The Optimization of Biochar for the Removal of Phosphorus from Water

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Abstract

Phosphorus (P) pollution from anthropogenic activities is contributing to increases in eutrophication in freshwater systems. In addition, the demand for plant-available P sources continues to increase globally. Biochar, a substance created through biomass pyrolysis, has shown potential for removing P from wastewater. Numerous published studies indicate that chemically modified biochar is more effective at P removal than unmodified biochar. To identify the most suitable type of biochar for future modification for P removal and storage, several characterization experiments were conducted. After conducting the characterization experiments on fourteen biochar types, four were chosen for further experimentation. These biochars were then chemically altered to optimize P adsorption. The modification agents used were Ca, Mg, Fe cations, and cationic polymers. 4% Fe-modified biochar was determined to be the best and it was incorporated into a bench scale continuous flow reactor with dairy effluent wastewater to simulate real wastewater treatment applications. The biochar was then recovered from the reactor and experiments were done to determine the quantity of recoverable plant available P and total P. The Fe-modified biochar treatment had a significant increase in plant available P from 27 to 138 mg/kg. However, this was still lower than the initial value of unmodified biochar, which was 646 mg/kg and increased to 680 mg/kg after treatment. Total P was highest in the Fe-biochar post-treatment with the flow reactor at 1224 mg/kg, while the unmodified biochar had a total P of 993 mg/kg. Results from the research will enable P recycling using modified biochars that can be used as a soil amendment.

To test biochar use for P recycling, a pilot study was conducted at Elk Mountain Farms, Idaho, to assess the effectiveness of Fe-modified biochar in removing P from groundwater impacted by agriculture. The University of Idaho Clean Water Machine, which uses reactive filtration technology, was utilized to remove and recover P from groundwater. For 4% Fe-modified Pacific Biochar, total P in the water dropped from 0.166 mg/L to 0.019 mg/L between the influent and effluent samples, while ortho-phosphate decreased from 0.102 mg/L to 0.008 mg/L. Total P for the unmodified biochar dropped from 0.091 mg/L to 0.025 mg/L between the influent and effluent samples, and ortho-phosphate decreased from 0.049 mg/L to 0.003 mg/L. Both the unmodified biochar and the Fe-modified treatment showed an increase in total P after being used in the reactive filtration. The unused unmodified biochar had an initial P amount of 725 mg/kg, which increased to 1108 mg/kg after water treatment. Similarly, the Fe-modified treatment had an initial P amount of

614 mg/kg, which increased to 995 mg/kg after water treatment. These results indicate that biochar has the potential to be used to remove P from water.

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Dedication

This thesis is dedicated to my dog Zulu who has been my constant companion throughout my academic career.

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Chapter 1: Characterization of Commercial Biochars for Potential use in Phosphorus Removal from Wastewater

1.1. Abstract

Phosphorus (P) release from wastewater treatment plants and agricultural industry is causing degradation of surface water quality. In addition, the demand for plant-available P sources continues to increase globally. Biochar, a substance created through biomass pyrolysis, has shown potential for removing and storing P from wastewater. Numerous published studies indicate that chemically modified biochar is more effective at P removal than unmodified biochar. To identify the most suitable type of biochar for future modification for P removal and storage, several characterization experiments were conducted. These experiments included adsorption isotherms, pH measurements, EC measurements, water desorption, and formic acid extractions. After conducting the characterization experiments on 14 biochar types, four were chosen for further experimentation, CharBliss, Pacific Biochar, BC Biocarbon, and Wakefield Biochar.

1.2. Introduction

1.2.1. Research Goals for the Project

A team of researchers from the University of Idaho have developed a carbon-negative water treatment technology that uses biochar and produces clean reuse water. This system also recovers the phosphorus (P) and nitrogen (N), which are limiting nutrients in many terrestrial and aquatic systems. The treatment uses ozone to kill pathogens and oxidatively destroy organic molecules such as pharmaceuticals. The water treatment technology is used in municipal wastewater treatment, as well as agricultural (e.g., dairy effluent) and industry water (e.g., food processing). For the technology to be improved, the optimization of water treatment with regards to P removal and P recovery for the potential use as a nutrient-upcycled fertilizer must be developed. To achieve this goal, the team is using modified biochar as the medium for P pollution removal and for the potential to reuse the biochar as a soil amendment and fertilizer.

A major impact on water quality is non-point source pollution caused from excess nutrients from agriculture (Worsfold et al., 2016). Dairy farms in particular face major challenges managing solid and liquid manure nutrients. In dairy-dense regions, the use of imported feed and fertilizer has concentrated N and P to levels that overwhelm local soils. This leaves the local water systems and plants with excessive nutrient levels. Therefore, this research focused on the removal of P from dairy production and other agricultural activities to create useful bioproducts that can be transported and used in more distant areas for crop production (Gelardi et al., 2021). This research was part of a larger project from a USDA Sustainable Agricultural Systems grant to integrate bio-economic research with industry needs of dairy production. The project goal is to support adoption of technologies and processes that transform nutrients in dairy manure into commercial fertilizers and other value-added bioproducts to improve soils, sustain agricultural productivity, reduce environmental impacts, provide alternative income streams, and create new employment opportunities. Specifically, this research addressed the investigation of new technologies to remove P from wastewater, such as dairy, and other point and non-point sources. The research also investigated the feasibility of using the recovered P as a nutrient fertilizer, which is a major need for making the dairy bioeconomy and limited P resource more sustainable (Bakshi et al., 2021).

The scope of this research aims to answer two important questions related to the future use of biochar.

1. How can biochar be optimized for the removal of phosphorus from wastewater?
2. Can the recovered biochar from wastewater applications be reused as a soil amendment to improve agriculture production?

To answer these questions, the reactivity of modified biochars for P adsorption was investigated for use in water treatment. Several objectives were completed to achieve these research goals:

1. Characterize the biochar so the best biochar can be selected for future experimentation and trials.
2. Determine methods to modify biochar with Ca, Mg, Fe, and a cationic polymer (PDADMAC) to optimize P recovery.

Maximum P removal by the biochar requires modification using either Ca, Mg, Fe, and cationic polymers to promote phosphate adsorption on the biochar surface. Modifications were necessary to improve the adsorption properties of biochar to increase efficiency when used in wastewater treatment. Another part of this objective was to determine the efficiency of P removal using the modified biochars. This was done from adsorption isotherm experiments and from simulated and/or real dairy wastewater in a benchtop flow system to emulate pilot-scale systems. This allowed for the evaluation of biochar's P removal capabilities in a controlled environment. The third objective is to determine P availability when amended to soil by evaluating P release from P-recovered biochar. By measuring this, the ability of the recovered biochar to be used as a soil amendment can be evaluated. After these objectives were tested and evaluated in a laboratory setting, a pilot scale experiment was carried out on agricultural wastewater to evaluate the effectiveness of the modified biochar in a real-world scenario.

1.2.2. Potential for Using Biochar in Wastewater Treatment

Phosphorus (P) pollution is a major concern for freshwater resources (Wetzel, 2015). Urbanized areas and regions of high use agriculture have increased P loading into their surrounding ecosystems (Walsh, 2000). Commercial agriculture applies large amounts of P-bearing fertilizers to stimulate the production of crops for human and livestock consumption. Other sources of P in agriculture are associated with livestock animals and their waste (Worsfold et al., 2016). This waste can enter water systems and infiltrate into soil systems. Soils can store P and release excess P that is not readily available for plant uptake (Rowland and Haygarth, 1997). Due to this, soils are increasingly acknowledged as a source of P discharges in surface water. Agricultural soils can also provide a measure of nutrient loss and an early warning of levels discharging into surface drainage water (Rowland and Haygarth, 1997). The amount of P in soils can vary drastically across regions depending on use. Phosphorus is also present in other parts of the terrestrial environment. Phosphorus, although less mobile than other nutrients such as nitrate, is mobile in environments that receive excess P, causing P fluxes from the soil into surface waters. (Worsfold et al., 2016). This mobility of P is a natural cycle that has been enhanced in several places due to human activity, which is causing P to become concentrated in some aquatic ecosystems and, creating serious environmental and public health issues.

Existing agricultural practices have caused significant effects on water quality from the loss of P into water bodies. This happens from agricultural run-off, which causes elevated levels of P in water systems. Such increases lead to eutrophication, harmful algal blooms, oxygen depletion and mortality of biota (Worsfold et al., 2016). When P is present at levels greater than 30 µg/L in a natural water system is categorized as eutrophic (Wetzel, 2015). Eutrophic water systems can become anoxic and are habitat for nitrogen fixing cyanobacteria. Cyanobacteria can produce toxins that can harm and even kill animals that encounter them (Wetzel, 2015). The increased eutrophication of water systems continues to be a problem surrounding anthropogenic activity. Excessive use of fertilizers is severely damaging water quality. The P that is not taken up by plants or immobilized in the soil often enters water ways in excess and contributes to eutrophication. This process can make the water anoxic and create “dead zones” (Bakshi et al., 2021). Dead zones can cause entire ecosystem collapse if turnover of the water bodies happen. Turnover, a natural phenomenon where the thermal stratification of water bodies reverses, is common in dimictic lakes (Wetzel, 2015). Turnover in dimictic lakes happen twice a year presenting the opportunity for massive kill offs twice a year. Cyanobacteria and their deadly toxins can be present in moving freshwater. Rivers and streams can also experience ecosystem collapse if the toxins become concentrated enough. In drought-stricken areas, which are becoming more common across the US, moving water systems are losing flows causing increases in the toxin levels (Bakshi et al., 2021).

A major focus for reducing P is on wastewater treatment facilities that must deal with the excess P and N in their systems to prevent the excess nutrient loading to surface waters. Water quality management facilities must determine the loads and fluxes of P species in water bodies to control internal cycling processes, restore eutrophic ecosystems and evaluate the effects of P runoff on the ecological health of receiving waters (Worsfold et al., 2016). This burden has drawn the attention of policy makers and reshaped regulations surrounding wastewater treatment. The possible adverse impact of increased phosphorus concentrations in natural waters has led to the inclusion of phosphorus mandates in numerous national and international legislative frameworks and guidelines (Worsfold et al., 2016). Population growth and increased industrialization are contributing to the elevated P inputs to natural waters. Both diffuse and point source pollution are common in urbanized areas. This has led to “cultural eutrophication”, which is the accelerated anthropogenic enrichment of the environment with nutrients and the concomitant production of undesirable effects (Worsfold et al., 2016).

Currently, several biological, chemical, and physical treatment technologies exist to capture P and to reduce runoff from agricultural soils, but the current technologies are often expensive to implement (Bakshi et al., 2021). New technologies that are affordable and easily integrated into current systems need to be developed and implemented as soon as possible. If not, the problem will continue to grow and a breaking point in many ecosystems could be reached (Walsh, 2000). This problem led to interests in using biochar for wastewater treatment and for soil amendment applications.

In recent years, many studies have been devoted to the potential applications of biochar. Potential benefits of biochar production and use are of interest in energy production, agricultural production, remediation, product substitution, waste management, and climate change mitigation.

This diverse range of potential uses has led to nearly 5000 scientific publications and nearly 4000 US patent applications just in 2020 (Gelardi and Parikh, 2021). To further our understanding of biochar and help industry develop efficient and effective uses, more research is needed to understand biochar properties and how it behaves in various applications, ranging from water treatment to soil amendments.

Biochar possesses chemical and physical properties that make it highly effective for removing chemicals from solution via sorption, as well as helping bioremediation processes (Gelardi and Parikhn, 2021). The type of biochar feedstock and production conditions can be tailored to the specific contaminants to improve remediation efficiency. Wood derived biochars typically have greater surface area and carbon content than those from manure or grass (Gelardi and Parikhn, 2021). Manure and grass biochars generally have more abundant oxygen-containing functional groups and mineral constituents (Downie et al., 2009). The activated carbon within the biochar is generated through the pyrolysis processes. This makes biochar a good immobilizer of pharmaceuticals in wastewater, and retardant for the mobility of pesticides. There is also increasing evidence that biochar can facilitate biodegradation of organic compounds (Qin et al., 2013). In addition to these traits, numerous studies have shown that biochars can bind trace metals. Metal and metalloids do not degrade, so immobilizing them is the best method of remediation. Biochars can immobilize metals by chemisorption and electrostatic adsorption reactions (Zhou et al., 2013).

Biochars are frequently modified to improve their properties for use in remediation of water treatment (Shepherd et al., 2016). Common modifications include adsorbing cationic polymers (Wang et al., 2020), magnesium (Fang et al., 2014), or iron (Siddiq et al., 2021). Oxidants, acids, or alkalis are also used as modifiers to improve the reactivity of biochars (Wang et al., 2019). Iron-modified biochar can be used to remove P from aqueous solutions including livestock manure, industrial and municipal wastes, and agricultural effluents. Biochar is similar to activated carbon, which is a common substance used in remediation. Both substances possess high cation exchange capacity, aromaticity, and high surface area. This makes biochar a favorable adsorbent for a range of trace metals (O'Connor et al., 2018), organic compounds (Zhang et al., 2010), and pesticides (Liu et al., 2018).

