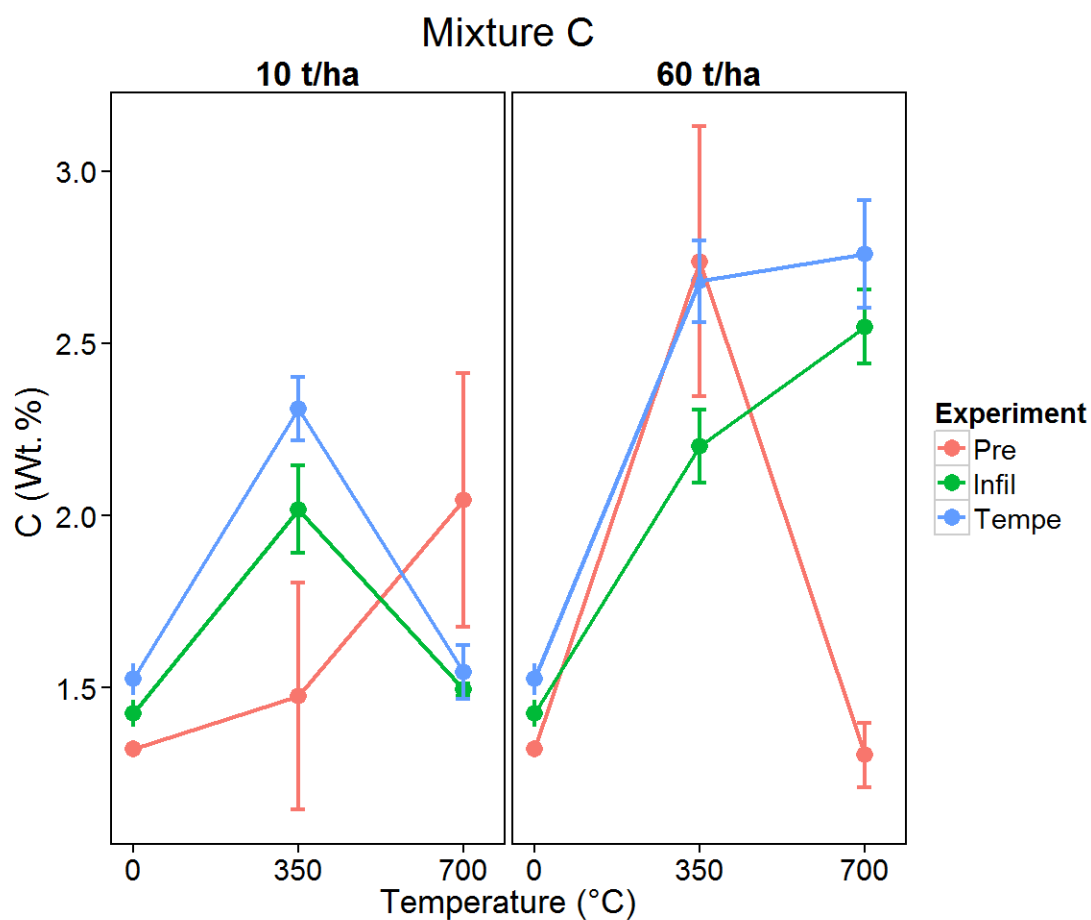


Figure 4-11 - Changes in C content of pre- and post-incubated soil-biochar mixtures. A temperature of 0°C represents the control soil, where no biochar was added. Lines represent the hydraulic experiment conducted, where "Pre" represents soil-biochar mixtures before incubation. Means are represented with standard error bars (n = 3).

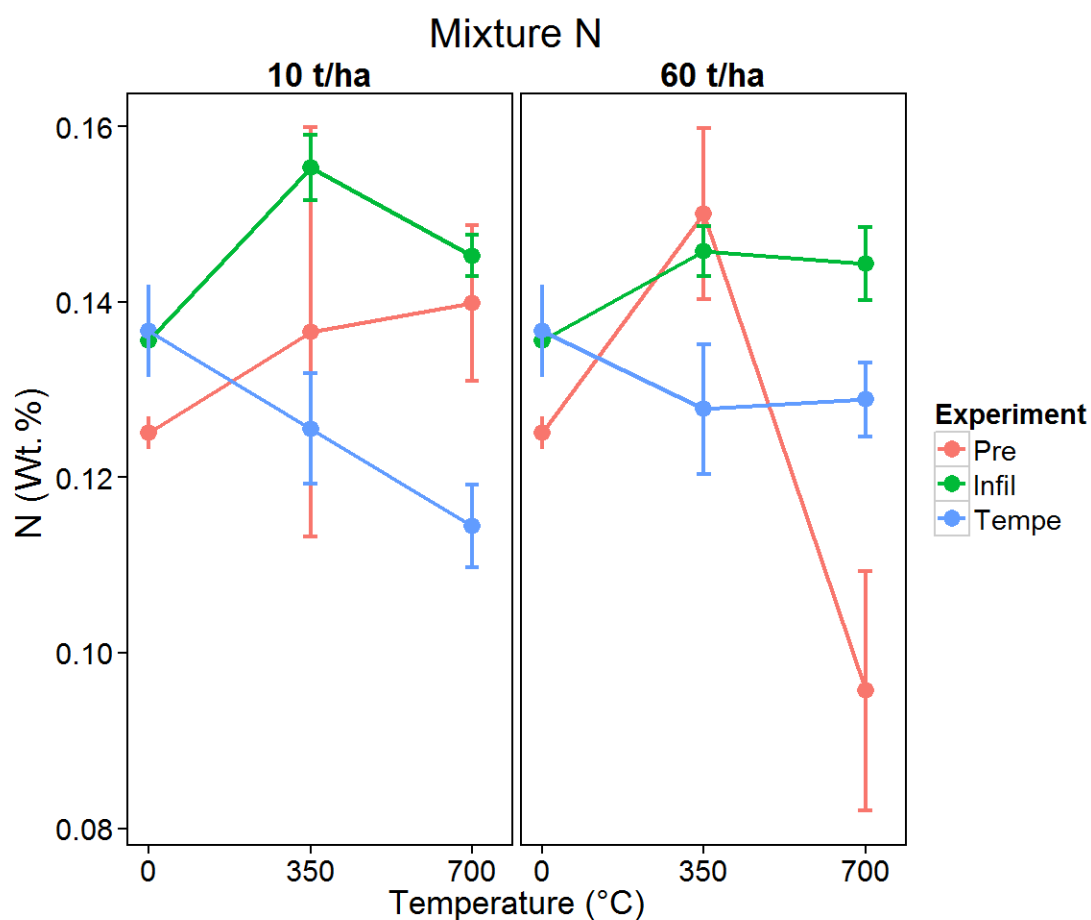


Figure 4-12 - Changes in N content of pre and post incubated soil-biochar mixtures. A temperature of 0°C represents the control soil, where no biochar was added. Lines represent the hydraulic experiment conducted, where "Pre" represents soil-biochar mixtures before incubation. Means are represented with standard error bars (n = 3). Means are represented with standard error bars (n = 3).

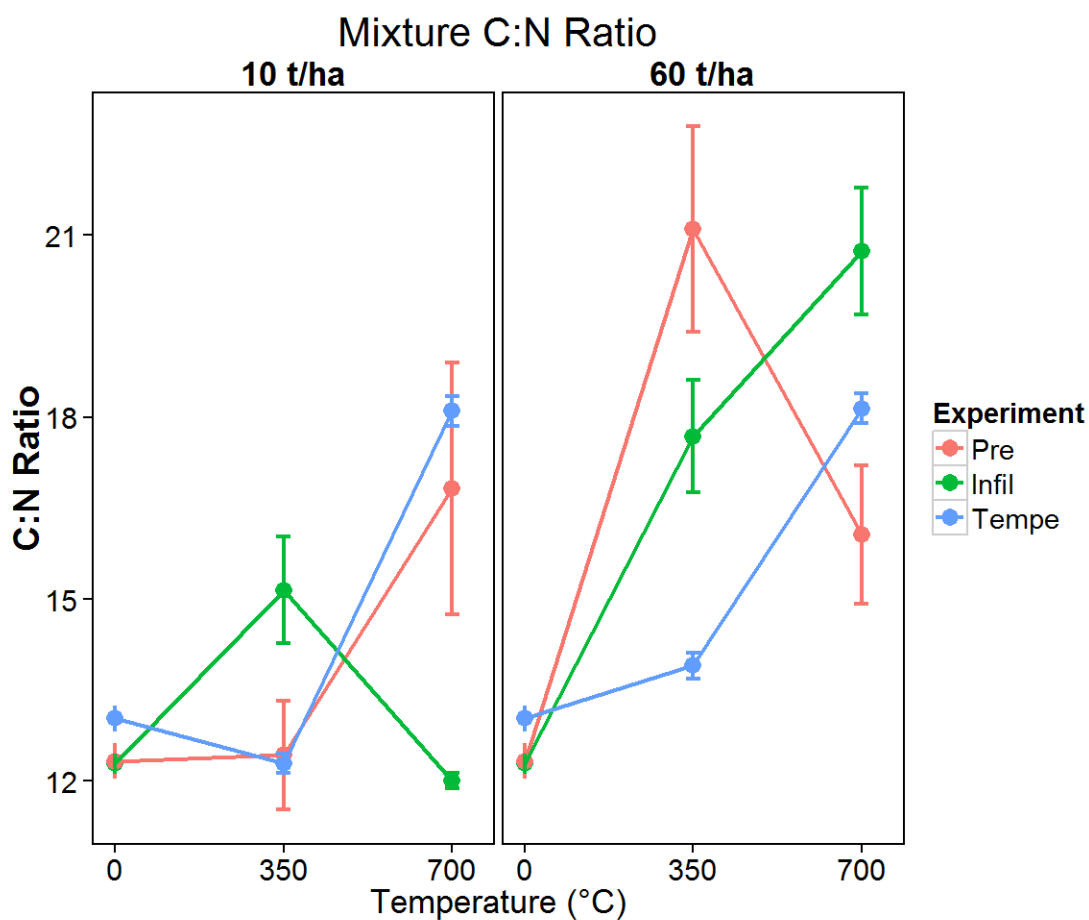


Figure 4-13 - Changes in the C:N ratio of pre and post incubated soil-biochar mixtures. A temperature of 0°C represents the control soil, where no biochar was added. Lines represent the hydraulic experiment conducted, where "Pre" represents soil-biochar mixtures before incubation. Means are represented with standard error bars (n = 3). Means are represented with standard error bars (n = 3).

4.2.2.2. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ Ratios

Biochar amended soil $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ stable isotope ratios are presented in Figure 4-14 and Figure 4-15, respectively. Unamended soils averaged -22.5‰ and became depleted of the heavier isotope with the addition of 350°C char. An even greater depletion was observed when adding 350°C char at a rate of 60 t/ha. The depletion of the heavier isotope in amended soils was likely due to the addition of a more depleted biochar, which had a ratio averaging -27.8‰ (Figure 4-4). Soils amended with high temperature biochar added at a low rate became more enriched (less negative), while at high rates, the mixtures remained more depleted. The soil-char mixtures likely remained depleted when biochar was added at high rates because the depleted biochar was more concentrated in the soil, reducing the ratio from ~23.5‰ (unamended) to ~25‰.

Without incubation, biochar $\delta^{15}\text{N}$ stable isotope ratios were observed to start at approximately 9.9‰ and become slightly more depleted of the heavier isotope with the addition of biochar; this trend is mirrored in mixtures from the Tempe Cell experiment, but at a relatively more depleted isotopic ratio (8.2‰). Conversely, mixtures containing 350°C char added at low rates became slightly more enriched (10.2‰). At a higher application rate, there was no significant change between additions of 350°C or 700°C char of the amended soil, but soils amended with 700°C from the Tempe Cell experiment became enriched. The enrichment of these soils follows the trend observed in the biochar alone (see Figure 4-5), where 700°C biochar was enriched by approximately 6‰ relative to 350°C char.