In certain scenarios, biochar can serve as a low-cost alternative to remediation where costs are typically high (You et al., 2017). Biochar is also low-tech, which can make applications simpler and therefore save on costs. By being low cost and simple to use, biochar has the potential to be incorporated into on-site local systems (Allohverdi et al., 2021). This can save costs on transportation as well. Not to mention the possible benefit of carbon credits (Matuštík et al., 2020). Research is ongoing into successful and cost-effective strategies for implicating biochar in remediation. The research is promising and there is a lot of room for the technologies to grow. More cost-saving advantages could still be discovered.

Biochar has many potential benefits and uses across a diverse range of applications that are not limited to just wastewater application. These uses fall into several main categories, including climate change mitigation through the sequestration of biomass (Matuštík et al., 2020); waste management when manure and plant waste is converted into biochar (Nemati et al., 2015); and as a soil amendment (Miles, 2020; Oladele, 2019). Biochar is also used for water filtration, soil blending in composts, and home gardening (Miles, 2020). Recent research has shown that chemically or physically modified biochars can have greatly improved performance over regular biochar in numerous applications (Allohverdi et al., 2021). These modified biochars can have greater surface area, increased pore size, higher cation exchange capacity, more hydrophobicity, greater stability, and higher potential for adsorption of contaminants.

1.2.3. The Need to Characterize Biochar

Biochar is the major derivative produced from pyrolyzing biomass under oxygen depleted conditions. Biochar is a source of energy production from bio-oil, a substance that is also produced during biochar production (You et al., 2017). It can be applied to land for climate change mitigation through carbon sequestration, as a soil amendment, and to bolster waste management. Due to the environmentally friendly nature and financial low cost associated with it, the application of biochar has recently garnered considerable attention as a low cost and effective adsorbent for pollutants from aqueous solution (Jung et al.,2016). Biochar is a carbon-rich solid obtained by heating biomass with little or no oxygen (Tan et al., 2015). Biochar can be made from any agricultural or forestry biomass waste. Common biochar feedstocks are wood, manure, and grasses (Gelardi and Parikh, 2021). Not only does the production of biochar reduce waste in many industries, utilizing these waste materials means that biochar can be considered a value-added product. This can provide another source of income for agriculture producers. Wood waste material can also be salvaged from forest fire impacted zones. As fires continue to worsen in the Western US, the amount of burnt timber will continue to increase and biochar production is one possible use of this large biomass resource.

There are several production variables that can influence the characteristics of biochar. These include gasification, pyrolysis, flow-through, and batch production to name a few (You et al., 2017). Pyrolysis is the most popular method of producing biochar. The production temperature and feedstock source are also influencing variables (Hassan et al., 2020; Jung et al., 2016). Slow pyrolysis is the most used technology for production of biochar for wastewater treatment. Pyrolysis temperature must exceed 500 degrees Celsius to produce the most favorable properties to create biochar for use in wastewater treatment (Tan et al., 2015).

Biochar production capacity is increasing, with large scale operations that produce truckloads of material every day (Gelardi et al., 2021). New and old companies are ramping up production to meet the growing demand for the material. Biochar can also be made in smaller batches using Flame Cap Kilns to limit oxygen at base of the fire (Miles, 2020). These smaller batch systems allow to produce biochar directly on-site of the waste generating facilities. A closed system of waste generation and reuse can then be implemented.

The properties of biochars that are affected by production methods and conditions include pyrolytic temperature, residence time, feedstock, and pyrolysis technology. Biochar has a high degree of variability because of these variables. Biochars made under high temperature pyrolysis have been shown to have high surface area, increased pore size, higher ash content, more hydrophobicity, and greater stability (Hassan et al., 2020). These traits are desirable for use in wastewater treatment. Biochars made under high temperature pyrolysis have higher pH (compared to low temperature biochars), an overall neutral to basic pH, stable carbon, and increased reactive surface functional groups (Downie et al., 2009). Biochars also contain high cation exchange capacity, which can result in increased exchangeable cations (Lehmann et al., 2011). A high cation exchange capacity will increase the potential of ion adsorption to the biochar. In addition to high CECs, some biochars also have measurable anion exchange capacity, which disappears over time in soil (Lehmann et al., 2011). This can facilitate some phosphorus adsorption from wastewater. These physiochemical traits are due to biochars molecular structure that is carbon rich, porous with oxygen functional groups, and full of aromatic carbon structures (Tan et al., 2015). Depending on the feedstock, there are also a variety of other solids in biochar, which vary as widely as the feedstocks themselves. The structure of biochar creates a large surface area and many potential bonding sites for contaminants to interact with the functional groups. Biochar can exchange cations via electrostatic attraction, form surface complexations, physically adsorb organic compounds, or form surface precipitates (Tan et al., 2015). The variety of potential reactions due to its structure makes biochar beneficial in many wastewater treatment applications.

Biochar is an extremely diverse substance due to the wide range of pyrolytic temperatures, residence times, feedstocks, and pyrolysis technologies used in its production. The chemical differences between various types of biochar make it challenging to conduct detailed, repeatable experiments on, leading to potential inconsistencies in the analytical information obtained. It is essential to characterize biochar physically and chemically, allowing for comparison of results to similar biochars. Therefore, the rest of Chapter 1 describes the experiments and measurements conducted on a variety of biochars to characterize them for future experimentation and study. Based on this data, certain biochars were selected for modification and testing for their use in removing phosphorus from wastewater (Chapter 3).

1.2.4. Biochar and Potential Health Hazards

Further research and investigation are necessary to better understand the potential risks and impacts of biochar on human health and the environment. This includes evaluating the potential health risks for agricultural workers, neighboring farm communities, livestock, and wildlife, as well as assessing the long-term effects of biochar application on water and air quality. Proper management and monitoring measures should be put in place to minimize any potential adverse effects and ensure the safe and sustainable use of biochar in agricultural practices. Governments have a significant role in developing and enforcing policies that ensure the safe production and handling of biochar. The United States currently does not have required regulatory standards for contaminant levels in biochar, such as polycyclic aromatic hydrocarbons (PAHs) and trace metals. However, maximum threshold values for a limited number of toxicants have been established in frameworks proposed by the European Biochar Certificate (EBC) and the International Biochar Initiative (IBI) (IBC, 2021). Currently, there are four certified biochar types in the United States that meet these safety and quality standards set by the ECB and IBI.

The adoption of a unified regulatory framework for biochar in the United States would greatly benefit the communication and coordination among academic sectors and the evolving biochar market. Education and outreach efforts can play a crucial role in ensuring the safe application of biochar to working lands, especially when biochar is used in government cost-share or incentive programs as part of climate change mitigation strategies. Regardless of the application method or government regulations, it is recommended that farm operators and workers handling biochar, including those approved to meet safety standards, use appropriate personal protective equipment (PPE) such as respirators, eye protection, gloves, long sleeves, and pants. Taking necessary precautions can help minimize potential risks associated with handling biochar and ensure the safety of farm operators, workers, and the environment.

1.3. Materials and Methods

1.3.1. Sources of Biochar

The need to develop standard biochar characterization methods led to the publication of "Biochar: A Guide to Analytical Methods," edited by Balwant Singh, Marta Camps-Arbestain, and Johannes Lehmann (Singh et al., 2017). This book provides background information on biochar and several peer-reviewed methods of preparing and analyzing biochar for analytical studies.

The biochars characterized in this chapter were purchased from several suppliers across North America and were made from various feedstocks (Table 1). The companies that provided biochars and the various feedstocks are listed below. Some of the biochars were determined to be modified by the suppliers. This was either listed in the product description or determined from extractable elements during characterization experiments. The exact modifications that these biochars underwent are unknown since that information was not disclosed to our research group. However, the biochars were modified for various purposes depending on their intended applications. For example, both the Logic Growth and Logic Starter biochars were modified with various plant nutrients to stimulate seedling growth for use as a soil amendment.

Table 1**.** Biochar providers and the feedstocks used.

Company	**Location**	**Commercial Product**	**Date Purchased**	**Modified by Supplier**	**Feedstock**
Oregon Biochar Solutions (CharBliss)	White City, OR	Yes	May-21	No	Forest Soft Wood Waste
Karbonous Inc. (PAC)	City of Industry, CA	Yes	May-20	Yes	Coconut Husks
Biochar Now (Powdered)	Berthoud, CO	Yes	May-21	No	Forest
Biochar Now(Granular)	Berthoud, CO	Yes	May-21	No	Forest
ARTi	Prairie City, IA	Yes	Feb-22	No	Corn Stover
National Forest Service (CharBoss)	USFS NE, OR	No	May-21	No	Forest Soft Wood Waste
Carbon Logic (Growth)	Spokane, WA	Yes	Mar-22	Yes	Crop Residue
Carbon Logic (Stater)	Spokane, WA	Yes	Mar-22	Yes	Wheat
NCT	St. Gwinn, MI	Yes	Mar-22	Unknown	Unknown
Pacific Biochar (Blacklite Pure)	Santa Rosa, CA	Yes	Apr-22	No	Forest Soft Wood Waste
Genesis Biochar	Somers, MT	Yes	May-22	No	Forest Soft Wood Waste
BC Biocarbon	McBride, BC	Yes	May-22	No	Lodgepole Pine Forest
Seneca Farms Biochar	Odessa, NY	Yes	May-22	No	Hard Wood Waste
Wakefield Biochar	Columbia, MO	Yes	May-22	No	Forest Soft Wood Waste

1.3.2. pH of Biochar Slurry

The method for measuring pH followed the protocol described in Singh et al. (2017). The biochars were first air-dried for 72 hours in the laboratory. The dried biochars were then crushed to a particle size of less than 2 mm using a stainless-steel rolling pin. Ground biochar was then physically separated using a number 10 sieve (2-mm opening). The material that passed through the sieve was kept while material that was retained was crushed again until it passed through the number 10 sieve. All equipment used to crush the biochar was cleaned with 18 megohm deionized water and 70% by weight ethanol before and between samples to eliminate cross-contamination.

The less than 2-mm biochars were weighed out to quantities of 5.0 grams. The biochar was then transferred to 250 mL HDPE bottles, and 50 mL of 18 megohm deionized water was added. The bottles were then sealed and mechanically shaken for 1 hour at approximately 23 degrees Celsius on a Glas-Col end-over-end shaker rotating at 30 rpm. After 1 hour, the slurry was allowed to rest for 30 minutes. The slurry pH was then measured using a Denver Instrument Model 250 pH probe that was calibrated using pH 4, 7, and 10 buffer standards. The pH of each sample was then recorded. The electrode probe was triple rinsed with DI water between sample measurements. Each sample was measured in triplicate, and the averages of the three were reported with standard deviations.

1.3.3. Electric Conductivity of Biochar Slurry

The method for measurement of electric conductivity (EC) followed the protocol described in Singh et al. (2017). Measuring EC is a common method of determining salinity of a solution and is recorded in micro siemens or milli siemens per cm. To measure EC, 5.0 g of the less than 2 mm air dried biochars were weighed and mixed with 50 mL of 18 megohm deionized water to create a slurry that was also used to measure pH (described above). An Oakton S/N2329707 EC probe was then inserted into the solution, and EC was recorded. The probe was triple rinsed using DI water and calibrated to the closest standard available for the first measurement. The standard that was closest to the measurement varied depending on the type of biochar. After calibration, the probe was triple rinsed again, and the measurement was retaken. The final post-calibration measurement was recorded, and then the probe was triple rinsed again before measuring the next sample. Calibration was done for each sample as necessary to reduce error in EC measurements across a large range. Each sample was measured in triplicate, and the averages of the three were reported with standard deviations.

1.3.4. Single Point Adsorption Isotherm for Phosphate

To evaluate adsorption potential of 14 different biochars a single point adsorption isotherm experiment was conducted. The experimental design was modeled after the method described by Kovar and Pierzynski (2009). A 25-mg/L concentration of the sodium phosphate (Na_2HPO_4) solution was used and a solid to solution ratio of 1:50. The experiment was carried out in triplicate, with an additional "burner" replicate for pH adjustment determination.

0.2 g of air dried < 2mm biochar was added to 5 mL of DI water in a 15 mL centrifuge tube to prepare each sample replicate, and the weights were recorded for future calculations. Then 0.25 mL of 1000 mg/L P from Na_2HPO_4 was pipetted into each replicate. After vortexing the samples for 30 seconds, they were allowed to rest for 1 hour. The pH of each non-burner replicate was adjusted to 6.5 using drops of 0.01 M HCl, with the amount of HCl determined using the burner replicate. The samples were then shaken for 24 hours at approximately 23 degrees Celsius on an end-over-end shaker.