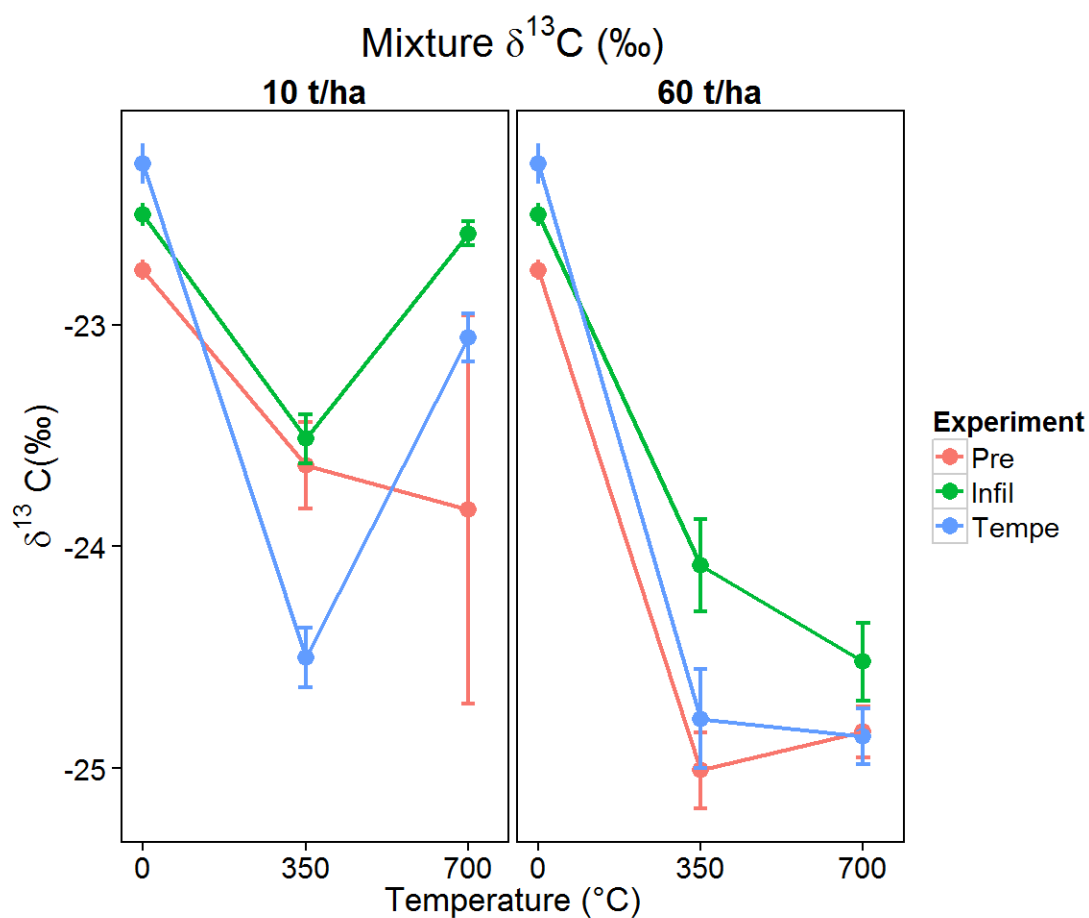


Figure 4-14 - Changes biochar C stable isotope tracings of pre and post incubated soil-biochar mixtures. A temperature of 0°C represents the control soil, where no biochar was added. Lines represent the hydraulic experiment conducted, where "Pre" represents soil-biochar mixtures before incubation. Means are represented with standard error bars (n = 3).

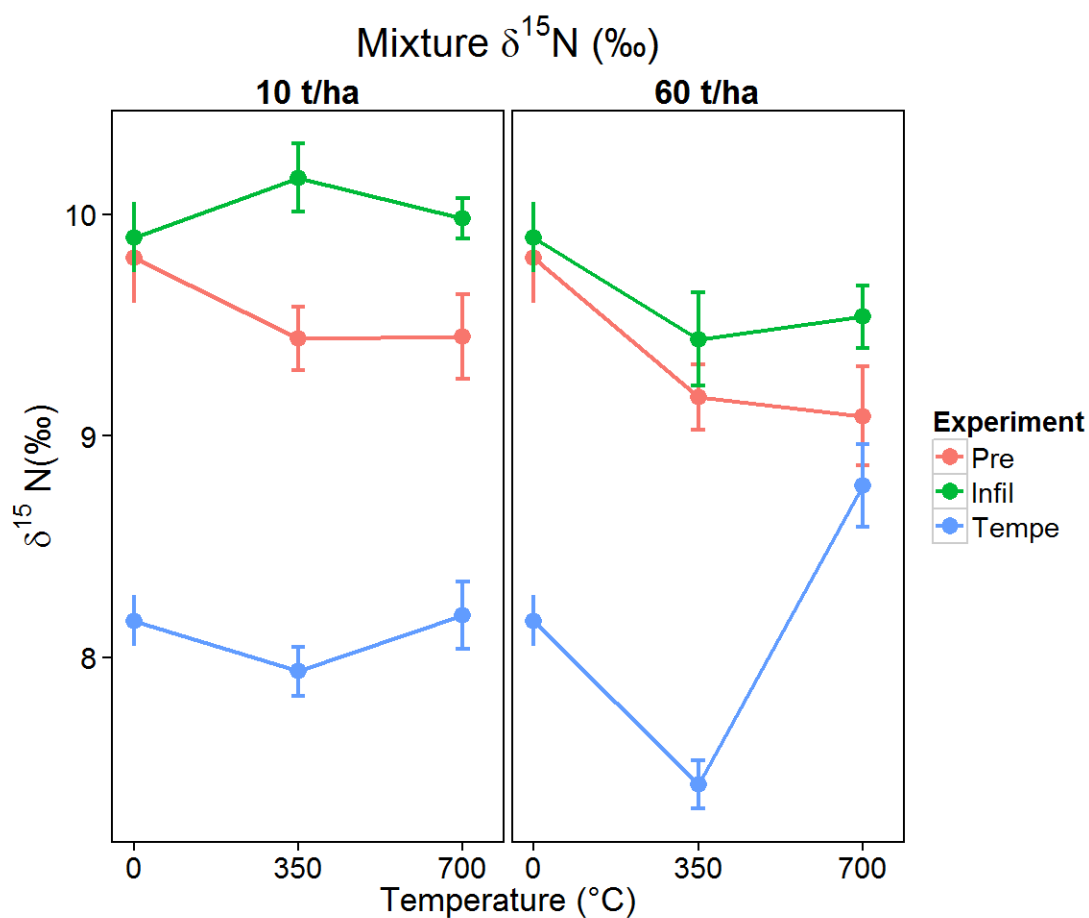


Figure 4-15 - Changes in biochar N stable isotope tracings of pre- and post-incubated soil-biochar mixtures. A temperature of 0°C represents the control soil, where no biochar was added. Lines represent the hydraulic experiment conducted, where "Pre" represents soil-biochar mixtures before incubation. Means are represented with standard error bars (n = 3).

4.2.2.3. Incubation CO₂ Flux

Carbon dioxide flux for experiments conducted in Tempe Cells and using the Infiltrometer are represented in Figure 4-16 and Figure 4-17, respectively. In the Tempe Cell experiment (Figure 4-16), there were no detectable significant differences between treatments (pyrolysis temperature and/or rate), although there was significance among all treatments over time (ANOVA, $F = 410.142$, $p < 0.001$). Soil amended with 60 t/ha of 700°C char contributed the greatest emissions (0.81 ± 0.08 g C-CO₂/g soil), whereas soils amended with 10 t/ha of 700°C char emitted the least at the final time point in the experiment (0.66 ± 0.04 g C-CO₂/g soil).

In the Infiltration experiment (Figure 4-17), significant effects were observed for the interaction between temperature, size, and time (ANOVA, $F = 3.588$, $p < 0.01$). Coarse char pyrolyzed at 700°C and amended at both rates had greater emissions than coarse char pyrolyzed at 350°C, whereas in the fine char fraction, 350°C char had greater emissions than soil amended with 700°C char. The greatest emission of carbon was observed for 350°C fine char at 60 t/ha at the end of the incubation period (1.72 ± 0.26 g C-CO₂/g soil). Coarse char pyrolyzed 350°C and added at 10 t/ha had the lowest emissions at the end of the incubation period, where 1.13 ± 0.09 g C-CO₂/g soil was released.

The release of carbon between both experiments was also significantly different (ANOVA, $F = 43.02$, $p < 0.001$). Across all treatments, excluding the fine char additions in the Infiltration experiment, Tempe Cell incubations released about 38% (350°C, 10 t/ha) to 56% (700°C, 10 t/ha) less g C-CO₂/g soil on average on the final day of the incubation period (day 63-64).

Isotope ratios of the emitted carbon for the last three time points (Day 36, 50, 64) of the Infiltration experiment are presented in Table 4-6. Ratios varied from approximately -21.51‰ (control; Day 36) to -19.18‰ (700°C, Coarse, 60t/ha; Day 64), with an overall average of -20.4‰. These values are enriched relative to the biochar ratios themselves, suggesting that microbes were not respiring biochar C. There were no significant differences of char addition over time for any treatment, with the exception of 700°C coarse char added at 60 t/ha, where day 36 was significantly different from day 64 (ANOVA, $F = 10.72$, $p < 0.05$).

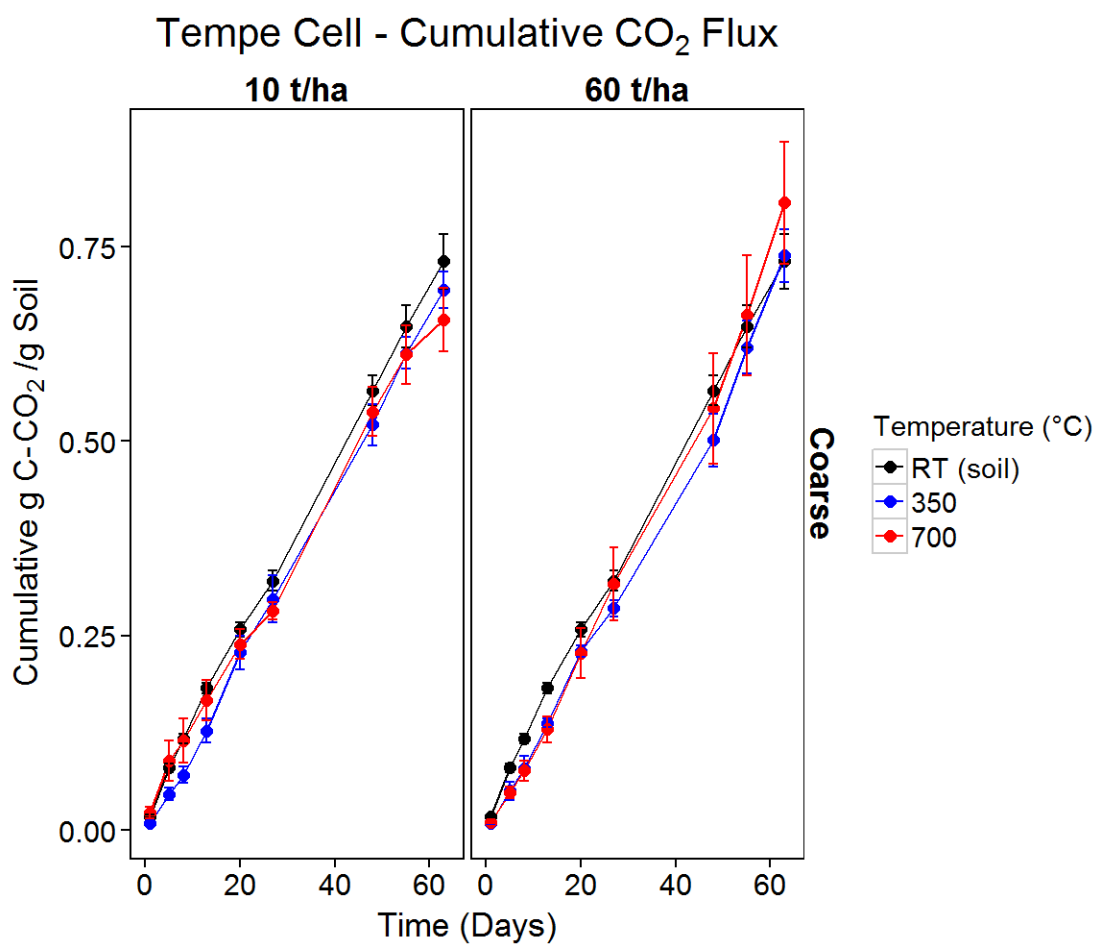


Figure 4-16 CO₂ flux from the Tempe Cell experiment after a 64 day incubation. The left and right panel represent treatments where char was added at rates of 10 t/ha and 60 t/ha, respectively. Only coarse char was added to this treatment, therefore no “fine” panel will be represented. Error bars show the standard error (SE) of the means (n = 3).