After 24 hours, the samples were centrifuged, and the liquid fraction that passed through the 0.45 µm PES membrane filters was collected and acidified with 1 drop of 1 M nitric acid. The samples' phosphorus concentrations were analyzed using ICP-OES (Agilent 5110, Santa Clara, California). The adsorption (Q) of each replicate was calculated using the equation below and normalized by the mass of biochar (M) and volume (V). The replicates were then averaged and reported with standard deviations:

Equation 1. Formula and units for determining adsorption of P on biochar.

$$Q = (Ci - Ce) * \frac{V}{m}$$

where:

Q = adsorption capacity of biochar (mg/kg)
Ci = initial concentration of phosphate in solution (mg/L)
Ce = equilibrium concentration of phosphate in solution (mg/L)
V = volume of the solution (L)
m = mass of biochar used (g)

1.3.5. Water Desorption

The ability of biochar to release captured nutrients is one of the main criteria for its effectiveness as a beneficial soil amendment. To determine the amount of phosphorus (P) that could be released over time, a desorption experiment with water and biochar was conducted using a benchtop stirred-flow reactor. For this experiment, the same biochar used in previous adsorption isotherms was selected. The concentration of P adsorbed to the biochar samples was determined using total elemental digestion listed in Chapter 9 of Biochar: A Guide to Analytical Methods (Singh, et al., 2017), and pre- and post-adsorption isotherm biochar subsamples were compared. A subtraction of the initial P concentration from the final P concentration was done to determine the amount of P loaded onto the biochar post-isotherm. This calculated P value was then used as the initial P concentration for the desorption experiments. The remaining biochar was air-dried for use in the desorption experiments.

All equipment used in this experiment was acid washed with 1 M HCl and then triple rinsed with 18 megohm deionized water. All hosing that was used was purged with deionized water and tested with litmus paper for neutral pH after acid washing. The equipment was then completely air-dried before use.

The stir flow reaction chamber used for the experiment is a plastic cylinder with a screw top with entry and exit ports. The center of the reactor has a small bevel to hold a magnetic stir bar directly below a recessed lip that would hold the filter. When placed on a stir plate, the stir bar creates stirred flow directly below the filter as water passed through the cylinder. The reactor was custom machined by the University of Idaho for the purpose of these experiments.

A 0.45 µm polyether sulfone (PES) membrane filter was set in the stirred-flow reactor chamber. Once the filter was in place, it was wetted with 18 megohm deionized water to seat it in the recessed grooves and to prevent movement from static electricity. Then, 0.2 grams of biochar were used in the stirred-flow reactor. The biochar was then placed below the filter. The 8 mm × 2 mm × 1.5 mm stir bar was then inserted into the bevel at the bottom of the chamber. The reactor was then sealed by screwing on the top of the chamber and placed on a magnetic stir plate.

MasterFlex size 13 tubing was used to connect the stirred-flow reactor to a MasterFlex L/S Cole-Parmer peristaltic pump, Spectrachrom CF 1 fraction collector, and DI water reservoir. The tubing was connected so that DI water would be pumped out of the reservoir and past the pump.

Flow then enters the reactor chamber from the top, mixes with the biochar sample, goes through the filter, and out the top of the reactor to the fraction collector. Before the system was started, the pump was calibrated to a flow rate of 2 mL/min. The fraction collector was set to cycle every 3 minutes so that 6 mL effluent samples were collected in each tube.

Once the equipment was calibrated, the system was primed with water up to the effluent port for sampling. At the same time, both the peristaltic pump and fraction collector were activated so that the sampling was calibrated to 6 mL per sample. The stir plate was then set to level 7 to prevent clogging in the system while stirring the water in the reactor without creating a vortex to avoid dislodging the filter. The system was then inspected for leaks or air bubbles that could affect the calibration of the system, and any issues were immediately fixed. If the issue was significant, the experiment would be restarted.

Every 10 samples, a subsample of effluent water was taken for pH measurement. A total of 40 samples were collected for each biochar sample (1 every 3 minutes), with a total run time of 120 minutes and 240 mL of water pumped through the system. The 40 samples for each biochar type were then combined to make one single sample for ICP analysis. The phosphorus concentrations of the samples were analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent 5110, Santa Clara, California). The samples were averaged this way to reduce the number of samples tested with the ICP. The concentrations that were desorbed were then compared to the initial starting concentrations from the total elemental digestions to determine the percentage of total loaded P that was desorbed. These percentages were then converted to mg/kg which is how the data is displayed in Figure 5.

1.3.6. Formic Acid Extractions for Plant Available Phosphorus

Formic acid extractions are good indicators of plant available P (Wang et al., 2012b). Formic acid used in extraction procedures emphasizes the influence of soil pH and organic ligands on P complexation, dissolution, and precipitation, with a special focus on orthophosphate-P. Formic acid is a monocarboxylate organic acid that has low complexing ability but solubilizes phosphate by decreasing the solution pH and buffering it at a pH value less than 3 (Wang et al, 2012b). For this reason, biochar samples were extracted with 2% formic acid to evaluate their effectiveness as a possible soil amendment according to (Singh, et al., 2017). Biochars were first crushed and prepared in the same manner as the pH and electric conductivity tests. Once the biochars were air-dried and sieved to less than 2 mm, 0.35 grams were placed in 50 mL polypropylene tubes, and 35 mL of 2% formic acid was added. To make the 2% formic acid stock acid, Fisher Chemical 88% Formic Acid by weight was diluted using 18 megohm deionized water. After the formic acid was added, the bottles were then sealed and set to ultrasonicate at level 5 for 30 seconds in a Ultrasonik 57X made by Degussa-Ney to completely disperse the formic acid into the biochar pores. The bottles were then mechanically shaken for 30 seconds at approximately 23 degrees Celsius on a Glas-Col end-over-end shaker. After 30 minutes, the samples were centrifuged at 25000 × g for 10 minutes. Supernatants were then filtered with Whatman no. 41 filter paper, and then P concentration was determined following colorimetric analysis (Murphy and Riley, 1962). Concentrations were reported as mg/L. If other possible nutrients in the biochar were of interest at the time of extraction, then samples were analyzed with ICP-OES. To prepare samples for this analysis, they were filtered using a 0.45 µm polyether sulfone (PES) membrane filter instead of the Whatman no. 41 filter paper. Phosphorus concentrations were then analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent 5110, Santa Clara, California). Concentrations were reported as mg/L. Available P was then calculated using Equation 2:

Equation 2. Formula for Bio-available Phosphorus and Units

$$BAP = \frac{(Cp * V)}{(m)}$$

BAP = Bio-Available Phosphorus (mg/kg)
Cp = Extracted P (mg/L)
V = Volume of Formic Acid (L)
m = Mass of Biochar (kg)

1.3.7. Statistical Analysis

All biochar types tested were done in triplicate for measurements and analysis. All graphs and data tables were generated using Microsoft Excel Version 2301. All means, standard deviations, and coefficients of variance were calculated using Microsoft Excel Version 2301.

1.4. Results

1.4.1. Companies, Location, and Feedstocks

Table 2. provides a summary of characterization data for the 14 biochar types that were analyzed. The study included biochar products from 11 companies and the USFS, with two companies contributing 2 types each. All the biochars were commercially available for sale to the public, except for the CharBoss biochar provided by the USFS. The feedstock for the biochars varied, with wood waste from forest fires and logging activities being the main source. Agricultural waste from crops such as wheat, corn, and coconuts were also used as feedstock. However, the feedstock for National Carbon Technologies biochar was unknown as the company did not provide this information.

Table 2. Biochar characteristics for determination for future experimentation.

Company	pH	Electric Conductivity (µS/cm)	Q (mg/kg) at 25 ppm P	Water Desorb P (mg/kg)	2% Formic Ava. P (mg/kg)
Oregon Biochar Solutions (CharBliss)	10.36	1217	-45	-1245	469
Karbonous Inc. (PAC)	10.22	753	1033	-1	690
Biochar Now (Powdered)	9.30	477	218	-29	269
Biochar Now (Granular)	9.88	1506	17	-15	64
ARTi	11.26	813	-252	-204	314
National Forest Service (CharBoss)	5.19	77	-6	-9	29
Carbon Logic (Growth)	9.70	2310	-44	-74	196
Carbon Logic (Stater)	11.06	1137	1187	-1	1335
NCT	11.34	1366	248	-3	94
Pacific BioChar (Blacklite Pure)	8.92	1137	16	-56	221
Genesis Biochar	7.98	143	89	-32	620
BC Biocarbon	9.20	1325	371	-10	1518
Seneca Farms Biochar	9.44	1471	-12	-34	125
Wakefield Biochar	7.98	470	64	-3	17

1.4.2. pH of Biochars

pH measurements were conducted to assess the biochar's reactivity in solution. Figure 1 presents the pH values of the 14 biochar types, with mean values calculated from triplicate measurements. The error bars indicate the standard deviation around the mean for each type. Only CharBoss biochar had an acidic pH of 5.19, while all other biochars were alkaline with a pH of 7.98 or higher. The highest pH value of 11.34 was recorded for National Carbon Technologies (NCT). The average pH of all biochars tested was 9.40.

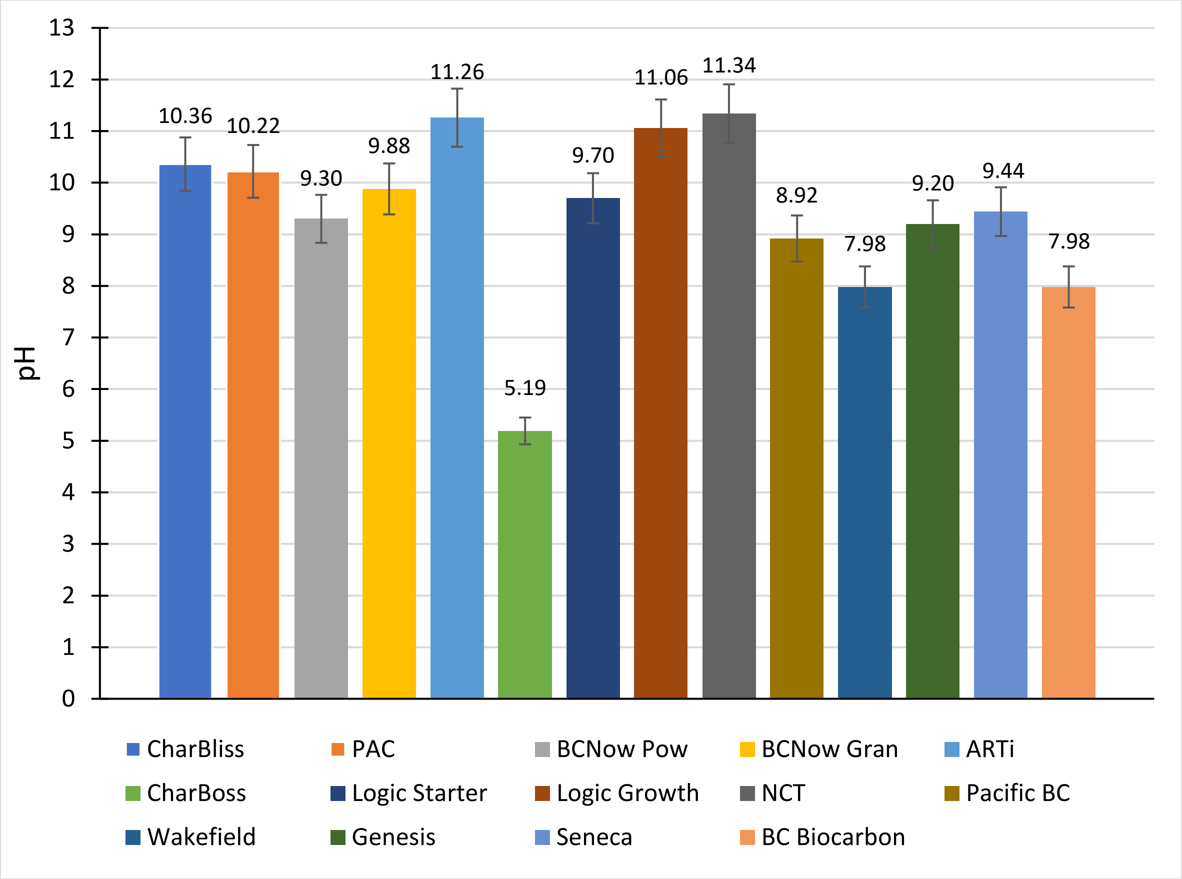

Figure 1. Biochar type and pH. (n=3)

1.4.3. Electric Conductivity

Electric conductivity (EC) measurements were taken to indicate the number of free ions in the biochar solution. The conductivity values varied widely between biochar samples, as shown in Figure 2. The mean values, reported from triplicate measurements, ranged from 77 µS/cm for

CharBoss to 2310 µS/cm for Wakefield. The error bars represent the standard deviation about the mean for each individual type. The mean value across all biochar types was 1007 µS/cm.