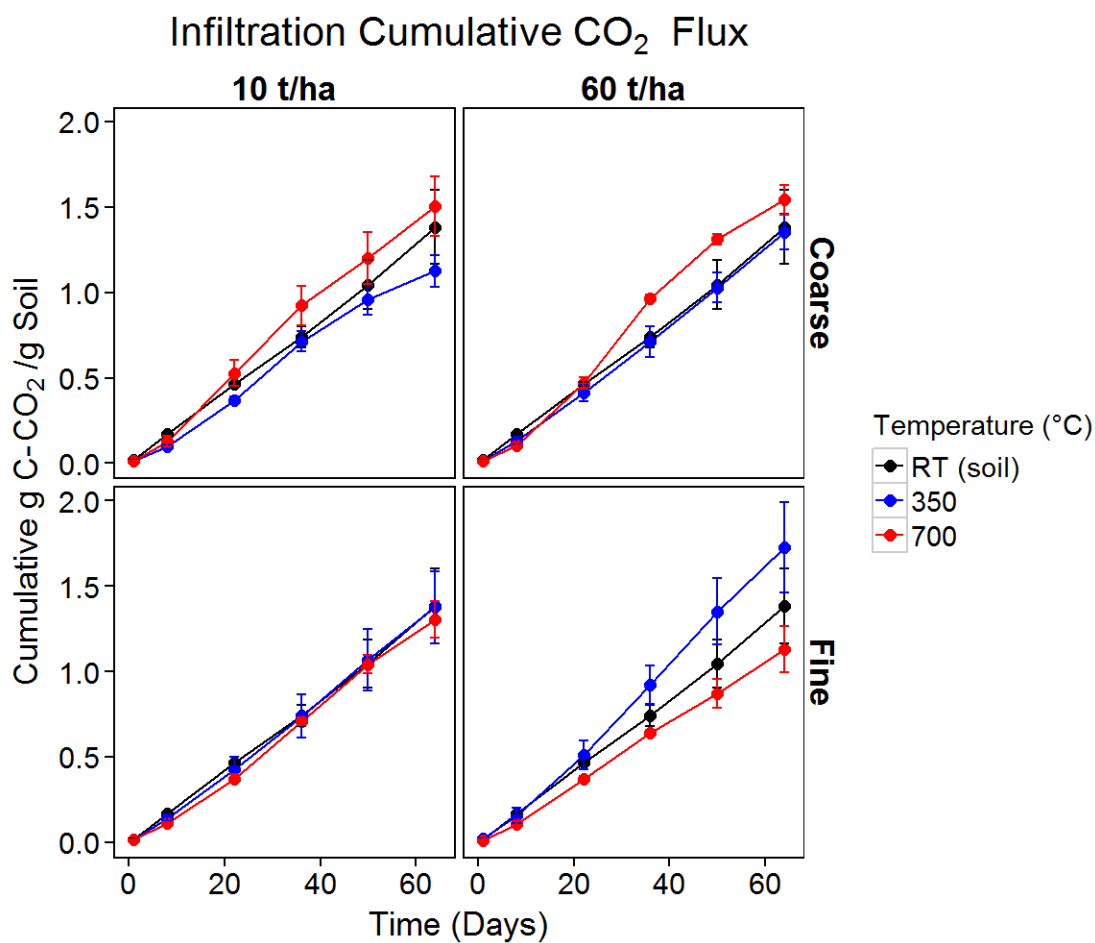


Figure 4-17 CO₂ flux measured from the Infiltration experiment after 64 days of incubation. Left panels show fluxes from 10 t/ha treatments, while right panels represent 60 t/ha treatments. Coarse and fine panels represent the char sizes added to a treatment. Error bars in all data panels represent the standard error (SE) of the means ($n = 3$).

Table 4-6 Infiltrometer experiment $\delta^{13}\text{C}$ ratios from CO_2 flux. Biochar additions include the varying biochar pyrolysis temperature, size, and rate of addition. Only the last three time points of the Infiltration incubation experiment are presented and available. The “N/A” label represents the control soil, in which no biochar was added. Average $\delta^{13}\text{C}$ ratios from CO_2 flux are presented with standard error values ($n = 3$). The only treatment that had a significant difference with the progression of time were the soils amended with 700°C coarse char added at 60 t/ha, as denoted by different letters. The presented letters are obtained from conducting a Tukey’s HSD post-hoc test, where different letters represent significant differences from each other ($p < 0.05$).

Biochar Additions				Day		
Experiment	Temperature ($^\circ\text{C}$)	Size	Rate (t/ha)	36 $\delta^{13}\text{C}$ (‰)	50 $\delta^{13}\text{C}$ (‰)	64 $\delta^{13}\text{C}$ (‰)
Infil	N/A	N/A	N/A	-21.10 (0.62)	-21.17 (0.63)	-20.47 (0.47)
Infil	350	Fine	10	-20.59 (1.15)	-20.71 (0.78)	-20.34 (0.53)
Infil	350	Fine	60	-21.51 (0.81)	-20.87 (0.65)	-20.53 (0.80)
Infil	350	Coarse	10	-19.68 (1.46)	-20.06 (0.73)	-19.97 (0.62)
Infil	350	Coarse	60	-19.84 (1.00)	-19.67 (0.65)	-19.78 (0.67)
Infil	700	Fine	10	-21.23 (0.84)	-19.89 (0.39)	-20.10 (0.44)
Infil	700	Fine	60	-21.28 (0.86)	-20.66 (0.76)	-20.44 (0.41)
Infil	700	Coarse	10	-20.92 (0.95)	-20.08 (0.59)	-20.59 (0.48)
Infil	700	Coarse	60	-21.41 a (0.44)	-19.58 ab (0.72)	-19.18 b (1.13)

4.3 Soil Physical Properties

4.3.1. Water Drop Penetration Time (WDPT)

Water drop penetration time of the soil biochar mixtures is reported in Table 4-7. No soil-biochar mixtures were observed to be strongly hydrophobic or repellent. Slight repellency, as indicated by a WDPT > 1 second, was observed for 350°C fine char added at a rate equivalent to 60 t/ha and the control soils in the Tempe Cell experiment.

Table 4-7 Water drop penetration time for soils and soil-biochar mixtures. The Tempe Cell experiment did not include any treatments with “Fine” char and is thus reported as N/A in the table. Measurements were conducted in duplicate after water contents were <0.1. Means and standard error are reported.

Material	Pyrolysis Temperature (°C)	Rate (t/ha)	Size	Infiltration WDPT (s)	Tempe Cell WDPT (s)
Soil	0	0	0	<1	4.5 (0.5)
Mixture	350	10	Coarse	<1	<1
Mixture	350	60	Coarse	<1	<1
Mixture	700	10	Coarse	<1	<1
Mixture	700	60	Coarse	<1	<1
Mixture	350	10	Fine	<1	N/A
Mixture	350	60	Fine	1.1 (0.01)	N/A
Mixture	700	10	Fine	<1	N/A
Mixture	700	60	Fine	<1	N/A

4.3.2. Saturated Hydraulic Conductivity (K_{sat})

Saturated hydraulic conductivity values for the Tempe Cell Experiment are visually depicted in Figure 4-18. The lowest K_{sat} was observed for the control at the start of the experiment ($3.44E-04 \pm 8.92E-5$ cm/s). The greatest K_{sat} was observed for soil amended with 350°C coarse biochar at 60 t/ha before incubation ($2.92E-02 \pm 2.92E-02$). However, there were no statistically significant effects of temperature, rate, or time on saturated hydraulic conductivity.

Infiltrometer hydraulic conductivity values are shown in Figure 4-19. Control measurements had a K_{sat} of $1.66E-04 \pm 6.51E-05$ cm/sec and $1.66E-04 \pm 6.41E-05$ cm/s at initial and final times, respectively. The greatest K_{sat} was observed for soil amended with 350°C coarse biochar at 60 t/ha before incubation ($8.18E-4 \pm 5.69E-05$

cm/s). Significant differences were observed between “Initial” and “Final” measurements (ANOVA, $F = 13.321$, $p < 0.0001$). Pyrolysis temperature was also observed to be significant among means, where soils amended with 350°C and 700°C char were significantly different from the control (ANOVA, $F = 10.31$, $p < 0.001$). The two pyrolysis temperatures, rate, and size had no statistically significant effects on saturated hydraulic conductivity.

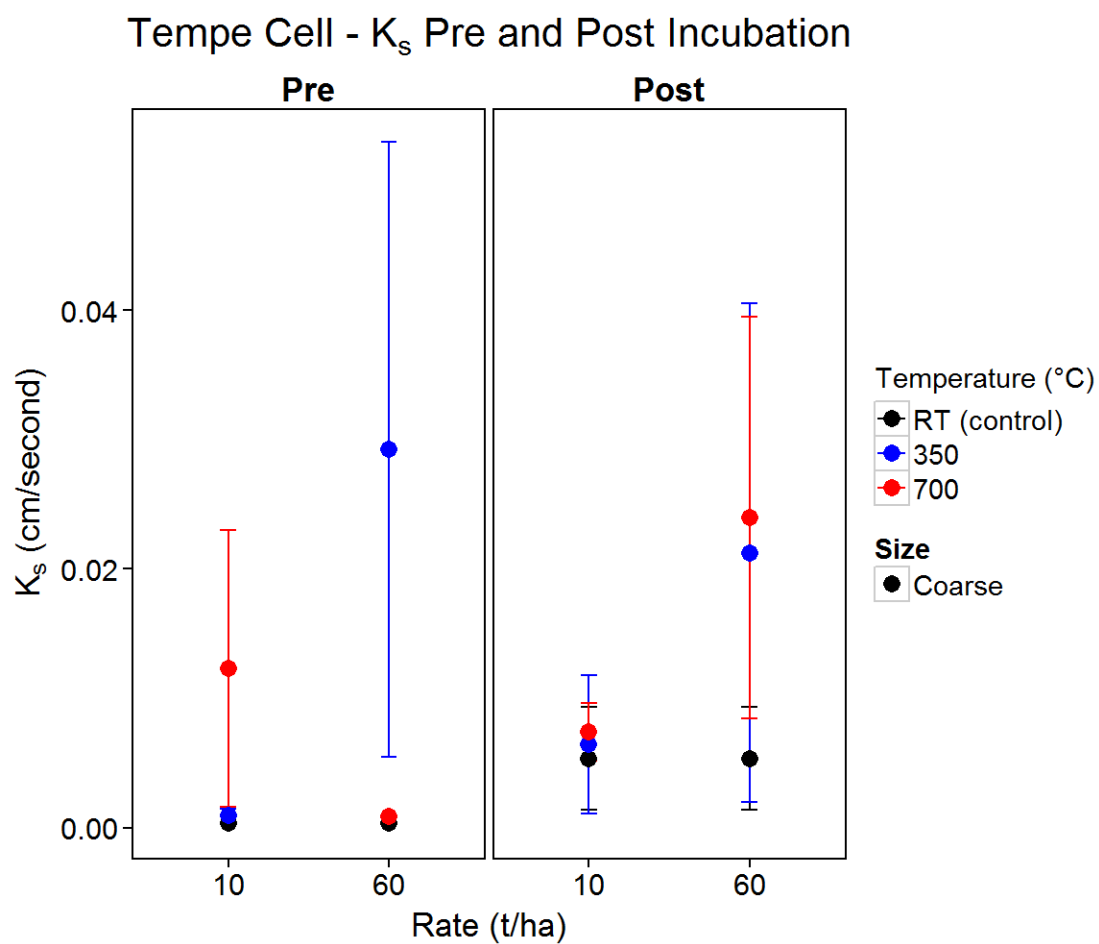


Figure 4-18 Tempe Cell hydraulic conductivity determined by inverse modeling in HYDRUS 1D. Means and standard errors are presented (n=3). Controls (black) are shown in each rate category for comparison against other treatment values, but are not associated with any rate.