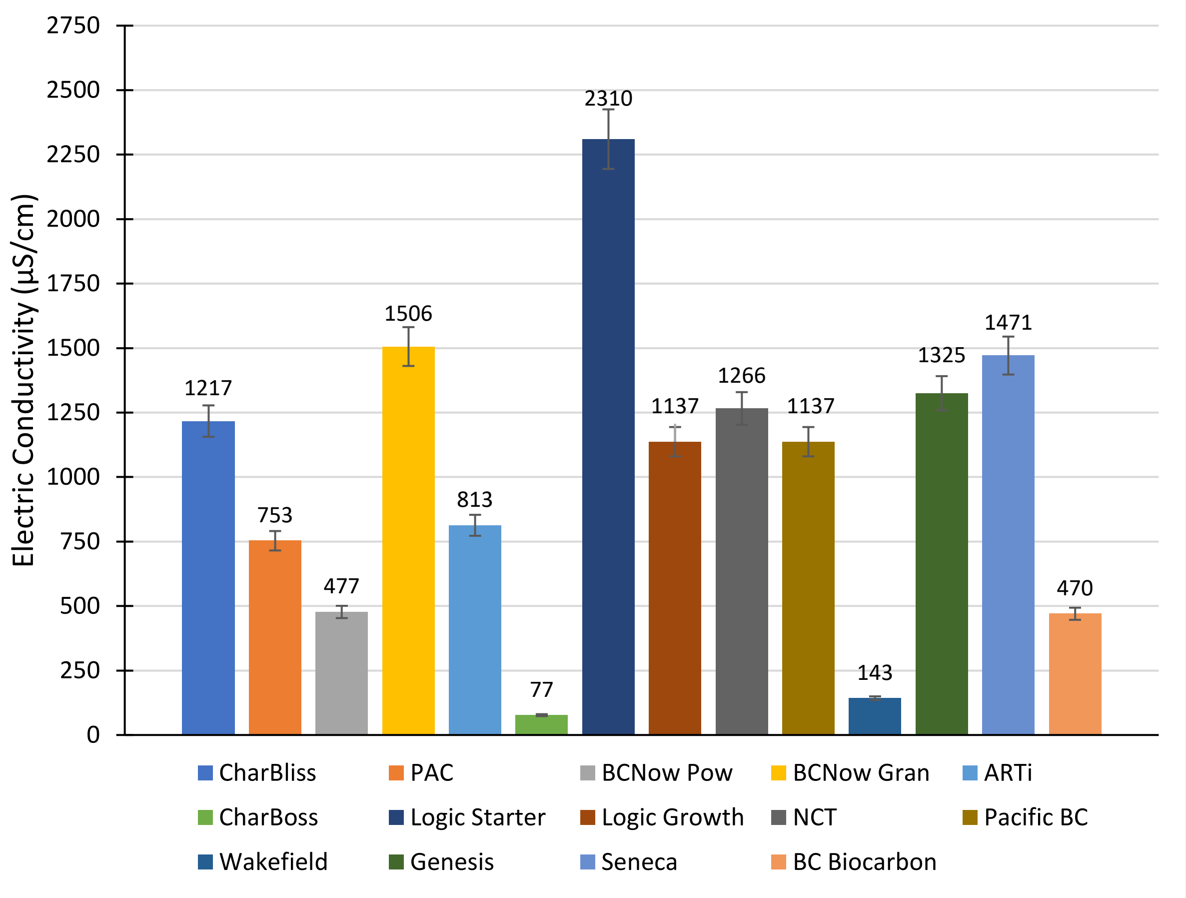

Figure 2. Electrical conductivity of different biochars. (n=3)

1.4.4. Single Point Adsorption Isotherm

A single point adsorption isotherm was done to determine the adsorption potential (Q) for the biochars in their “raw” state (Figure 3). Results are recorded as milligrams of P per kilogram of biochar. Mean values are reported from triplicate sample measurements. The error bars represent the standard deviation about the mean for each individual type. Adsorption varied widely across biochars, where some even showed negative adsorption or desorption of P, indicating that they release P into effluent water even when a 25 mg/L P solution was added to the suspension.

The three best performing biochars had chemical modifications done by their suppliers. These were included in the raw unmodified characterization isotherms because they had not been modified by our research group. There is a drastic reduction in the adsorption potential of the biochars between the modified and unmodified biochars. It is not known if NCT is modified or not due to the lack of information provided by the supplier. It had the fourth highest adsorption of the biochars that were tested. Of the known unmodified biochars, Biochar Now Powdered had the highest adsorption while ARTi had the lowest with desorption of P instead of adsorption. The initial and final pH of each biochar type is also shown in Figure 4. Initial pH was adjusted to as close to 6.5 as possible.

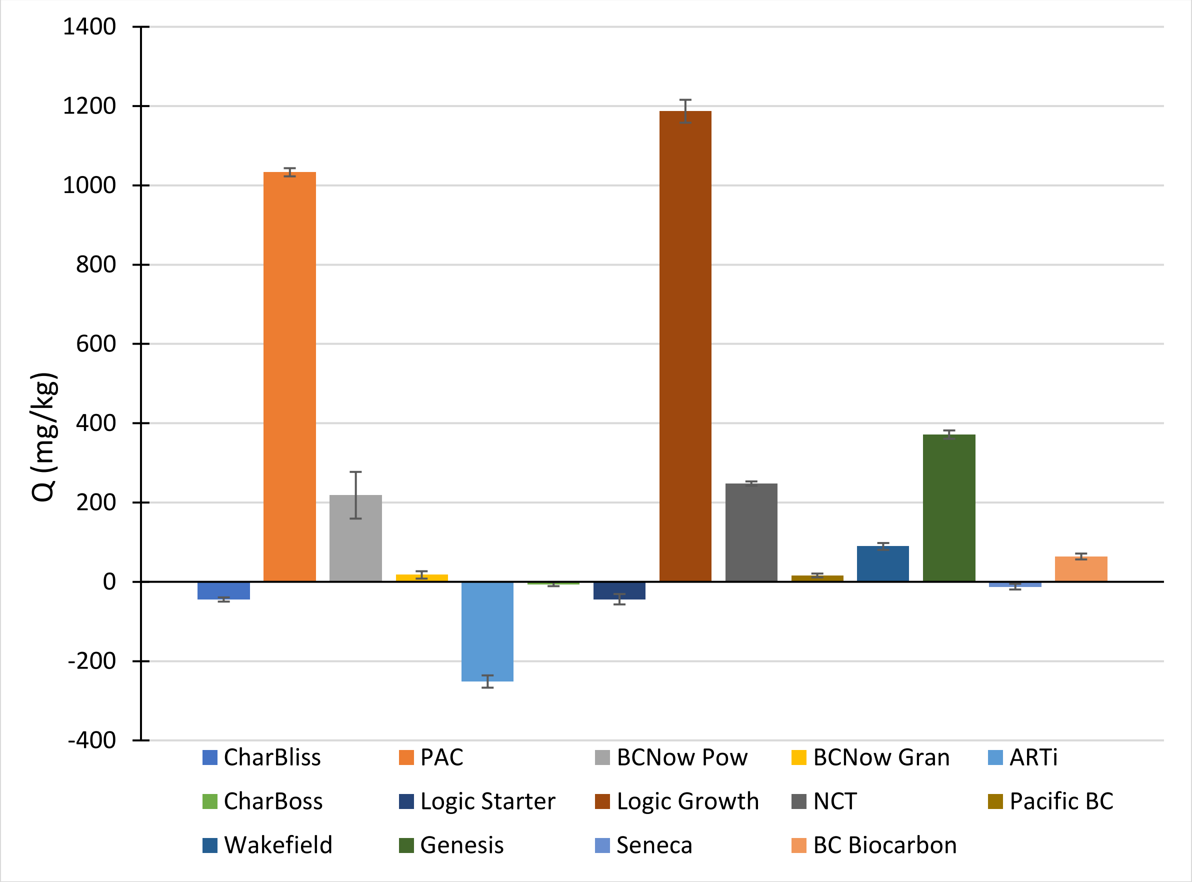

Figure 3. Phosphorus adsorption on "raw" biochar from a 25 mg/L P solution, Q is P adsorbed to biochar. (n=3)

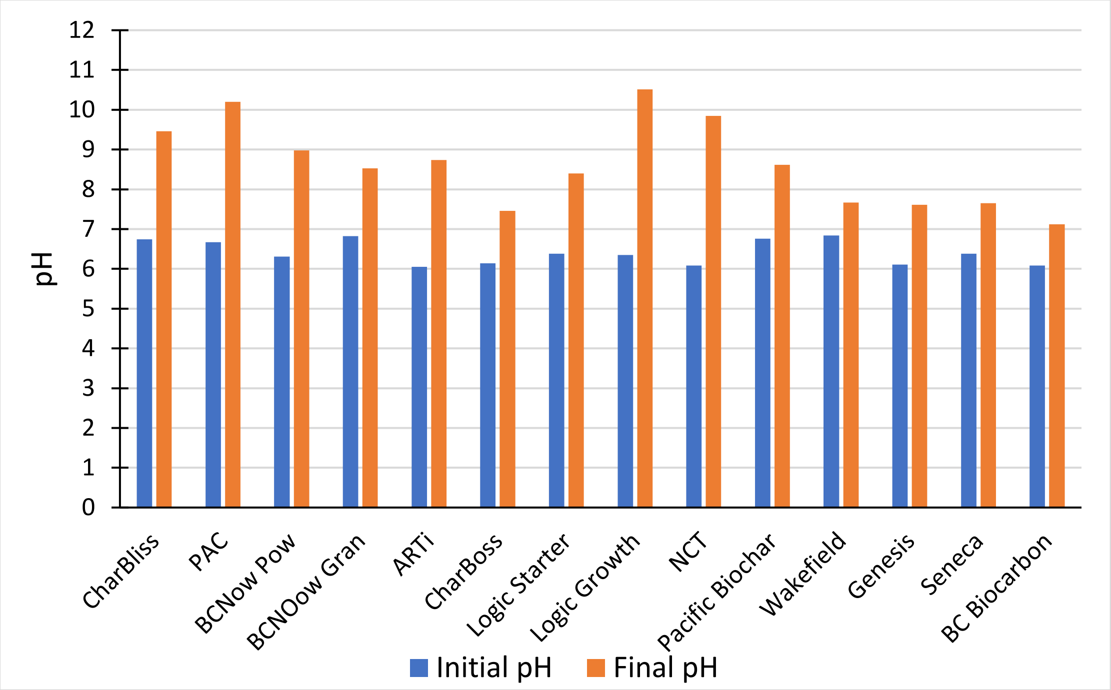

Figure 4. Initial and final pH of biochar types during the single point adsorption isotherm experiment. (n=3)

1.4.5. Phosphorus Extractions with Deionized Water

Phosphorus release from the biochars was tested in the stirred-flow reactor using deionized water to quantify the amount of phosphate that could be released from the biochars. This test was also used as an indication of the ability of the biochars to release other nutrients post-treatment with wastewater. The amount of P desorbed is reported as desorption (Q). Results are recorded as milligrams of phosphorus desorbed per kilogram of biochar. Mean values are reported from triplicate sample measurements, and the error bars represent the standard deviation about the mean for each individual type. While all biochars released phosphate, there was a wide distribution between biochar types. Like the single-point adsorption isotherm, the modified biochars behaved differently from the unmodified biochars, releasing the least amount of P, with the 3 worst desorption results coming from these modified biochars. Logic Growth released the least amount of P at 0.49 mg/kg, and ARTi released the most at 204 mg/kg. The mean P released for all biochar types was 42 mg/kg.

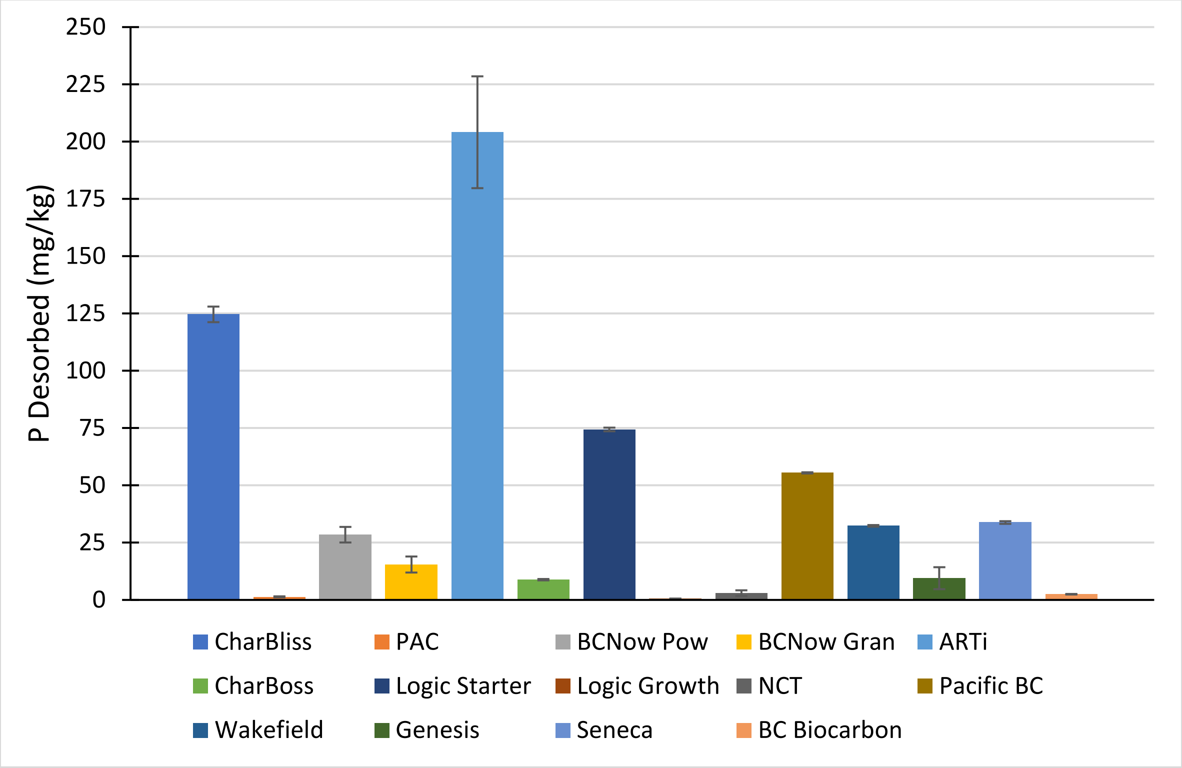

Figure 5. Phosphorus desorbed from "raw" biochar types using a water extraction. (n=40)

1.4.6. Plant Available Phosphorus Extraction with Formic Acid

Formic acid extractions were done to mimic the organic acids that would encounter the biochar in an agricultural setting released from plant roots. Formic acid is a good substitute for other organic acids because it is less reactive and safer to handle compared to other acids like EDTA (Singh, et al., 2017). Mean values are reported from triplicate sample measurement. The error bars are standard deviation about the mean for each individual type. The amount of P released from the extraction is reported as milligrams of phosphorus per kilogram of biochar. This was done to normalize sample mass and for easy determination of possible nutrient potential. All biochar tested released P but there was considerable variation between biochar types. Genesis biochar released the most P at 1518 mg/kg. BC Biocarbon released the least amount with 17 mg/kg. The mean amount of P released for all biochar types was 426 mg/kg.