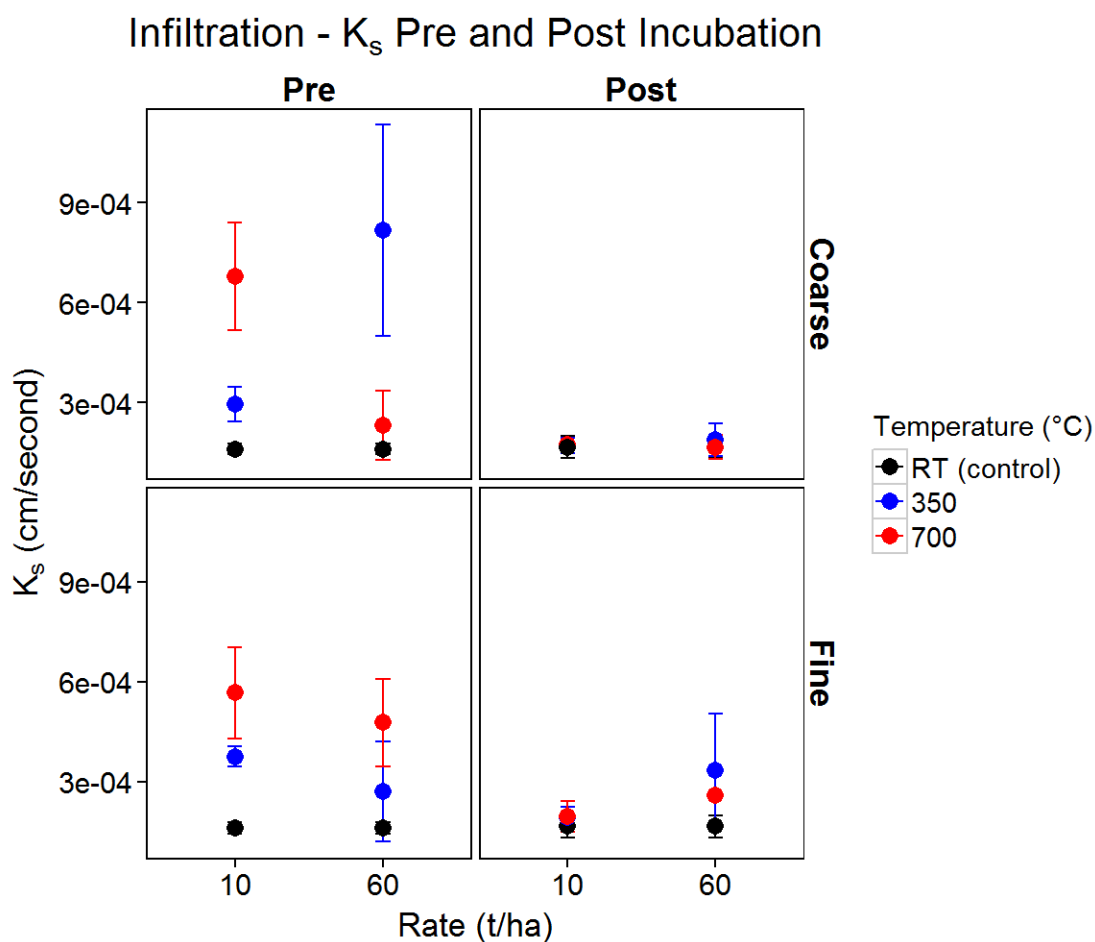


Figure 4-19 Infiltration experiment hydraulic conductivity as determined using Decagon Devices, Inc. macrosheet. Means and error bars are presented (n =3). Controls (black) shown in each rate category, but are shown for comparative purposes against the treatments. The x-axis facet (left/right) demonstrate measurements conducted before and after incubation, while the y-axis facet separates the biochar size fractions.

4.3.3. Water Retention Curve

The water retention curve generated from the Tempe Cells is shown in Figure 4-20. There is a general reduction in water retained with an increase in temperature and rate as time progressed. The most reduced water content was observed at time C, in soils amended with 60 t/ha of 700°C char (11% loss in water relative to the control; 0.38 ± 0.007). Volumetric water content at field capacity (θ_{fc}) was used to determine change across all WRCs and is shown in Table 4-8. At time A (before incubation), temperature and/or rate had no significant effects ($p < 0.05$) on water retention. At time B (during incubation), soils amended at a rate of 10t/ha were significantly different from 60 t/ha amended soils (ANOVA, $p < 0.05$). At time C (after incubation), both temperature and rate had significant effects on θ_{fc} (Temperature: ANOVA, $F=25.741$, $p < 0.001$; Rate: ANOVA, $F=18.122$, $p < 0.001$). Across the entire data set, there was a significant effect of time on water retention (ANOVA, $F=35.140$, $p < 0.001$). The α shape parameter (related to air-entry pressure) was observed to significantly increase with an increase in time, rate, and temperature as is observed in Table 4-8. The n parameter (related to pore distribution) was not observed to change across time, temperature, or rate, while saturated water content was observed to increase with increasing temperature and application.

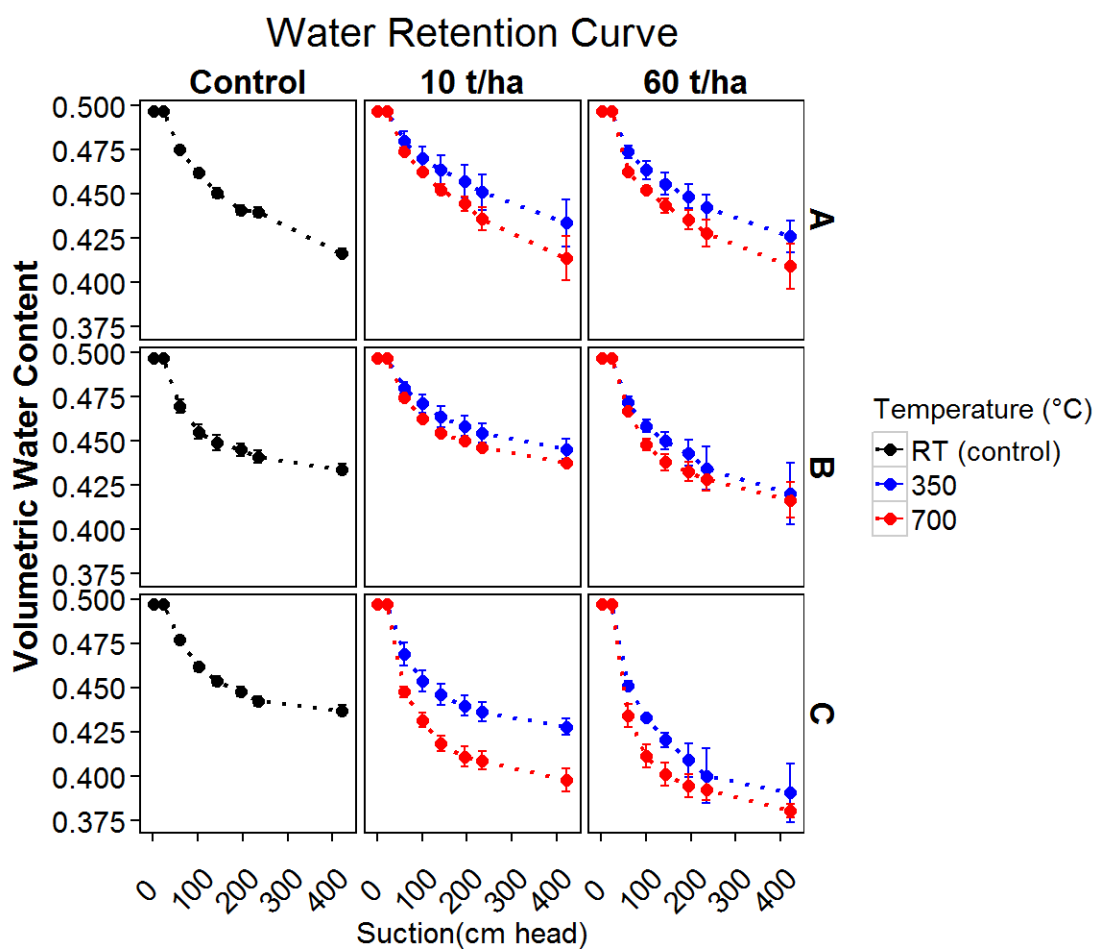


Figure 4-20 Water retention curve generated from Tempe Cells. Time "A", "B", and "C" correspond to before, during, and after an incubation period of 64 days. The facet on the x-axis describes increasing rates of char added, where "0", "10" and "60" correspond to 0, 10t/ha, and 60 t/ha, respectively. Means are shown with standard error bars (n=3).

Table 4-8 Fitted Van Genuchten parameters and volumetric water content at field capacity for Tempe Cell biochar amended soils. Time A, B, and C correspond to before, during, and after the incubation period, respectively. Columns containing “N/A” are controls, with no biochar addition. θ_r and θ_s are the residual and saturated water contents (cm^3/cm^3), respectively; α is related to the inverse of the air-entry pressure (cm^{-1}); n is related to the pore-size distribution (dimensionless). θ_{fc} is the water content at field capacity (100 cm head).

Time	Temp	Rate	Size	θ_r	θ_s	α	n	θ_{fc}
A	N/A	N/A	N/A	0.000 a	0.501 def	0.009 b	1.102 a	0.463 a
A	350	10	Coarse	0.000 a	0.500 f	0.007 b	1.087 a	0.472 a
A	350	60	Coarse	0.000 a	0.501 def	0.012 ab	1.082 a	0.465 a
A	700	10	Coarse	0.000 a	0.500 ef	0.009 b	1.122 a	0.464 a
A	700	60	Coarse	0.000 a	0.502 def	0.018 ab	1.095 a	0.455 ab
B	N/A	N/A	Coarse	0.000 a	0.502 de	0.032 ab	1.056 a	0.460 a
B	350	10	Coarse	0.000 a	0.500 ef	0.016 ab	1.056 a	0.472 a
B	350	60	Coarse	0.000 a	0.501 def	0.017 ab	1.092 a	0.461 a
B	700	10	Coarse	0.000 a	0.501 def	0.025 ab	1.056 a	0.465 a
B	700	60	Coarse	0.000 a	0.503 bcd	0.024 ab	1.079 a	0.453 ab
C	N/A	N/A	Coarse	0.000 a	0.502 def	0.021 ab	1.061 a	0.465 a
C	350	10	Coarse	0.000 a	0.502 cde	0.027 ab	1.066 a	0.458 a
C	350	60	Coarse	0.000 a	0.505 abc	0.028 ab	1.116 a	0.438 bc
C	700	10	Coarse	0.000 a	0.505 ab	0.032 ab	1.090 a	0.437 bc
C	700	60	Coarse	0.000 a	0.506 a	0.036 a	1.104 a	0.423 c

4.3.4. Water Stable Aggregates

Water stable aggregate results from the Tempe Cell experiment are shown in Figure 4-21. Soil amended with char added at 60 t/ha was slightly greater than char added at 10 t/ha. Rate was the only factor with statistically significant means (ANOVA, $p < 0.05$). Relative to the control, char added at higher rates increased aggregate stability by approximately 5.3% and 3.8% for 350°C and 700°C char, respectively.

Figure 4-22 shows the percent water stable aggregates from the Infiltration experiment. Overall, pyrolysis temperature had significant effects relative to the control (350°C: ANOVA, $p < 0.001$; 700°C: ANOVA, $p < 0.05$), although the trend was not consistent between both char sizes. An increase in pyrolysis temperature and rate increased aggregate stability in the coarse char fraction, but reduced aggregate stability in the fine char fraction. The greatest water stable aggregate content was found in the control ($76.19 \pm 1.56\%$) and soils amended with 60 t/ha of coarse 700°C char ($75.79 \pm 1.65\%$). The remainder of the treatments reduced aggregate stability by 5% (700°C coarse char applied at 10 t/ha) to 21% (700°C fine char applied at 60 t/ha).