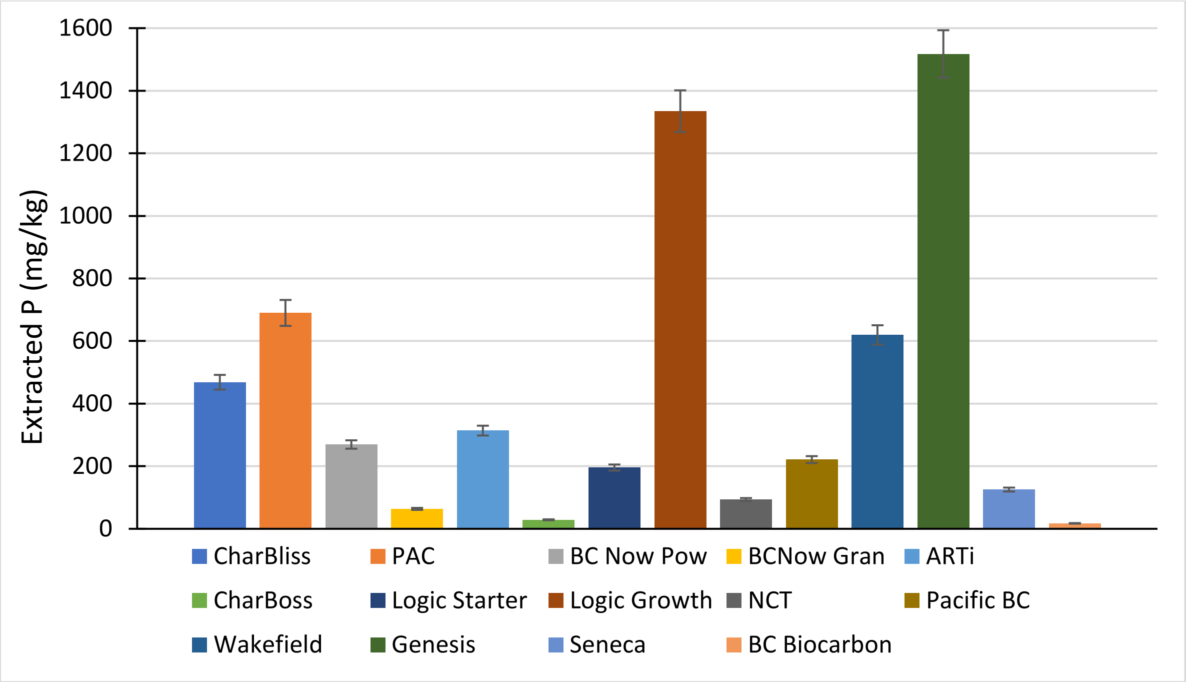

Figure 6. 2% formic acid extraction of biochars to for available P in biochar. (n=3)

1.5. Discussion

1.5.1. Raw Biochar and Modified Biochar

During the process of characterizing the different types of biochar, it was observed that a few performed significantly better for P adsorption than the others. Specifically, PAC, Logic Growth, and Genesis biochars showed phosphorus adsorption capacities of 1033, 1187, and 337 mg/kg respectively. It should be noted that these biochars, along with Logic Starter, are "raw" biochars as defined in this study. For this study's definition, raw biochars are those that have not undergone any chemical modifications post-pyrolysis. Furthermore, PAC is an activated carbon and not a biochar. It was included in this study for a comparison and is referred to in a similar manner with the other biochars. The exact modification to the PAC was not shared with our research group but the activated carbon is modified for the purpose of wastewater remediation.

In the 2% formic acid extractions, biochars that were modified by the suppliers, along with PAC and Genesis, all had concentrations of calcium and magnesium that were orders of magnitude higher than those of the raw biochars (Table 3). The exact mechanism behind biochar modified with calcium and magnesium for the removal of P was not determined from this extraction, but complexation of phosphate with calcium and magnesium is known to promote increased removal of phosphate. This is explored further in Chapter 2 of this thesis with both a review of relevant literature and experiments involving Ca and Mg modified biochars.

Table 3. Ca and Mg amounts from 2% formic acid extractions.

Biochar Type	**Ca Availability (mg/kg)**	**SD**	**Mg Availability (mg/kg)**	**SD**
CharBliss	9805	181	714	6
PAC	15347	36	2676	3
BCNow Pow	9241	154	725	32
BCNow Gran	1655	83	226	4
ARTi	605	68	221	10
CharBoss	902	2	25	1
Logic Starter	5685	527	303	29
Logic Growth	61905	680	1910	22
NCT	5050	183	132	3
Pacific BC	3031	13	320	2
Wakefield	8068	25	896	11
Genesis	48255	1304	2692	90
Seneca	20670	6747	894	212
BC Biocarbon	899	124	101	1

Optimizing the adsorption of P onto biochar by removal from wastewater is the primary objective of this research. To eliminate any unknown variables, it was decided that modifications must start with previously unmodified biochar or “raw” biochar. The need to understand the mechanism of the modification is also important. Therefore, even though the PAC, Logic Growth, and Genesis biochars showed the best adsorption from the single-point isotherm experiment, they were not selected for further experimentation. Similarly, NCT was excluded from further experiments as feedstock and possible modification information was not shared. However, the high P adsorption performance by Logic growth due to added amounts of Ca and Mg complexed with the biochar led us to try Ca and Mg modification of raw biochar for increased P adsorption; results of this trial are included in Chapter 2.

1.5.3. Effects of Particle Size on Biochar Characterization

All the raw biochars were standardized to a particle size of less than 2 mm using a stainless-steel rolling pin to crush the biochar into small particles. The biochar was then physically separated using a number 10 sieve. Normalization of particle size was necessary for characterization since adsorption reactions can be greatly influenced by surface area, which is largely influenced by particle size (Downie et al., 2009). To confirm this, Biochar Now granular and powdered materials were tested. Although the biochar was chemically similar, the powdered material was expected to have a much larger surface area compared to the granular material and therefore more adsorption. Adsorption for the biochar increased from 17 mg/kg in the granular to 218 mg/kg in the powdered. Based on this, all other biochars were normalized for particle size, and the two Biochar Now particle sizes were both included in the data set to quantify this action.

While reducing biochar particle size increases adsorption, it is important to consider the practicality of recovering the biochar after wastewater treatment for use as a soil amendment. Therefore, a particle size that balanced increased surface area with ease of mechanical separation was chosen for experiments. This was especially crucial for the pilot-scale application discussed in Chapter 3 of this manuscript.

1.5.2. Selection of Biochar for Further Study

After conducting characterization experiments on 14 biochar types, four were chosen for further experimentation, namely CharBliss, Pacific Biochar, BC Biocarbon, and Wakefield Biochar. The first set of modified isotherms with a 2% Fe-modification, detailed in Chapter 2, was conducted on these four biochars based on the criteria specified within this chapter. All four biochars were selected because they are commercial products available for purchase at a large scale, which could meet the needs of commercial applications. Additionally, they were all made from forest waste feedstock, which was not a requirement, but aligned with the project's objective of using biochar from waste material. The pH of the selected biochars ranged from 7.98 to 10.36, which were not at extremes on either end of the tested range. Electric conductivity ranged between 1137 and 1325 µS/cm, except for Wakefield, which was only 470 µS/cm.

The selected biochars exhibited positive adsorption in the single point isotherms in their raw states, except for CharBliss, which had a desorption of 45 mg/kg P. It was determined that biochars with positive adsorption in their raw state would be suitable for increasing adsorption through modification. However, this assumption needed to be tested so CharBliss was included in the subsequent experiments to determine if its negative raw adsorption would significantly affect the adsorption of modified biochar. CharBliss was selected over other biochars with negative adsorption because it shared the other traits listed above with the other biochars selected including commercial availability, feedstocks, pH, and EC.

All four chosen biochars released P during the water desorption experiment, which was essential to ensure that the biochar could be used as a possible P bearing soil amendment. Some biochars almost had no P released, while others released comparably high amounts. Biochars with either very low or very high P release would have been poor candidates as soil amendments, as they either lack soil amendment potential or have the potential to become sources of P pollution.

To assess soil amendment potential, formic acid extractions were conducted. All four chosen biochars released P through extraction, with a wide range from 17 to 1518 mg/kg. It was determined that the potential to release P was more important than the quantity of P released since the amount of potential P released through extraction of modified biochars post-treatment with wastewater would be considerably different from that of raw biochars.

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Chapter 2: Modification of Biochar for the Removal of Phosphorus from Wastewater

2.1. Abstract

Phosphorus (P) pollution from anthropogenic activities is contributing to increases in eutrophication in freshwater systems. Sustainable sources of P such as recycling it from wastewater are important to study because phosphate-bearing minerals are a limited resource. Biochar, a substance that is created through the pyrolysis of biomass shows promise in removing P from wastewater. Chemically modified biochar is significantly more efficient at removing P than unmodified biochar. This chapter evaluates biochar modifications that optimize P adsorption of P to biochar. The modifications used Ca, Mg, Fe cations, and cationic polymers.

The best performing modified biochar which was 4% Fe-modified biochar was incorporated into a continuous flow reactor with dairy effluent wastewater to simulate real wastewater treatment applications. The biochar was then recovered from the reactor and formic acid experiments were done to determine the quantity of recoverable P. The Fe-modified biochar treatment had a significant increase in plant available P from 27 to 138 mg/kg. However, this was still lower than the initial value of unmodified biochar, which was 647 mg/kg and increased to 680 mg/kg after treatment. Total P was highest in the Fe-biochar post-treatment with the flow reactor at 1224 mg/kg, while the unmodified biochar had a total P of 994 mg/kg. It is the hope that P recovered from our modified biochars with this method can be reused as a soil amendment. Sustainable agriculture will have to utilize other sources of P in the future and these modified biochars could be a resource of recycled P.

2.2. Introduction

2.2.1. Phosphorus as a Limited Resource

Humans have currently created a non-sustainable P system, where there is large scarcity of the element available in agriculture and substantial waste at the same time. Waste exists in nearly all stages of the current food system, therefore there is a lot of potential to address this issue with the recovery and redistribution of P from various types of wastewaters (Shepherd et al., 2016).

Many P recovery technologies, such as chemical precipitation, biological P uptake, and adsorption, have been developed (Fang et al., 2015). Despite this, not all technologies have the same potential. Many chemical precipitation methods require expensive chemicals and can create large amounts of chemical waste. Struvite ($Mg(NH_4)(PO_4)\bullet 6(H_2O)$) is a mineral precipitate that is used for the removal of P (Stolzenburg et al., 2015). A main limitation in struvite precipitation in small wastewater treatment facilities is that the water conditions are undersaturated with respect to struvite, as well precipitation kinetic limitations (Halles et al., 2019). Struvite precipitation is dictated by physio-chemical factors affecting both nucleation and crystal growth. These include temperature, mixing energy, pH, the concentrations of Mg, NH_4, and H_3PO_4, and the presence of competing ions (Halles et al., 2019). If conditions are favorable, then struvite can be recovered for P reuse, but these conditions can be hard to maintain. In a study by Halles et al. (2019), four wastewater treatment plants were tested for improvements in P recovery that occurred when Mg concentrations were increased. The addition of Mg and pH adjustment caused struvite to precipitate. Although one of the plants achieved 97% removal of PO_4 (initial concentration of 400 ± 141 mg/L and thus reducing P effluent concentration to ~12 mg/L), another only achieved 43% removal of PO_4 with an initial concentration of 120 ± 33 mg/L, showing the variability in struvite precipitation efficiency. Further, the effluent water still is high in total P concentration with remaining risks for P loading to surface waters.

Biological P removal may be limited due to a lack of carbon sources and the difficulty of sustaining microorganisms in removal systems. It can be difficult to balance the conditions necessary to sustain microbial productivity (Rittmann et al., 2011). For instance, many microorganisms such as Didymosphenia *geminata*, that can uptake P require alternating aerobic and anaerobic conditions. Most wastewater treatment facilities rely on anaerobic conditions thus preventing the additions of these microorganisms without costly upgrades to current systems. Phototrophic microorganisms (i.e., photosynthetic bacteria and algae) also have difficulty being implemented in wastewater treatment plants because their microbial cells cannot be removed easily from treated water (Rittmann et al., 2011).