Both experiments were also noted to be significantly different from each other (ANOVA, $F = 79.94$, $p < 0.001$). Only the coarse fraction was analyzed because both experiments shared the coarse treatment (fine char was not added in the Tempe Cell experiment). On average, the Infiltration experiment had about 11% (700°C, 60 t/ha) to 40% (350°C, 60 t/ha) less water stable aggregates than the Tempe Cell experiment.

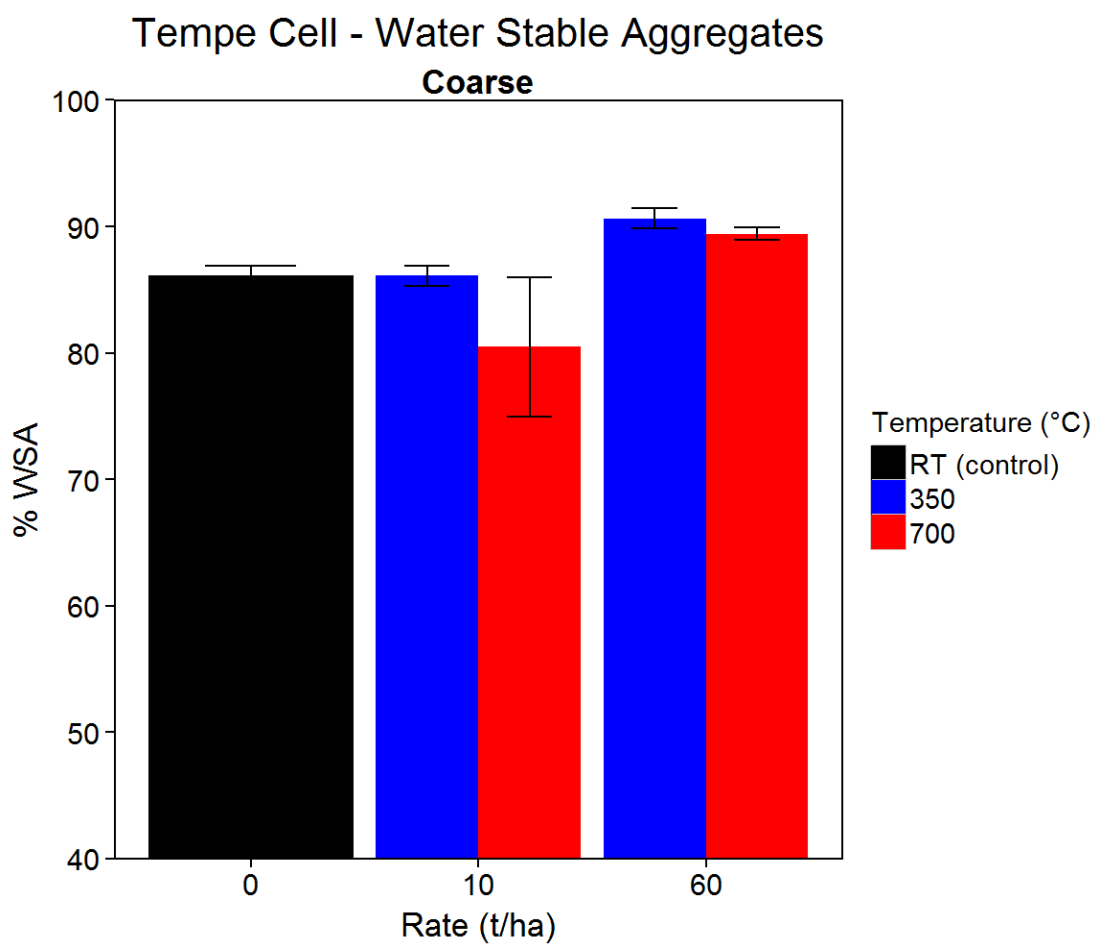


Figure 4-21 Tempe Cell experiment percent water stable aggregates (%WSA). Bars represent means with standard error bars (n=3). Bars with the same letters are not significantly different at $p < 0.05$ using Tukey's Honest Significant Difference (HSD) test.

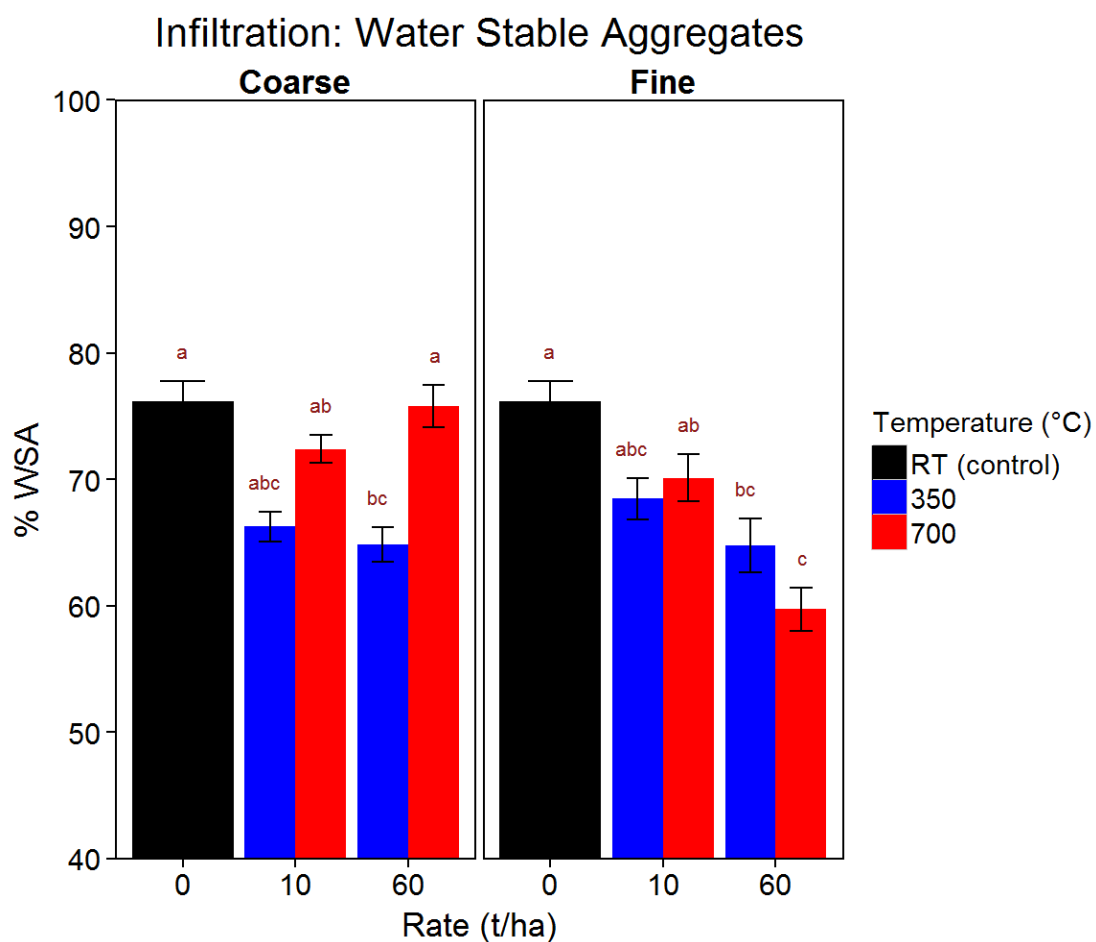


Figure 4-22 Infiltration experiment percent water stable aggregates (%WSA). Bars represent means with standard error bars (n=3). Bars with the same letters are not significantly different at $p < 0.05$ using Tukey's HSD.

CHAPTER 5. Discussion

Here, main findings of this study are re-presented and discussed. The main findings of this experiment include distinctive changes in biochar quality primarily mediated by an increase in pyrolysis temperature, reductions in water retention at the end of a 63-64 day incubation period, and a change in soil structure (aggregation) that varied with experiment type.

5.1 Biochar Quality

Biochar yield was greatest at a lower pyrolysis temperature as shown in Table 4-1. Pyrolysis was observed to recover approximately 33% to 18% of the original biomass as pyrolysis increased from 350°C to 700°C, respectively. Almond shell biochar yields of around 30-40% between 300-400°C have been observed by other studies using almond residues as feedstock (Gonzalez et al. 2005). Greater recovery is attributed to a reduced loss of volatiles (CH_4 , H_2 , and CO) relative to char produced at higher temperatures (Novak et al. 2009). With increasing temperature, there was an increase in moisture loss, ash, and fixed C, while volatile matter loss from the proximate analysis was highest in the 350°C char. These trends have been confirmed by other studies (Antal & Grønli 2003; Keiluweit et al. 2010; Cantrell et al. 2012). A reduced volatile matter loss from the proximate analysis indicates that more volatile matter was lost during the pyrolysis process, producing a greater content of fixed carbon as a result.

The pyrolysis process also created higher contents of C and N, while simultaneously reducing the O and H contents (in weight percent). N was observed to be conserved in biochar, with the exception of 700°C char from the Infiltration experiment. Similar results were obtained in a study by Gaskin et al. (2008) and Almendros et al. (2003) for pine nuts/peanut hulls and peat, respectively. The conservation was attributed to N incorporation into aromatic and heterocyclic structures as temperature increased ((Gaskin et al. 2008; Almendros et al. 2003). Despite a higher content of N, carbonization of N may make it unavailable for plants (Knicker et al. 2005; Gaskin et al. 2008). C:N ratios relatively high in this study, with higher C:N ratios in the coarse fraction. This suggests greater immobilization of N by microbes during biochar decomposition, reducing N availability for plants (Sullivan & Miller 2001). Relative to the raw feedstock, 350°C char lost an average of 33% H

and 700°C char lost approximately 80% H. Similar losses in H have been reported elsewhere (Cantrell et al. 2012). O losses followed a similar trend, where an average of 39% O and 76% O was lost for 350°C and 700°C char, respectively.

O:C ratios have been suggested as a reliable measure of stability and half-life (Spokas 2010; Hedges et al. 2000). Our study saw a reduction in O:C ratio with increasing temperature, where raw almond residues were 0.56 and 350°C and 700°C char averaged 0.22 and 0.08 respectively. The O:C ratios describing different forms of black carbon, including biochar, range from 0.0 to 0.6, as is observed in Figure 5-1. Char produced within this range has been proposed correspond to half-lives ranging from 100 to 1000 years, indicating that the char produced in this study are relatively stable carbon products (Mimmo et al. 2014; Spokas 2010). Although our almond residue O:C molar ratio is within the 0 to 0.6 range, the separation values are not static and vary with the biomass utilized; peach pit and fir biomass were observed to have a similar O:C ratios, despite being uncharred (Spokas 2010).

O:C ratios are also used as indicators of hydrophobicity. As previously mentioned, the O:C ratios of char in this study were reduced, implying an increased hydrophobicity as temperature of pyrolysis was increased. A reduction in the O:C ratio suggests losses of surface polar functional groups that contribute to hydrogen bonding and, thus the attraction to water. Hydrophobic char also contains a lessened capacity to capture and retain nutrients (Yam et al. 1990). A combination of both these characteristics may generate char less capable of water storage and nutrient holding capacity, reducing its usefulness as a soil amendment, especially in sandy soils. However, studies provide evidence that biochar created under 700°C is rapidly oxidized in soil, creating a more negatively charged environment to attract cations and reduce hydrophobicity (Cheng et al. 2008; Nguyen et al. 2010).

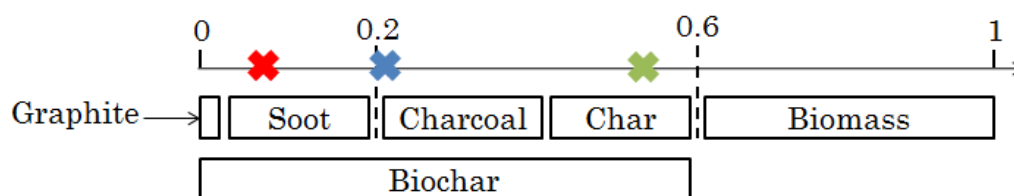


Figure 5-1 Oxygen:Carbon (O:C) molar ratios corresponding to the black carbon continuum. An O:C ratio of 0 is indicative of graphite, while 0.6 and beyond is typical of uncharred biomass. Biochar encompasses all forms of black carbon with O:C molar ratios below 0.6. The red, blue and green 'x' denote where our 700°C, 350°C, and raw almond residue lie along the continuum. This figure was modified from Spokas and others (2010).

An H:C ratio can be used estimate the content of H-C bonds, graphene clusters, and resulting stability of biochar (Ronsse et al. 2013). Our results show a declining H:C ratio with increasing temperature, where 350°C char has an average H:C of 0.78 and

700°C char averages 0.21. Our values are comparable to wood biochar produced at 300°C and 750°C in a study by Ronsse et al. (2013), in addition to other studies by Keiluweit et al. (2010), Schimmelpfennig and Glaser (2012), and Sun et al. (2012). The lower the ratio, the more graphene-like and stable the char is assumed to be. A biochar H/C ratio averaging 0.3 has been noted to be associated with condensed aromatic ring structures and pyrolysis temperatures ranging 500-1000°C; ratios greater than 0.7 are associated with the presence of non-condensed aromatic structures (Hammes et al. 2006; Mimmo et al. 2014). Because there is a declining content of hydrogen as a function of pyrolysis temperature and a coinciding increase in fixed C, heating likely removes a greater content of volatiles containing H.

A combination of O:C and H:C ratios have been suggested to be a proxy for the stability and carbonization of biochar (Schimmelpfennig & Glaser 2012). High stability and carbonization of biochar are proposed to occur with O:C ratios < 0.4 and H:C ratios < 0.6. This study presents biochar with O:C ratios under 0.4 (350°C – 0.22, 700°C – 0.08); however, H:C ratios of 350°C char were all observed to exceed the proposed H:C ratio (Table 4-2). As previously mentioned, H:C ratios above 0.7 may suggest the presence of non-condensed aromatics that were unable to be thermally converted at 350°C (Mimmo et al. 2014). This suggests that pyrolysis at 350°C maintains more structural similarity to the uncharred almond biomass than char produced at 700°C. The Van Krevelen plot (Figure 4-7) elucidates the trend of increasing carbonization with increasing temperature.

The stable C, N and H isotope composition varied across temperature and the experiment the samples underwent. The C ratio of uncharred almond residue was -27.6‰ and became depleted as pyrolysis temperature was increased to 350°C. High temperature char in the Tempe Cells became slightly enriched, but was not significantly different from 350°C char. Depletions and enrichments were all within ca. 2‰, which has been reported in the literature (Ascough et al. 2008; Turney et al. 2006). The “Pre” char, which was unincubated, showed no significant change from raw almond feedstock to char pyrolyzed at 350°C or 700°C, suggesting that thermal degradation has minute effects on the C isotope fractionation in char. Similar conclusions were derived in studies by Czimczik et al. (2002) and Schleser et al. (1999) for wood, where charring above 340°C had minor changes. In contrast to pyrolysis temperature, incubation seems to have a greater impact on $\delta^{13}\text{C}$ changes. Microbial preference for the lighter isotope can be a possibility the slight depletion of $\delta^{13}\text{C}$ seen for low temperature char in Figure 4-4 that was greater for the Tempe Cell incubated char. Biochar decomposition has been reported by Kuzyakov et al. (2009), where grass biochar (200-400°C) was found to have a decomposition rate of 0.5% biochar/year. However, microbial mineralization was likely not occurring as $\delta^{13}\text{C}$ from CO_2 was observed to have an isotope ratio of -20.4‰ on average, more exact values of which can be observed in Table 4-6. Biochar uptake would have presented $\delta^{13}\text{C}$ - CO_2 ratios that were relatively more depleted if microbes were respiring C from biochar, but they are slightly more enriched than soil (-23.3‰). It is most likely that our samples were soil ‘contaminated’, as our char pieces were picked directly from sample cells and not thoroughly dusted prior to measurement. Soil had an isotopic ratio of -23.3‰, which is more enriched relative to the unincubated char pieces (ca. -

27.6‰). The mixing of the isotope ratios may explain why the incubated mixtures had ratios more depleted than char that was unincubated (“Pre”).

The N stable isotope was observed to become enriched (loss of light N) with pyrolysis temperature, where the greatest jumps were found for 700°C char relative to the original almond feedstock. High temperature char from both incubation treatments were also found to be enriched by ca. 5‰ relative to their unincubated counterparts, suggesting an effect from incubation. However, similar to what was observed in the C isotope, the char analyzed may have had been affected by N isotopic ratios from soil, which was 8.15‰. Despite this, there was still an apparent slight enrichment in 700°C unincubated char (“Pre”), which was not exposed to soil. In a study by Huber and others (2013), they found that charred organic matter material after fire was also slightly enriched, attributing the enrichment to combustion discrimination against the heavier isotope. On the other hand, others have reported that cereal grain feedstock charred up to 300°C had unchanged N isotopic composition from the original feedstock (Bogaard et al. 2007; Aguilera et al. 2008; Bird & Ascough 2012). The discrepancy in results may be a function of the low N content of char, as the low N content of char warrants a greater level of uncertainty (Bird & Ascough 2012). It is also possible that there was a loss of lighter isotopes from leaching induced by the hydraulic experiments, as a more enriched isotope ratio is present after exposure to hydraulic experiments (Figure 4-5).

H isotope had the most consistent trend across the isotope analysis. The starting almond feedstock had a ratio of ca. -60‰. As pyrolysis temperature increased to 350°C, the δD ratio became more negative, indicating a depletion of the heavy H species. The cause of this depletion is unclear, although it may be related to the rapid H exchange that occurs on organic molecules, where a heavy H may be exchanged for a light H. The presence of hydroxyl and carboxyl groups still present on 350°C char (See Figure 4-8) may suggest this, as these H-bound functional groups can exchange rapidly at room temperature (Schimmelmann et al. 2006). Sessions and others (2004) reported that organic H could be depleted in D by 50-300±100‰ as a function of this exchange. Char pyrolyzed at 700°C significantly shifted, becoming less negative. The enrichment of D (loss of lighter H) in 700°C char may be attributed to a combination of volatile matter loss and moisture loss (see Table 4-1); 700°C char had greater contents of moisture loss relative to 350°C char, thus possibly fractionating from evaporation loss. Lighter H isotopes are preferentially lost in volatilization and evaporation because of their lower molecular weight, thus leaving the residual matter (char) D-enriched (Schimmelmann et al. 2006). Microbial uptake may be able to explain the differences between “Pre”, “Tempe”, and “Infil.” Biochemically, microbes prefer to take up the lighter isotope and thus leave the heavy isotope, enriching the remaining matter (Schimmelmann et al. 2006). Because the general overall trend was consistent whether incubated in soil with microbes or not (see Figure 4-6), this suggests that microbial fractionation did not have as significant an impact on D fractionation as temperature did. There is a scarcity of studies looking at H isotopes in pyrogenic/black carbon and char. Cheng and others (2006) measured the δD of black locust char (350°C; 6 hours) and found a ratio of -110.7 for unincubated char, which was similar to our 350°C almond residue

char. Unlike our study, they found that incubated char became enriched (less negative), which became more pronounced as their incubation temperature increased (Cheng et al. 2006). However, they offered no explanation to this result, as the study was more geared towards effects of oxidation. This topic is heavily understudied in biochar and/or pyrogenic carbon, as the studies cited to explain my results were looking at isotope fractionation in fossil fuels. The knowledge deficit is attributed to the difficulty in analyzing H isotope results because H is easily exchanged with an external source (Schimmelmann et al. 2006). A review on isotopes in pyrogenic carbon by Bird and Ascough (2012) report no studies on H isotopes in pyrogenic carbon, stating that the topic remains in its “infancy.” This statement emphasizes the need for further studies on H isotopes in black carbon.

The pH of the char also increased with increasing pyrolysis, increasing from 4.78 as raw biomass to 9.77 and 12.42 for 350°C and 700°C, respectively. The increase in pH has been well documented (Mimmo et al. 2014; Ronsse et al. 2013). Ronsse and others (2013) speculate that at higher pyrolysis temperatures there is a deprotonation of carboxyl (-COOH) groups resulting in a greater content of basic ions in solution; however at lower pyrolysis temperatures, more oxygenated and protonated carbon is available, creating less basic conditions. A more alkaline pH may also be due in part to the ash content of char. Both pH and ash content increased as a function of temperature (Table 4-1).

Surface Area

Biochar surface area is often a measure associated with a biochar's effectiveness in a soil. A greater surface area provides greater opportunity for chemical activity, including cation exchange capacity and adsorption, and implies greater porosity, thus also having implications in soil water flow and storage. As determined by BET-N₂ sorption analysis, the surface area of our char was observed increase with increasing temperature for the fine fraction; our highest char value was 15.02±0.40 m²/g for 700°C fine char. This trend is supported in a study lead by Lua and others (2004), who found that temperature of pyrolysis had the most significant effect on surface area. Greater surface area is observed with an increase in temperature because a greater content of volatiles are lost during thermal conversion as a function of temperature, forming pores in the resulting product (Zabaniotou et al. 2008). Lower pyrolysis biochars are speculated to have lower surface area because volatiles condensate at this temperature, clogging pores (Pignatello et al. 2006). Temperature dependency cannot be elucidated for the coarse fraction because results for 700°C char were unable to be obtained. Few studies have analyzed the efficacy of almond shell residue biochar. Another study reporting slow-pyrolysis almond residue biochar reported BET-N₂ surface area of 2±2 m²/g at a residence time of 60 minutes, as was conducted in this study (Thomas Klasson et al. 2014). The same study observed a significant increase in surface area ranging from 201±9 to 493±40 m²/g when increasing residence time to 240 minutes for ash-containing and ash-less biochars (Thomas Klasson et al. 2014). This study suggests that the residence time of our char may have been insufficient to form enough micropores that contribute significantly to surface area. Other authors using almond shells

have reported 4.9 to 133.1 m²/g surface areas for 850°C char at different residence times (Marcilla et al. 2000). Gonzalez and others (2005) found surface areas of 6 m²/g, 93 m²/g, 78 m²/g, 20 m²/g for fast pyrolysis almond residue chars produced at 500°C, 600°C, 700°C, and 800°C, respectively. Keiluweit (2010) looked at wood-based slow pyrolysis char (1 hour residence time) and reported a surface area of 392±11 m²/g and 347±11 m²/g for 600°C and 700°C, respectively. This study, despite having similar pyrolysis peak temperature and residence time, had a surface area 26 times greater than the surface area reported in our study, pointing to the importance of feedstock chosen for biochar creation (Keiluweit et al. 2010). The previous almond shell studies mentioned also suggest that duration of heating has a significant role in determining the extent of biochar surface area, more so for almond residues and less so for wood-based biochars.

Surface area is typically measured using BET-N₂ adsorption analysis. While this method is widely used, its use alone is not sufficient to provide an accurate picture of surface area and has been noted to be unreliable (McLaughlin et al. 2012). Brewer and others (2014) emphasize caution when choosing a method of surface area analysis because biochar pores, the primary contributors to surface area, span five orders of magnitude (sub-nano to several microns). BET-N₂ gas adsorption captures micro and meso-pores (<2 nm-50nm), and thus do not provide a full measure of biochar porosity. Additionally, it does not provide a good measure of pore diameters useful for plant available water and water flow, which is found in pores greater than 0.1µm (Brewer et al. 2014). Brewer and others (2014) suggest using pyconmetry and mercury porosimetry methods that are more able to capture macroporosity when measuring pore surface areas relevant to water interactions. Macroporosity is also important to aeration, root movement, and microbial habitat, thus emphasizing the importance of measuring macroporosity. Larger pores can also be observed using SEM imagery and are shown in Figure 5-2. Gas adsorption methods, including BET-N₂ and CO₂, may be more suited to measure pore surface area less than 0.1 µm that may be more beneficial in studies focusing on chemical interactions and less so for water (Brewer et al. 2014; Antal & Grønli 2003). Knowing this, the results of this study imply that fine char, especially at 700°C, has a greater content of micro-and-nano pores, while coarse char surface area may have been less detectable because of a greater content of macropores that were unable to be captured by BET-N₂.