As opposed to struvite removal and biological removal, adsorption has the advantage of being easier to control and cost efficient (Fang et al., 2015). When adsorption is done using iron, the reactions are easier to predict due to the high affinity of iron oxides for ortho-phosphate (Wilfert et al., 2015). Research done by Newcombe et al. (2008) suggest that adsorption to hydrous ferric oxide during the reactive filtration process is stable within a normal municipal wastewater pH range of 6.0 to 9.0 and stable, despite highly varying alkalinity, temperature, and sulfate concentrations. The surface charges stayed stable with a constant acidity despite differing influent water quality, which allows for similar sorption mechanisms regardless of the concentrations of influent reactive contaminants. Adsorption also offers the possibility of P recovery and the reuse of the adsorbents, which adds a value to the waste material making it more cost effective (Wilfert et al., 2015).

Regardless of the method of P removal, the recycling of P is important if societies are going to achieve sustainable P production. Global P needs continue to increase but it is uncertain how much longer P reserves will last considering future predictions. In 2000 alone, 19.7 Mt of P was mined from phosphate-bearing rocks (Gilbert, 2009). The majority, 15.3 Mt, was used to produce fertilizers. Researchers have estimated that total international reserves of P will be adequate for almost a hundred years (Gilbert, 2009). Depending on use, discovery of new sources, and technologies to recycle P, some researchers state that there might only be approximately 50 more years of P resources available (He et al., 2017). If these estimates are true, then it will be crucial for the agriculture industry to find alternative sources of P-based fertilizer. Regardless of the need to recycle P, removal of P from wastewater to reduce P pollution is imperative (Hallas et al., 2019). Therefore, a cyclic use of P and continued advancement of technologies that achieve the recovery of P from secondary sources is required. Globally, about 1.3 Mt P per year is treated in municipal wastewater treatment plants. This potential untapped resource could provide a major secondary source of P (Wilfert et al., 2015). The benefits of recycling P can also help reduce the costs of P fertilizers. For instance, the cost of fertilizer products in the state of Illinois increased by over 50% in 2021 alone. Fertilizer prices across the rest of the United States have been on an upward trend since 2006, with a peak in 2008. (Schnitkey et al., 2021). Recycling P would reduce the amount of P required from mineral reserves . It would also allow more P to be available domestically and reduce dependency on foreign sources, which are subject to costly tariffs that can raise the costs of fertilizers.

2.2.2. Wastewater Treatment Using Biochar for Phosphorus Removal

Biochar possesses chemical and physical properties that make it highly effective for removing chemicals from solution via sorption, as well as help bioremediation processes (Gelardi and Parikhn, 2021). The type of biochar feedstock and production conditions can be tailored to the specific contaminants to improve remediation efficiency. Wood derived biochars typically have greater surface area and carbon content than those from manure or grass. Manure and grass biochars generally have more abundant oxygen-containing functional groups and mineral constituents (Downie et al., 2009). The activated carbon in biochar is generated through the pyrolysis processes. This makes biochar a good immobilizer of pharmaceuticals in wastewater, and retardant for the mobility of pesticides. These traits also mean biochars can serve as a sink for petroleum-based compounds. There is also increasing evidence that biochar can facilitate biodegradation of organic compounds (Qin et al., 2013). In addition to these traits, numerous studies have shown that biochars can bind trace metals. Metal and metalloids do not degrade so immobilizing them is the best method of remediation. Biochars do this through their high surface area and cation exchange capacity by mechanisms of chemisorption and electrostatic interactions (Zhou et al., 2013).

Biochars are frequently modified with the desire to improve their remediation properties (Shepherd et al., 2016). This is most common when they are applied to nutrient removal. Common modifications include cationic polymers (Wang et al., 2020), magnesium (Fang et al., 2014), and iron (Siddiq et al., 2021). Oxidants, acids, or alkalis are also used as modifiers to improve the remediation potential of biochars (Wang et al., 2019). Iron modified biochar can be used to remove P from aqueous solutions including livestock manure, industrial and municipal wastes, and agricultural effluents. Biochar is similar to activated carbon, which is a common substance used in remediation. Both substances possess high cation exchange capacity, aromaticity, and high surface area. This makes biochar a favorable adsorbent for a range of trace metals (O'Connor et al., 2018), organic compounds (Zhang et al., 2010), and pesticides (Liu et al., 2018).

In certain scenarios, biochar can serve as a low-cost alternative to remediation. Biochar is also low-tech, which can make applications simpler and therefore save on costs. By being low cost and simple to use, biochar has the potential to be incorporated into on-site local systems. This can save costs on transportation as well. Research is ongoing into successful and cost-effective strategies for implicating biochar in remediation. The research is promising and there is a lot of room for the technologies to grow. More cost-saving advantages could still be discovered.

2.2.3. Phosphorus Adsorption with Iron Oxides

Adsorption of P is a technology that is applied in wastewater treatment. Current technologies attain low P concentrations in effluent waters by utilizing iron-based adsorbents (Wilfert et al., 2015). These technologies can be up to 99% effective at removing P from wastewater (Newcombe et al., 2008). Iron adsorbents are used due to the high affinity of oxides for orthophosphate, the simplest of the phosphates (Wilfert et al., 2015). Adsorption of P also offers the opportunity of P recovery and the reuse of the adsorbent materials (Genz et al., 2004). Ferrous and ferric ions can be hydrolyzed by increasing pH and precipitate out of solution as numerous insoluble iron oxides, including goethite, hematite, ferrihydrite and hydrous ferric oxide (HFO) (Cornell and Schwertmann, 2003). When these iron oxides are used in wastewater treatment facilities, they react with phosphate to form either iron phosphate minerals such as strengite or adsorption complexes (Smith et al., 2008). Iron oxides have varying degrees of crystallinity (Guzman et al., 1994), which controls properties such as specific surface area, porosity, the quantity of exposed surface sites, solubility, and reducibility.

Amorphous iron oxides have greater phosphate adsorption capacities than crystalline iron oxides, and this is credited to amorphous iron oxides having higher surface areas (Parfitt et al., 1975). These properties in turn affect the phosphate binding properties of the iron oxides and the bioavailability of adsorbed phosphates (Guzman et al., 1994). These various oxide properties cause differences in the amount and ways that P is adsorbed (Wilfert et al., 2015), and can also affect the strength of P bound to Fe or Ca. The strength of the chemical bonds on P can then affect desorption rates and capacities of the oxides (Wilfert et al., 2015). Mechanisms through which Fe-phosphates can be altered resulting in P release vary just like the oxides themselves. This emphasizes the underlining importance of differentiating between any Fe-phosphates for applications involving adsorption (Wilfert et al., 2015).

Mechanisms behind phosphate adsorption onto oxides are mainly through ligand exchange with the surface OH groups. This happens when the Fe beneath the surface hydroxyl acts as a Lewis acid (Cornell and Schwertmann, 2003). When phosphate is bound directly to an iron oxide surface through a ligand exchange mechanism there is no water between the oxide and phosphate; the resulting complex is called an inner sphere complex (Abdala et al., 2015). The mechanisms of inner sphere complexation vary based on the types of iron oxides and the conditions during the formation reactions. Variables such as the initial phosphate concentration and pH can change these conditions (Abdala et al., 2015). Therefore, phosphate adsorption and desorption properties vary for different iron oxides. This makes adsorption to oxides a very versatile process (Wilfert et al., 2015). For these reasons iron was combined with biochar for removing P from wastewater. Through combing ferric chloride and biochar, a modified biochar rich in iron was created for experimentation. The iron on the biochar exists as adsorbed cations and hydrous ferric oxide, which is an amorphous iron oxide species.

2.2.4. Phosphate precipitation in wastewater with Ca (Apatite) and Mg (Struvite)

Phosphate precipitation is a method utilized by wastewater treatment facilities in the removal of P from water. Laboratory experiments have shown that P concentrations in controlled systems rapidly decrease due to precipitation as Ca-P minerals (e.g., hydroxyapatite ($Ca_5(PO_4)_3OH$)) (Cao and Harris, 2008). One such experiment involved manure-amended soil leachate solutions and flushed dairy manure wastewater. In these solutions the pH was adjusted to between 8.50 and 9.50 to precipitate hydroxyapatite from solution (Cao and Harris, 2008). Phosphate precipitation occurs rapidly where the bulk of the reaction happens in the first 10 minutes, followed by a slow decline until 60 minutes when a leveling off occurred. This observation agreed with previous work done by (Cao et al., 2007). The most stable Ca-phosphate mineral that can be precipitated is hydroxyapatite (Cao and Harris, 2008) except for fluorapatite, but F is not added to wastewater.

The formation of more soluble Ca-phosphates may be favored kinetically because of faster nucleation (Cao and Harris, 2008). If Ca is in solution with P this does not mean it will always produce Ca-phosphates. There are a variety of ions that can impede Ca-P precipitation due to surface complexation on the newly forming surfaces that interrupt nucleation. These impeding ions are called inhibitors and may include organic acids, CO_3^- , and Mg^{2+}. Of particular interest is the inhibitory effect of Mg^{2+} from its adsorption at active growth sites (Ferguson and McCarty, 1971). Spontaneous precipitation experiments imply that Mg^{2+} kinetically hampers nucleation and the succeeding growth of hydroxyapatite by occupying structural sites larger Ca^{2+} ions would normally fill (Ferguson and McCarty, 1971). This mechanism has also been described as the consequent reduction of long-range order due to the smaller size of Mg^{2+} and its greater tendency to bond covalently. This site replacement coprecipitation of Mg^{2+} with Ca-phosphate encourages formation of amorphous Ca-phosphate over hydroxyapatite. (Suchanek et al., 2004). X-ray diffraction (XRD) analysis discovered that precipitates where soluble amorphous Ca-phosphate contained Mg^{2+} in solution, had the overall effects of reducing Ca-phosphate precipitation (Cao and Harris, 2008). This resulted in higher P concentrations in solution. The integration of Mg^{2+} into the precipitated Ca-phosphate phase was supported by XRD analysis of heat-treated solids (Cao and Harris, 2008). The importance of this mechanism is the existence or addition of Mg^{2+} can enable Ca-phosphate precipitation and potential P recovery from wastewater systems to be improved. This is especially true in waste waters with high alkalinity (Cao and Harris, 2008).

Example Reaction of Apatite Precipitation (Wang et al., 2018)

$3PO_4^{3-} + 5Ca^{2+} + OH^- \rightarrow Ca_5(PO_4)_3(OH)$ (a)

$3HPO_4^{2-} + 5Ca^{2+} + 4OH^- \rightarrow Ca_5(PO_4)_3(OH) + 3H_2O$ (b)

$3H_2PO_4^{-} + 5Ca^{2+} + 7OH^- \rightarrow Ca_5(PO_4)_3(OH) + 6H_2O$ (c)

Struvite, a Mg-phosphate mineral, is another precipitate that is utilized by wastewater treatment facilities in the removal of P from water. A general equation for struvite is:

$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4 + 6H_2O$

Anaerobic wastewater treatment plants have used struvite precipitation for P recovery (Halles et al., 2019). However, not all anaerobic systems can utilize struvite precipitation due to conditions that are not thermodynamically favored (Halles et al., 2019). Generally, Mg is the limiting reagent during struvite production so treatment plants must add Mg. This is usually done with the addition of $MgCl_2$, requiring care to prevent the treated water from becoming saline. A study by Halles et al. (2019) observed that competing ions such as Al^{3+}, $Ca^{2+,}$ and Fe^{3+} did not interfere with the formation of struvite. pH was around 8 for all these trials, which is in the lower range for struvite to precipitate, optimal pH is around 10. However, it was found that a pH of around 8.5 was best to precipitate struvite, which decreased the formation of Ca and Mg co-precipitates (Lew et al., 2010).

2.2.5. Biochar modifications with Ca, Mg, Fe, and Catatonic Polymers (pDADMAC)

Unmodified biochar has favorable traits for the use in wastewater treatment and as a soil amendment, but for some uses, modification of the biochar is required to achieve certain properties (Bakshi et al., 2021). There are several types of modifications done to biochars depending on the desired traits. A common one currently in practice is to adsorb reactive ions to the surfaces of biochar (Chen et al., 2011). These reactive ions then adsorb more nutrients from wastewater. The increase in reactive ions is also favorable as a soil amendment because the biochar may release the ions into the soil for the potential uptake by plants. Biochars are modified using Ca, Mg, and Fe. These modified biochars have been tested for their uptake and release of P (Zhang et al., 2018; Dalahmeh et al., 2020; Fang et al., 2015).

Wang et al. (2020) created MgO-doped biochars and tested their adsorption capacity for orthophosphates from wastewater. The MgO biochar was close to one hundred times more efficient at binding to the orthophosphate than unmodified biochar. These MgO biochars are good at immobilizing P but they do not readily release the bound P. This is because the MgO binds with the orthophosphate principally by forming an amorphous Mg phosphate species (Wang et al., 2020).

Yang et al. (2021), used nuclear magnetic resonance spectroscopy to investigate the biochar surfaces and observed oxygenation of carbon compounds that creates reactive O functional groups with greater CEC and thus co-adsorption of P via ternary complexation. Oxygen modified biochars made from thermal oxidation during pyrolysis were ten times more efficient at adsorbing P from wastewaters than untreated biochars (Yang et al., 2021).

Cationic polymer modifications differ from other modifications listed so far because the process involves reversing the charge on the adsorbent, which irreversibly binds a cationic polymer (Wang et al., 2020). Poly(diallyldimethylammonium) chloride (pDADMAC) is a polymer that has been studied when it is adsorbed to biochar (Wang et al., 2020). This polymer could bind with the activated carbon on the biochar’s surface and be introduced in wastewater treatment industries for flocculating small particles, algae, bacteria, viruses, microbes, and dissolved organic matter. This flocculation settles organic waste material out of suspension through adsorption at low pH (Wang et al., 2020). Applications with other polymers such as cationic polymer C-496 were shown to be suitable for tannery wastewater treatment at a dose of 20 mg/L (Haydar and Aziz, 2009). This polymer removed contaminants with 91-95% efficiency. Another cationic polymer, poly-epichlorohydrin-dimethylamine (PED) which was immobilized onto fly ash was able to adsorb 1.5 more dye wastewater than standard commercial activated carbon (Zhou et al., 2021). The polymer was also able be reused for multiple treatments. This polymer has the potential to be adsorbed with biochar. Further study on biochars modified with these or similar polymers could be a benefit to removing P from wastewater. For this reason, pDADMAC was used in adsorption isotherm experiments with biochar.

Ca-Mg-modified biochar is another type of modification that has been shown to possess the ability to reach high P adoption capacities. Adsorption amounts in a range of 294 - 326 mg/g of P have been recorded (Fang et al., 2015). This was done in a system that only required agitation and applied heat to the modified biochars and wastewater. A simple process like this allows for easier application and implementation of these modified biochars. The P selectivity of the Ca-Mg biochar also was not significantly influenced by the typical pH levels of fermentation liquid. This would allow these modified biochars to be resistant to various pH changes in native soils. The modified biochar was also able to continually release P after it was done being used in biogas fermentation liquid treatment. The P release was stable and found to be most suitable in an acid environment (Fang et al., 2015). The specific surface area of Ca-Mg-modified biochars increases with synthesis temperature. Results of Fourier Transformed Infrared Spectroscopy (FT-IR) analysis show that the Ca–Mg biochar becomes rich in organic functional groups of hydroxyl, carboxyl, carbonyl, and methoxyl (Geng et al., 2009). Adsorption isotherm data has also indicated that the Freundlich adsorption model is the main adsorption type for Ca-Mg biochars. Adsorption extraction of P in modified biochars has the advantage of being easily controlled. Continuous extraction experiments have shown that the P release rate of post sorption Ca–Mg biochars is slow (He et al., 2017). The amount of P released was greatly increased in slightly acid DI water, which indicates the Ca-Mg biochars could be a good soil amendment for acidic soils. For this reason, modification to biochar with Ca and Mg were done and tested to see the efficiency of removing P from wastewater.

In addition to the Ca- and Mg-modified biochars, Fe-modified biochar has the potential to greatly increase the amount of P uptake from wastewater. Biochar can be modified with iron several ways but a common one is submerging biochar is an acidic solution with $FeCl_3$ to create hydrous ferric iron coated biochar (Pattammattel et al., 2019; Zheng et al., 2018). HFO biochar is then used in isotherm experiments. Langmuir isotherms produced by Bakshi et al. (2021) showed that Fe-modified (7.5 wt% solution of $FeSO_4$ at 1:1 ratio) biochar to be 11-12 times more adsorbent of P than unmodified biochars. The possible mechanisms for P adsorption to biochar surfaces have been described to be inner-sphere ligand exchange and electrostatic attraction between P anions and positive surfaces on the biochar. Precipitation mechanisms have also been inferred after ligand exchange in specific experimental conditions (Bakshi et al., 2021). The ligand exchange mechanisms favor monodentate or bidentate and mononuclear or binuclear complex formation. Studies have also shown that these iron-coated biochars have no change in oxidation state, which can make maintaining a suitable environment for their adsorption to be easier to maintain and predict (Pattammattel et al., 2019). pH has an integral effect on the surface charge of Fe oxides, which can influence P adsorption (Bakshi et al., 2021). pH may impact P complexes on the Fe oxides to be monodentate, which is easier for the release of P than bidentate complexes. This will allow for the release of P back into the soil, which is a desired trait. P adsorption will increase with concentration until saturation has been reached. This has been shown by well-defined isotherm plateaus (Bakshi et al., 2021; Fang et al., 2015; He et al., 2017; Shepherd et al., 2016). This could allow Fe-biochars to adsorb high concentrations of P from wastewaters despite the concentrations present. All these physical and chemical traits have made Fe-modified biochar stand out as potential candidates in the use of wastewater treatment and soil amendments.

2.2.6. Testing Iron Modified Biochar in Circular Flow Dairy Effluent Reactor

To assess the performance of Fe-modified biochar in non-laboratory settings, a circular flow reactor was constructed for testing the biochar with dairy effluent water. It was crucial to test the efficiency of biochar in removing phosphorus from real wastewater. The previous laboratory experiments were conducted with simulated P-bearing wastewater that contained few competing ions and consistent pH. In contrast, dairy effluent water provided numerous competing ions and a range of pH, which is more consistent with real-world applications.

2.3. Material and Methods

2.3.1. Iron Modified Biochar Experiments

Equations from chapter 1 used again in this chapter:

Equation 1. Formula and units for determining adsorption of P on biochar.

$$Q = (Ci - Ce) * \frac{V}{m}$$

where:

Q = adsorption capacity of biochar (mg/kg)
Ci = initial concentration of phosphate in solution (mg/L)
Ce = equilibrium concentration of phosphate in solution (mg/L)
V = volume of the solution (L)
m = mass of biochar used (g)

Equation 2. Formula for Bio-available Phosphorus and Units

$$BAP = \frac{(Cp * V)}{(m)}$$

BAP = Bio-Available Phosphorus (mg/kg)
Cp = Extracted P (mg/L)
V = Volume of Formic Acid (L)
m = Mass of Biochar (kg)

2.3.1.1. Modification of Biochar to Create Fe-Biochar

All biochar used in this study was prepared using the particle size reduction method described in Chapter 1, Section 1.3.2. of this thesis, resulting in a particle size less than 2 mm. To produce iron-modified biochar, the following procedure was followed. First, biochar was slowly added to approximately 500 ml of ultrapure 18 megohm water while stirring on a stir plate without heat. The amount of biochar added was determined by referring to Equation 3, which calculates the amount of biochar required to achieve a desired weight percentage of Fe. The pH of the biochar/water slurry was then gradually lowered to around 3 using drops of 1 M HCl and a Denver Instrument Model 250 pH probe calibrated with pH 4, 7, and 10 buffer standards. If needed, 0.1 M HCl was used in place of the 1 M HCl. Once the desired pH was reached, the desired volume of $FeCl_3$ was added to the slurry while stirring, as determined by Equation 3. For these experiments, the density of $FeCl_3$ used was 1.415 g/ml and the %Fe in solution was 13.6%. The pH of the solution decreased to around 2 upon addition of $FeCl_3$ due to the concentrated HCl used to keep $FeCl_3$ in solution.

Next, 1 M NaOH was added dropwise to the slurry while monitoring the pH until a pH range of approximately 3.25-3.50 was reached. 0.1 M NaOH was then added dropwise until a final pH range of approximately 6.00-6.50 was achieved. The use of 0.1 M NaOH after a pH of 3.25-3.50 prevented exceeding the buffering capacity of the solution. Additionally, adjusting the pH slowly allowed for adequate hydric ferric oxide coating of biochar particles. The slurry was then divided evenly between four 250 ml centrifuge bottles and centrifuged at 25000 × g for 10 minutes at 23°C. After centrifugation, the slurry was carefully decanted while retaining as much biochar as possible in the bottle. If loss was expected, a Whatman 42 filter was used. Approximately 200 ml of ultrapure water was added to each bottle, capped, and inverted twice before centrifuging again. This process was repeated twice for a total of two rinse cycles to ensure no aqueous Fe remained. After the second rinse, the biochar was transferred to plastic weigh boats and allowed to air dry under the fume hood for 48-72 hours. The modified biochar was then transferred to an HDPE bottle and stored for use in future experiments. This protocol was used to create Fe-modified biochar at concentrations of 2%, 4%, and 6%.

Equation 3. Formula for Calculating Volume of %Fe to Make Modified Biochar by Weight

$$V = \frac{(m * W)}{(P * D)}$$

where:

V = Volume of $FeCl_3$ to add to biochar/water slurry (mL)
m = Mass of biochar (g)
W = The desired weight % Fe-modification for the biochar (unitless)
P = The % Fe in the $FeCl_3$ (unitless)
D = Density of $FeCl_3$ (g/mL)

2.3.1.2. Adsorption Isotherms with Fe-Biochar to Test Optimal Percent Fe, Range of pH, and Solid Solution Ratios

To set up an adsorption isotherm for the Fe-biochar, a gradient of 9 phosphorus concentrations was used. For each P concentration treatment, 3 replicate aliquots were prepared, along with 1 “burner” for pH adjustments, 1 spike for each concentration (to compare Ci and Ce), and a DI 18 megohm water blank. Each incremental concentration had 5 total replicates associated with it, along with a DI water sample as a method blank. To prepare each replicate, 0.2 grams of Fe-biochar were weighed out using a Mettler AJ100 analytical scale and added to a 15 mL centrifuge tube. The volume of 1000 mg/L P stock solution required to make 0, 0.5, 1, 5, 10, 25, 50, 75, and 100 mg/L P was added to the tubes. Next, the appropriate amount of 1000 mg/L P stock solution was added to the 15 mL centrifuge tube for each desired concentration. Finally, 18 megohm DI water was added to each replicate to bring the final volume up to 10 mL.

The “burner” replicates were first used to adjust the pH of all replicates to 6.5. The number of drops of 0.1 M HCl added to the burner replicate for each concentration was recorded to standardize the pH adjustment. Then, the same number of drops were added to each replicate for each concentration level as needed. To prevent contamination, pH measurements were not taken directly from regular replicates. Instead, it was assumed that the buffering capacity amongst replicates in each concentration level would be the same. All pH measurements were taken with a Denver Instrument Model 250 pH probe calibrated using pH 4, 7, and 10 buffer standards.

The samples were then incubated for 24 hours on a Glas-Col end-over-end shaker rotating at 30 RPM. After incubation, the pH of all "burner" replicates was measured again to compare the initial and final pH. The samples were then centrifuged at 25000 × g for 10 minutes and filtered using a 0.45 µm PES membrane filter syringe. One drop of 1 M nitric acid was added to each replicate. The phosphorus concentrations of the samples were analyzed using ICP-OES (Agilent 5110, Santa Clara, California), and the adsorption capacity was calculated using Equation 1 from chapter 1 of this thesis. This experiment was repeated with various biochar types and different weight % Fe values to generate various adsorption isotherms for comparison.

The adsorption isotherms with different pH and solid solution ratios were conducted similarly with some variable changes. For the isotherm measuring the effects of pH, a single concentration of 5 mg/L P was used across all replicates, and the initial pH values were adjusted to 5.5, 6, 6.5, 7, 7.5, 8, 8.5, and 9. All replicates were adjusted to this pH range before incubation, as in the first isotherm with Fe-biochar. For the adsorption isotherm with various solid solution ratios, a single concentration of 0.75 mg/L P was used across all replicates, reflecting concentrations present at pilot-scale experimentation. Replicates were set up to have solid-to-solution ratios of 1:20, 1:50, 1:100, 1:250, 1:500, 1:1000, 1:1500, and 1:2000 by adding or decreasing the amount of biochar in each replicate. The pH of each sample was adjusted to 6.5, like the first isotherm with Fe-biochar, and all other variables and steps were kept constant for this isotherm. This was done to determine the effects of adsorption capacity at various solid-to-solution ratios that could be used during pilot-scale experimentation detailed in Chapter 3 of this thesis.

2.3.1.3. Total Elemental Digestion for Biochar (Dry-Ash Method)

The following method was adapted from the book Biochar: A Guide to Analytical Methods, edited by Balwant Singh, et al. (2017). All biochar samples were prepared using the method described in section 1.3.2 before experimentation, whether unmodified or modified. Prepared biochars were stored in a desiccator before use to prevent moisture from rehydrating the dried samples. The labware was prepared by washing digestion tubes, funnels, and sample vials with laboratory detergent and rinsing them thoroughly in 18 megohm DI water. The labware was then soaked in an acid bath of 10% HCl for at least 1 hour, thoroughly rinsed with DI water several times, and dried at 105°C.

Weighing 200 mg of each sample was done using a Mettler AJ100 analytical scale . Once the biochar was weighed, it was transferred to a crucible. The weighing paper was then reweighed after transfer to account for material not transferred due to adhesion from static charge. The weights were recorded to 0.1 mg, and all samples were done in triplicate. Crucibles were placed in a Thermo Scientific F47925 muffle furnace, and the location of each sample was noted. The crucibles were marked with a high-temperature grease pen. The samples were heated from ambient to 500°C at 5°C per minute, then the temperature was held at 500°C for 8 hours. They were then cooled to ambient at 5°C per minute. This was done to minimize physical loss to the samples due to convection. The crucibles were weighed after they returned to ambient, and the weights were recorded to 0.1 mg.