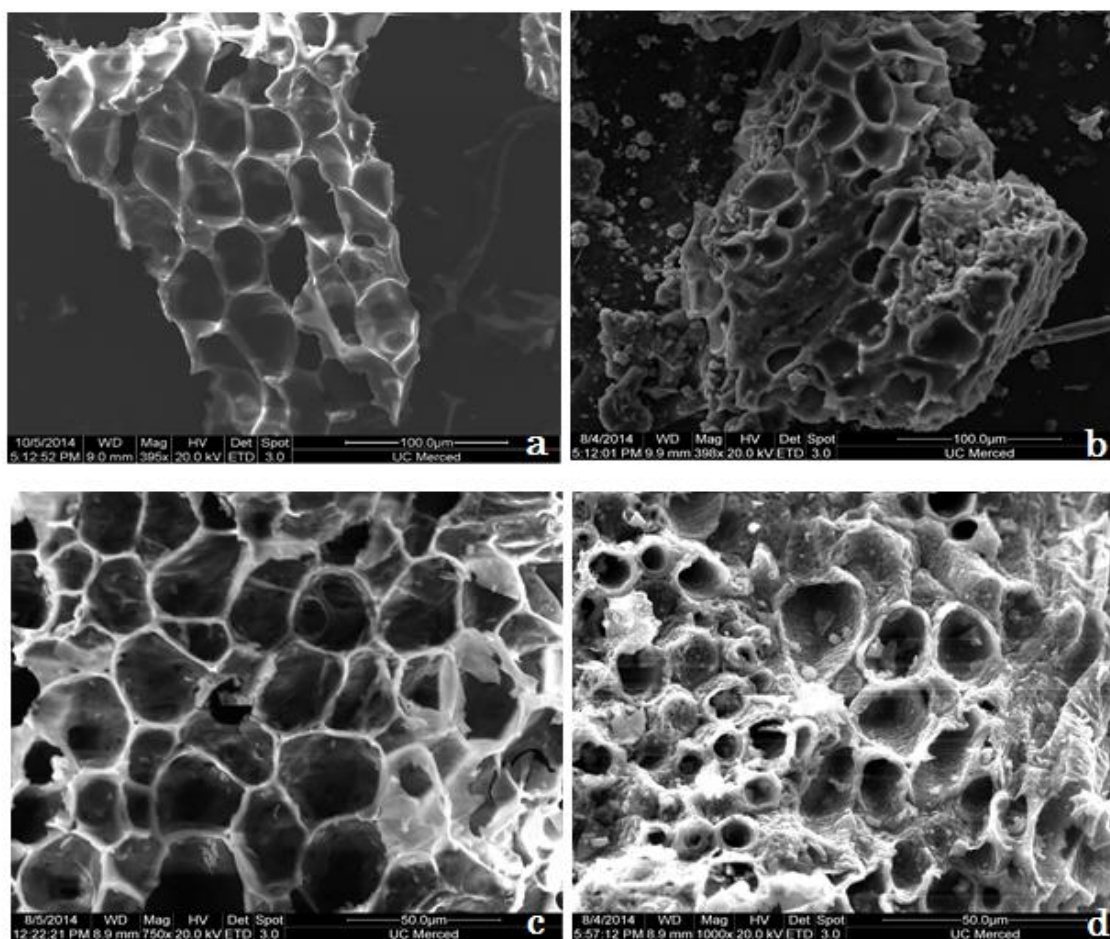


Figure 5-2 Scanning Electron Microscope (SEM) images of (a) 350°C fine, (b) 700°C fine, (c) 350°C coarse, and (d) 700°C coarse char produced by slow pyrolysis for at peak temperature for 60 minutes. Samples were imaged with an electron beam energy of 20 kV. The scale bar is 100 μm for (a) and (b) and 50 μm for (c) and (d).

FTIR

FTIR results were also strongly dependent on temperature, as has been observed for proximate analyses, ultimate analyses and pH. Size was not differentiated here because the resulting spectra were the same. When comparing the raw almond residue spectra with that of the 350°C spectra seen in Figure 4-8, it is clear that the surface functionalities from the raw biomass are present, but have been reduced. With further pyrolysis, the FTIR spectra shows little trace of the original feedstock spectra, implying a nearly complete loss of traceable functional groups. Water-based O-H stretches spanning 3500-3200 cm^{-1} are significantly reduced at 350°C, showing

the gradual loss of hydration as thermal conversion progresses. Alkyl C-H stretching at 2935 cm^{-1} has been reported to be correlated with hydrophobicity (Kinney et al. 2012). Gradual loss of this group indicates reduction of hydrophobicity as a function of pyrolysis temperature, which may have positive implications in soil. This study also observed losses in aromatic functionalities found at 1600 cm^{-1} and 1710 cm^{-1} , losses of which begin around 650°C and are completely removed by 750°C (Antal & Grønli 2003). Carboxyl C=O and ester C-O-C groups ($1740\text{-}1700\text{ cm}^{-1}$, $1270\text{-}1250\text{ cm}^{-1}$) also disappeared with increasing pyrolysis temperature. These functional groups contribute to a biochar's negative functional sites, enhancing the ability of char to attract cations in a soil. This feature has positive implications for nutrient dynamics in coarse soils that have high leaching rates. The reduction of these groups in our spectra suggests that as pyrolysis temperature increases, the cation exchange capacity may be reduced and may be less beneficial for plant growth.

However, the exchangeable cation exchange capacity trends presented in Figure 4-9 suggest otherwise. Cation exchange capacity describes a biochar's ability to hold positively charged ions, allowing them to be available for plant use. In this study, cation exchange capacity was shown to increase with decreasing size and increasing temperature. The ECEC was 97.57 cmol/kg and 43.13 cmol/kg for 700°C fine and 350°C coarse biochar respectively. Previous studies have reported CEC values of corn-stover biochar to be 100 mmol/kg (Lee et al. 2010) and straw biochar to have surface area up to 888 mmol/kg , depending on pH (Silber et al. 2010). These studies suggest that high ECEC of char may positively influence the ability of CEC-poor soils to retain more nutrients. This has been observed in a study by Laird and others (2010), who found a 30% increase in the ECEC of soil amended with slow pyrolysis hardwood charcoal. The ECEC was found to be weakly correlated with surface area ($R^2 = 0.71$) and strongly correlated to pH ($R^2 = 0.99$). It is well established in soils that as pH increases, there is an increase in negatively charged surface sites (deprotonation of functional groups), resulting in a higher CEC; a similar phenomenon appears to occur with biochar and has the capability to contribute positive effects to soil fertility. A study by Hossain et al. (2010) found an increase in the number of fruits produced per plant with an addition of 10 t/ha of biochar to an acidic soil, attributed to an increase in pH generating a slow release of nutrients to biochar. Caution is advised, however, as enhanced soil fertility from increased pH and CEC may only be beneficial to coarse-textured, low organic matter-containing soils (Silber et al. 2010).

5.2 Amended Soil Hydraulic and Physical Properties

CO₂ flux

Measurements of CO_2 flux allow visualizations of microbial respiration and are often used as a proxy for microbial activity. Results of this study saw little to no outstanding effects between pyrolysis temperature or rate in the Tempe Cell, which only had additions of coarse biochar (Figure 4-16). Maximum C release ranged from

0.66 to 0.81 g C-CO₂/g soil at the final time point of the incubation period (Day 63). Interestingly enough, the equivalent treatments (350°C or 700°C pyrolysis; 10 or 60 t/ha, coarse fraction) in the Infiltration experiment were observed to release 38% (350°C, 10 t/ha) to 56% (700°C, 10 t/ha) more g C-CO₂/g than the minimum and maximum emissions reported in the Tempe Cell experiment. The results from the incubation point out two main observations: (1) wetting/drying cycles may suppress microbial activity because of improved aggregate stability, regardless of biochar addition in Tempe Cells; and (2) under constant matric potential, pyrolysis temperature and char size influence how much C is respired.

The Tempe Pressure Cell experiment had lower overall C loss from CO₂ relative to the Infiltration experiment and there were no significant effects between biochar treatments. The depressed C emissions are speculated to be a result of an additional wetting/drying cycle generated as a function of monitoring changes in water retention over time in the Tempe Cell experiment. To generate an additional time point in the water retention curve, pressure cells were subjected to complete re-saturation and an eventual matric potential of 0.4 bar, thus drying the soil beyond field capacity. The samples were then re-saturated to field capacity and kept constant for the remainder of the incubation period. This process created an additional wetting/drying cycle. Previous studies looking at wetting/drying cycles report spikes in microbial activity immediately after rewetting, but a decline after a multiple rewetting events (Fierer & Schimel 2002; Fierer & Schimel 2003). This spike is attributed to a release of stored carbon within soil aggregates and can last for multiple days (Fierer & Schimel 2003). Rewetting causes a rapid intake of water; air is trapped & compressed in pores, causing aggregate swelling, disruption, and a release of aggregate associated organic matter (Denef et al. 2001; Kemper et al. 1985). However, a discernable spike in CO₂ flux was not observed in this present study, for either of our experiments; this may have been a result of lack of immediate CO₂ flux measurement after wetting. Our cumulative flux data was, however, greater in the Infiltration experiment by 38-58% relative to the same treatments in the Tempe Cell experiment. We speculate the difference to be a result of the additional wetting/drying cycle conducted in the Tempe Cell experiment, inducing the formation of water stable aggregates. The drying portion of the cycle causes nearby particles to be pulled together. As the soil dries, the remaining water is saturated in soluble adhesive compounds (i.e. silica, carbonates, organic molecules) and is pulled towards particle-particle interfaces, thereby cementing particles together and forming aggregates (Kemper & Rosenau 1986). Comparing water stable aggregate percentage (%WSA) in the Tempe and Infiltration experiments (Figure 4-21 and Figure 4-22, respectively), there were at least 11% more stable aggregates present in the Tempe Cell experiment, when analyzing the same treatments (coarse fraction only). This was also observed by Denef and others (2001), who reported more stable, slake-resistant aggregates after two wet-dry cycles. The increase in water stable aggregates in the Tempe Cell experiment provide greater physical protection of C against microbial activity and may explain why we observed reduced mineralisation rates in the Tempe Cell experiment. This suggests that soil physical alterations play a key role in determining C mineralization rather than the direct addition of biochar C.

While the Tempe Cell experiment saw depressed C loss and no changes as a function of biochar addition, the Infiltration experiment had the largest C loss with 350°C fine char added at the highest rates. Similar observations of enhanced C mineralization from low temperature char has been observed elsewhere (N. Ameloot et al. 2013; Zimmerman et al. 2010; Cross & Sohi 2011). Enhanced C mineralization in biochar amended soils has been suggested to be caused by microorganisms consuming biochar C, increased organic matter priming, and/or C release from abiotic oxidation (Cross & Sohi 2011; Bruun et al. 2008; Jones et al. 2011). Low temperature chars are speculated to have a greater content of labile, more mineralisable C, thus providing a greater energy source for microbial communities (Ameloot et al. 2013). Lower temperature char also has a greater content of volatile organic compounds (see Table 4-1) and macroporosity, supplying extra sources of C and microbial habitat, respectively (Keith et al. 2011). Other than changes with temperature, biochar size also had an interesting effect in this study. Coarse high temperature chars had greater C loss than their fine counterparts, whereas fine low temperature chars had greater C loss than coarse low temperature char (see Figure 4-16 and Figure 4-17). Fine char may have been more accessible for microbiota than coarse char and at lower temperatures; a greater content of mineralisable C could explain the greatest rates of C loss. However, the isotope ratios of C-CO₂ released in the final few time points, show no indication that biochar C was being respired by microbes, regardless of biochar pyrolysis temperature, size, or rate added (Table 4-6). Biochar $\delta^{13}\text{C}$ was depleted relative to the $\delta^{13}\text{C}$ -CO₂, where the most enriched char was ca. -25.5‰ (350°C char, Tempe Cell) and the respired $\delta^{13}\text{C}$ -CO₂ overall average ratio was -20.4‰. The enriched C flux indicates that biochar C was not mineralized, likely because of the short incubation period (9 weeks) and the suggested stability of char. Coarse chars (1-2 mm in this case) have the capacity to increase macroporosity, and thus increase aeration and microbial activity. The specific C source is unknown, but as previously mentioned, biochar C was not being respired based on the enriched $\delta^{13}\text{C}$ -CO₂ ratios relative to the ratios of char. Thus, soil structure alterations (porosity) from biochar addition may have induced the mineralization of existing soil C by increasing aeration in our coarse char amended soils.

Water stable aggregates

Biochar addition in both experiments had mixed results in terms of aggregate stability. Rate had the greatest effect in the Tempe Cell experiment, whereas additions of char generally reduced aggregate stability across all treatments in the Infiltration experiment. Similar to results in the Tempe Cell experiment, Ibrahim and others (2013) saw an increase in water stable aggregates with an increasing rate of char application (14 and 20 g/kg) and wetting/drying cycles. Observed increases in aggregate stability in the literature are attributed to (1) char acting as a binding agent, (2) char promoting organo-mineral complexes, and (3) biochar hydrophobic surfaces reducing the penetration of water into pores (Glaser et al. 2002). However in this case, it appears that the stability of aggregates was most affected by the number of wetting/drying cycles and was less influenced by char addition. This was observed in the overall increased content of water stable

aggregates in the Tempe Cell experiment (Figure 4-21) versus the Infiltration experiment (Figure 4-22). Previous studies looking at aggregate formation with biochar addition have observed increases in aggregate stability, attributing their results to biochar addition. Lei and Zhang (2013) reported increases in macroaggregate stability in a loamy soil amended with woodchip biochar after 30 days, attributing stability to an increase in microbial activity and increases in microbe-associated binding agents. Other studies reporting similar results have been documented with an increasing biochar rate (up to 20 g/kg) in a sandy loam soil (Ibrahim et al. 2013); commercial biochar added to a sandy soil (Awad et al. 2013); and woodchip and straw char (up to 60 g/kg) added to a clayey soil (Sun & Shenggao 2014). These results were obtained after incubation periods ranging from 30 to 180 days. Given what is found in the literature, it is possible that our incubation period was insufficient for the formation of binding agents between our specific almond residue char and soil particles, especially in the Infiltration experiment. Our results emphasize the necessity of further study on how various biochars affect aggregate formation and how this varies with time.

Soil Hydrophobicity

Hydrophobicity is a physical property associated with a material's repellency to water. Hydrophobic materials have the capacity to reduce infiltration rates and increase runoff in the process. While biochar hydrophobicity was not explicitly measured, the O:C ratio has been indicated as a relative measure of hydrophobicity (Lehmann et al. 2009). Despite speculations that high pyrolysis temperatures reduce O:C ratios and increase hydrophobicity, studies have reported little impact of biochar on soil hydrophobicity (Asai et al. 2009; Kinney et al. 2012; Abel et al. 2013). Similar results are reported here. In this study, amended soils were tested for hydrophobicity using the water drop penetration time (WDPT test). Results of the WDPT test are shown in Table 3-3 and report no significant water repellency. Soils amended with 350°C fine char in the Infiltration experiment and control soils in the Tempe Cell experiment had slight repellency, where water infiltration was >1 second but <5 seconds. A similar result was obtained using biochar made from feedstock maize pyrolyzed at 750°C (Abel et al. 2013). Biochar may not affect soil hydrophobicity because of the rapid removal of hydrophobic surface compounds by water, as conducted in a study by Briggs and others (2012). An interesting observation from conducting this experiment was that there were locally hydrophobic characteristics per sample. Traces of hydrophobicity from the localized spots and 'slightly repellent' soils are likely related to initial formations of microbial deposits and/or activity. This has previously been observed in a study by Abel and others (2013), in which they attributed spots of surface hydrophobicity in amended soils to surficial fungal hyphae; however, large bursts of fungal hyphal growth have been reported to be more pronounced in soils amended with hydrochar and less so as a function of biochar addition (Lehmann et al. 2011). Such microbial residues and exudates (including from bacterial sources) are well established sources of soil hydrophobicity. Compounds contributing to this phenomenon are typically various forms of aliphatic hydrocarbons (non-polar) and/or amphiphilic molecules (polar) that form a hydrophobic coating (Doerr et al. 2000). While microbial activity may

have contributed to the slight repellency observed in this study, overall there were no significant surface hydrophobic effects on biochar amended soils that would impact infiltration.

Water Retention

Water retention curves provide an idea of the capacity of a soil to store water. Biochar addition to soils has been reported to improve water storage by improving aggregation and pore size distribution (Downie et al. 2009), in addition to providing pores available for water storage (Downie et al. 2009; Chen et al. 2010). However, our biochar amended loamy sand soils showed a gradual reduction in water retention with increasing rate and temperature, as shown in Figure 4-20. Soils amended with 700°C char at 60 t/ha (2% w/v) were observed to have water contents approximately 11% less than the control after the incubation period (time C). Other studies have observed increases in water retention with biochar addition. Adding switchgrass char to a loamy sand (2% rate) was observed to increase water retention by 6.7-15.9% relative to the controls (Novak et al. 2009). Similar results in sandy, coarse-textured soils have also been reported elsewhere but as a result of greater additions of char (4-45% by volume) (Tyron 1948; Gaskin et al. 2008). It is speculated that adding high rates of biochar increase the content of soil microporosity due to biochar's extensive pore structure, thus increasing area for water storage. However, in the present study, high rates of char reduced the water content of soil relative to the control. This may be because we added 1-2 mm sized char, increasing the macroporosity of the soil; Tyron (1948) observed that water retention was enhanced with fine char (<1mm) over large char (2-5 mm). Moreover, our char may have been slightly hydrophobic, thus expelling water away through the soil core. These results suggest that high additions of almond shell char, regardless of temperature, may not be beneficial for these loamy sand soils if the sole purpose is to store water. However, it may be beneficial in the short term to pass water through a soil profile if it is heavily afflicted by saline or sodic conditions. In the long term, it is plausible to obtain water storage conditions from high biochar additions because char has been reported to become oxidated and less hydrophobic with time (Nguyen et al. 2010; Cheng et al. 2008). At lower rates of char addition, low temperature char may be most beneficial in retaining water, as it had comparable volumetric water contents to the control after the 63 day incubation period. Despite a study by Glaser and others (2002) noting that improved soil water retention using biochar may only work in coarse soils, this study provides evidence that water retention may also be reduced in coarse soils, especially if a high rate of coarse char is applied.

Infiltration

When adding char to sandy soils, it is expected that porosity will increase, thus enhancing a macroporous network. Infiltration rate, as measured by observing changes in saturated hydraulic conductivity (K_{sat}), differed between both of our experiments. In the Tempe Cell experiment, which only measured coarse char, no significant differences were observed between treatments. There were slight

reductions on average after the incubation period, which may be attributed to a greater aggregate stability, which was observed to increase by at least 3.8%. In the Infiltration experiment, char addition increased infiltration before the incubation period. The initial increase occurs because biochar increases macroporosity and preferential flow of water through soils (Sohi 2010). Additionally, the hydrophobic nature of the char will repel water, causing an increase in flow. Interestingly enough, the increased K_{sat} in coarse char was observed for 350°C and 700°C, whereas in fine char, the highest K_{sat} was observed for fine char at 700°C on average. This suggests that upon initial application, K_{sat} increases with char size (regardless of temperature) and with the addition of finer chars, K_{sat} increases with higher temperature. After the incubation, K_{sat} of all treatments reduced, becoming more similar to the control soil. The reduction of K_{sat} after incubation may have been attributed to an increase in soil structure; however, our aggregate stability results saw an overall reduction in aggregate stability with biochar addition (see Figure 4-22). For fine char, pore clogging may be a possible explanation as to why there was an observed reduction in K_{sat} ; reduced K_{sat} for coarse char is uncertain. Barnes and others (2014) mention reduced K_{sat} in sandy soils to be a function of biochar generating water flow pathways between sand and char and the other to be the addition of pore pathways from char itself. Our char was dominated by pores around 50 μm (see Figure 5-2) and was thus large enough for water molecules (0.28 nm) to pass through, making it plausible that this phenomenon existed in our soils. It is also possible that the complete drying before measuring K_{sat} resulted in soil compaction (higher bulk density), thus reducing the pore connectivity and infiltration (Zhang et al. 2006). Bulk density after the experiment was not measured in this study, but soil compaction was observed after drying the soil, especially in the control. Building on these observations, it may be possible that biochar initially increased the porosity of the soil (giving a higher initial K_{sat}) and then a combination of drying and biochar porosity resulted in final lower K_{sat} values that were more similar to the control. Other studies observing changes of K_{sat} in sandy soils have observed increases (Oguntunde et al. 2008), reductions (K. C. Uzoma et al. 2011; Barnes et al. 2014; Deveraux et al. 2012; Brockhoff et al. 2010) or no change (Hardie et al. 2013). Using powdered wood charcoal, Deveraux and others (2012) saw a reduction in K_{sat} with increasing rate (up to 62.5 t/ha) and similar results were observed by Uzoma and others (2011) with up to 20 t/ha char; rate had no effect in our study. These varied effects in the literature and in this study point to the necessity to further study how biochar will affect soil water flow. A lacking in the literature is a comparison of the behavior of different sized char particles in soil. While our study saw no apparent effect of size on K_{sat} before and after the experiment, there is a great need to explore this area, especially if biochar is to be optimized for a variety of soil systems.

CHAPTER 6. Summary and Conclusions

This study explored varying biochar properties and their effects on soil physical and hydraulic properties. The underlying motivation was to observe whether or not biochar would be able to improve water flow through arable soils both experiencing drought conditions and infiltration resistance.

Findings from this study revealed properties of almond residue biochar pyrolyzed at two different temperatures and two different sizes. Finer char was observed to have a lower C content than its coarse counterpart, but was not starkly different otherwise. Pyrolysis temperature had the greatest effect on resulting properties of the biochars. Increasing pyrolysis temperature increased C content, fixed C, ash and pH while reducing O and H content and yield. An increase in pyrolysis temperature also reduced functional group presence and increased the stability of biochar. Both effective cation exchange capacity and surface area increased with higher pyrolysis temperature and smaller size, which is likely attributed to an increase in porosity generated at higher temperatures.

After being mixed with an arable loamy sand soil and incubated for 9 weeks, soil properties changed. Two sets of hydraulic experiments were used to test these soils. The first was the Tempe Cell experiment, which used to generate a water retention curve. This experiment solely used coarse char at a high and low rate. The Infiltration experiment was used to obtain direct measurements of the infiltration of water into soil. This experiment used coarse and fine char at both application rates. Overall, there were significant reductions in water storage as temperature and rate were increased, indicating that high rates may be beneficial to flush out ions or other substances if there is a buildup. High temperature char applied at 60 t/ha, however, would not be beneficial if the purpose is to retain water, which is especially important to consider in times of drought. Low temperature char applied at a low rate was most beneficial for water retention, and thus is advised if seeking improved water storage. Infiltration was observed to increase prior to incubation because of enhanced macroporosity, but reduced after incubation from possible pore clogging. Aggregate stability may have caused an increase in infiltration, but increased stability was not observed in the Infiltration experiment; biochar addition generally

reduced aggregate stability with reduced biochar size. Increased aggregate stability was observed in the Tempe Cell experiment, highlighting the importance of wetting/drying cycles for improved soil structure.

Overall, biochar had varying effects on the hydraulic properties in this experiment. From this study, it appears low temperature char at low rate would be best for retention purposes, while high temperature char at any rate of addition would be most beneficial for infiltration purposes. It is crucial to note that the behavior of biochar in this soil will differ from others, as is the nature of using heterogeneous materials (i.e. soil and char). There is still extensive research that needs to be conducted to develop a database of biochar that elucidates what chars will be most beneficial in certain environments.

CHAPTER 7. References

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