Samples were then digested to ensure decomposition of pyrolytic carbon. To do this, 5 mL of 70% trace metal grade nitric acid (HNO_3) was pipetted into each crucible. The ash/acid solution was transferred to digestion tubes and set in an Environmental Express digestion block, which was set up in a fume hood to control harmful vapors. The samples were heated at 145°C to oxidize carbon and evaporate HNO_3 without physical losses due to aggressive boiling. The sample volume was then reduced over the next several hours to about 2 mL. The steps of adding HNO_3 and evaporating were repeated if concentrated digestate appeared brown, indicating excessive residual carbon.

Once the samples became clear, they were cooled to ambient, and 4 mL of 30% hydrogen peroxide (H_2O_2) and 1 mL HNO_3 were added. They were held at ambient temperature for 2 hours. Once effervescence had subsided, the samples were heated to 100°C and held at that temperature for 1 hour. After that, samples were heated at 145°C to oxidize carbon and evaporate the H_2O_2-HNO_3 mixture without physical losses due to aggressive boiling. The sample volume was then reduced in this manner over the next several hours to approximately 2 mL. The samples were then cooled back down to ambient.

The samples were diluted by adding 30 mL of DI water to the digestion tubes which were then heated one final time at 100°C for 30 minutes. Once the samples cooled down sufficiently for safe handling, they were transferred to a 50 mL volumetric flask using a long stem funnel. The digestion tubes were rinsed with DI water into the flask and the volume was brought up to 50 mL. From the 50 mL volume, 12 mL was aliquoted and filtered using a 0.45-micron PES membrane filter into a 15 mL centrifuge tube. The filtered samples were then stored in a refrigerator until analysis with the ICP-OES (Agilent 5110, Santa Clara, California).

2.3.2. Calcium Modified Biochar

2.3.2.1. Modification of Biochar to Create Ca-Biochar

The method used to create calcium-modified biochar (Ca-biochar) followed the same process used for making Fe-biochar, as described in section 2.3.1.1. The only variation was substituting $FeCl_2$ with $CaCl_2$ and using Equation 4 to determine the concentration of the $CaCl_2$ solution instead of Equation 3.

Equation 4. Formula for determining mass of $CaCl_2$ powder to make calcium solution at given molarity.

$$\boldsymbol{m} = (\boldsymbol{C} * \boldsymbol{V} * \boldsymbol{M})$$

where:

m = mass of $CaCl_2 * 2H_2O$ powder (g)
C = desired concentration (mol/L)
V = final volume of solution (L)
M = molar mass of $CaCl_2 * 2H_2O$ (g/mol)

2.3.2.2. Adsorption Isotherm with Ca-Biochar

The adsorption isotherm for Ca-modified biochar was conducted using the methods described in section 2.3.1.2. of this thesis, with the only difference being the substitution of Ca-biochar for Fe-biochar in the experiment. No other modifications were made to the method.

2.3.3. Calcium and Iron Modified Biochar

2.3.3.1. Modification of Biochar to Create Ca-Fe-Biochar

The method used to create calcium and iron modified biochar (Ca-Fe-biochar) was the same as the method used to make Fe-biochar, as described in section 2.3.1.1., and the method to make Ca-biochar, as described in section 2.3.2.1. The protocol was identical, except the biochar slurry was dosed with both $FeCl_2$ and $CaCl_2$, using Equations 3 and 4, respectively, at the same time. This created a solution with both Fe and Ca to adsorb with the biochar surface.

In one set of experiments, powdered aragonite was substituted for $CaCl_2$. This was done because aragonite is a calcium carbonate mineral ($CaCO_3$). The method to make the aragonite-Fe-biochar was done in the same manner as the Ca-Fe-biochar, but the 5% aragonite was added by weight percent instead of percent concentration.

2.3.3.2. Adsorption Isotherm with Ca-Fe-Biochar

The adsorption isotherm for Ca-Fe-biochar was done following the methods used in section 2.3.1.2. of this thesis. Nothing was changed from this method other than the biochar type that was used in the isotherm, in this case Ca-Fe-biochar was used.

2.3.4. Magnesium Modified Biochar

2.3.4.1. Modification to Biochar and Fe-Biochar with MgO (Struvite)

Magnesium oxide was utilized to modify biochar to precipitate mineral struvite. The MgO and biochar mixture was prepared using a 1:10 ratio, where 0.5 grams of powdered MgO (thermos scientific 98% pure) was mixed with 4.5 grams of biochar. The resulting mixture was added to an HDPE container and gently rotated for 5 minutes to ensure complete blending of the powdered materials. A similar process and ratio were used to create a MgO-Fe-biochar by mixing MgO with Fe-biochar, which was prepared following the procedure outlined in section 2.3.1.1. of this thesis.

2.3.4.2. Struvite Precipitation with Biochar to Remove Phosphorus

To test the efficiency of struvite precipitation in removing P from wastewater, several treatments were prepared. MgO modified biochar was added to a solution of mono ammonium phosphate (MAP) and $MgCl_2$ (struvite solution), and a treatment with MgO-Fe-biochar was also done with the (MAP) and $MgCl_2$ solution. To create a struvite solution with the desired concentration of

10 mg/L P and 200 mg/L Mg, Equation 4 was used to dilute $NH_4H_2PO_4$ and $MgCl_2*6H_2O$ stock solutions, respectively. In addition to the MgO-biochar and MgO-Fe-biochar in struvite solution treatments, treatments with in-situ Fe dosing were also included, and the amount of $FeCl_3$ to add for each sample was determined using Equation 3. Once the samples were prepared in triplicate, the following procedure was carried out on all replicates:

Experimental replicates were set up with a 1:20 solid solution ratio with various treatment permutations and 20 mL of the struvite solution. Method blanks were also set up for all treatments tested. Samples were shaken with vortex and settled for 5 minutes. If necessary, the pH of experimental replicates of the slurry was adjusted to between 7-8, and the pH was recorded after adjustment. The slurry mixture was then lightly agitated at 5 RPM in a Glas-Col end-over-end shaker for 8 hours. After incubation, the samples were removed from the shaker, and a final pH was taken. Then the samples were centrifuged at 25000 × g for 10 minutes at 23°C. The liquid fraction was carefully decanted off from the solid fraction, and the liquid fraction was transferred into syringes and filtered with a 0.45 µm PES membrane filter. The liquid fraction that passed through the filter was retained in HDPE tubes and then acidified with one drop of 1 M nitric acid. All sample replicates were then analyzed for P concentration using ICP-OES (Agilent 5110, Santa Clara, California).

2.3.5. Cationic Polymer (pDADMAC) Modified Biochar

2.3.5.1. Modification to Biochar with Polydiallyldimethylammonium Chloride (pDADMAC)

Biochar and Fe-modified biochar were prepared by following the protocol listed in section 1.3.2. of this thesis. To create pDADMAC-modified biochar, the method used by Wang et al. (2020) was followed. In a 50 mL HDPE centrifuge bottle, 5 grams of biochar, 16 grams of pDADMAC, and 16 mL of water were combined. The mixture was equilibrated on a Glas-Col end-over-end shaker for 24 hours. In addition to regular biochar, Fe-biochar was also modified with pDADMAC using the same ratios and incubation time. The samples were then removed from the shaker and centrifuged at 25000 × g for 10 mins at 23°C. The liquid fraction was carefully decanted from the solid fraction, and 18 megohm DI water was added to the tubes to bring the samples up to 50 mL. The centrifuging and decanting process was repeated four times to ensure all residual pDADMAC in solution was removed. Finally, a final centrifugation and decantation were performed to separate the solid fraction, which was set aside to dry for 72 hours. Once the pDADMAC-modified biochar was fully dry, it was ready to be used in experiments.

2.3.5.2. Adsorption Isotherm with pDADMAC-Biochar

For this isotherm, different treatments of biochar, Fe-biochar, pDADMAC-biochar, and pDADMAC-Fe-biochar were set up. 0.2 grams of biochar were taken to prepare a 1:50 solid to solution ratio. To each replicate, 0.25 mL of 1000 mg/L stock $NaPO_4 *7H_2O$ was added to achieve an initial concentration of 25 mg/L P in each sample. Each treatment was performed in triplicate and brought to a final volume of 10 mL with DI water. Method blanks were also prepared along with the experimental replicates. Similarly, to section 1.3.4. of this thesis, a "burner" of each treatment was also made for pH measurements.

The sample replicates were shaken with vortex for 30 seconds and settled for 5 minutes. The pH of the samples was adjusted to 8 using "burner" tubes. The pH for other replicates for each treatment was also adjusted to match the burner tubes. pH adjustment was done using either 0.1 M HCl or 0.1 M NaOH depending on the initial pH of the treatment. After pH adjustment, the slurry mixture was lightly agitated at 30 rpm in a Glas-Col end-over-end shaker for 24 hours. The samples were then removed from the shaker, and the final pH was recorded. Samples were centrifuged at 25000 × g for 10 minutes at 23°C. The liquid fraction was then carefully decanted off from the solid fraction. The liquid fraction was transferred into syringes and filtered with a 0.45 µm polyether sulfone (PES) membrane filter. The liquid fraction that passed through the filter was retained in HDPE bottles. Phosphorus concentrations were then analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Agilent 5110, Santa Clara, California).

2.3.6. Removing P with Fe-Modified Biochar in a Circular Flow Reactor

A bench-scale experiment was conducted to evaluate the efficiency of biochar and Fe-biochar (see section 2.3.1.1.) in recovering P from wastewater. A circular flow reactor was used to continuously pump dairy effluent material (manure solution) across Fe-biochar for a set period. The influent and effluent manure solutions were then analyzed to determine the effectiveness of the technology.

To create the flow reactor, a cylindrical Tempe Pressure Soil Moisture Cell #1400 (Santa Barbara, California USA) (flow cell) was cut to a length of 10 cm. Gasketed end caps were placed on each end to close the flow cell, and wing nuts were screwed down along machined rods inserted into the end caps to hold them in place. When tightened, the two end caps were pulled together to seal the flow cell. Holes were drilled through each cap in the center, and screw fittings were set in the holes. These fittings were the same diameter as MasterFlex size 15 hosing, which was then plumbed out from both ends. The flow cell was hung vertically when in use. The rest of the system included a MasterFlex L/S Cole-Parmer peristaltic pump, a reservoir of manure solution, and a stir plate.

To set up the system, an 80-micron mesh screen was inserted into the flow cell at the bottom. The flow cell was closed and sealed by tightening the wingnuts, and the effluent hosing that came out of the bottom of the flow cell was set into the reservoir of manure solution. The manure solution was constantly stirred using the stir plate and a magnetic stir bar for the entire experiment. Biochar was added directly to the manure solution at a 1:100 solid to solution ratio. A second hose was then set into the solution and plumbed to the MasterFlex L/S Cole-Parmer peristaltic pump. The hose was connected to the top of the flow cell using the fittings, and both fittings on the flow cell were clamped shut. The pump was set to a flow rate of 100 mL/min using calibration for a size 15 MasterFlex hose. The direction of flow was set so that manure solution was pumped out of the reservoir into the top of the flow cell. Gravity assisted the pump in pushing manure solution through the flow cell and out of the bottom, where the solution entered the reservoir again. As the system flowed, the biochar was captured in the screen in the flow cell, allowing for its recovery for later use. The system was set to flow, recirculating the manure solution for approximately 6 hours until the solution became visibly clearer. Once the solution was clear, effluent samples were collected for comparison with influent solution. The captured biochar and manure particulate material (filter cake) that accumulated were also collected for analysis and comparison with the influent and effluent samples. This experiment was conducted with both unmodified biochar and Fe-biochar.

Several tests were conducted to analyze the solutions and filter cake. The influent and effluent solutions were tested for pH using a Denver Instrument Model 250 pH probe, which was calibrated with pH 4, 7, and 10 buffer standards. Electric conductivity (EC) was measured using an Oakton S/N2329707 EC probe. Orthophosphate in solution was determined by filtering with Whatman no. 41 filter paper and subsequently analyzing P concentration by colorimetric analysis following the method described by Murphy and Riley (1962). Total P in solution was determined using EPA Method 3050B. To determine plant available P, the filter cake material was processed with formic acid in the same manner as in section 1.3.6. A CNS analysis was performed using an Elementar Vario Max Cube following the method outlined on pages 41-43 in Biochar: A Guide to Analytical Methods (Singh et al., 2017). Furthermore, total elemental digestion was carried out using the method described in section 2.3.1.5. Finally, the data obtained from all these analyses, along with the pH, EC, orthophosphate, and total P measurements, were compiled into tables.

2.3.7. Scanning Electron Microscopy of Unmodified and Fe-Biochars

All SEM images were taken at the University of Idaho Electron Microscopy Center using a Zeiss Supra 35 SEM and processed with Noran System Six EDS. All samples were powder coated in carbon prior to imaging to promote better imaging. Images were either taken with SE2 or QBSD band. Samples were analyzed with small area scans on the surface for chemical determination. Smaller “spot” checks were done on individual grains for chemical determination as well.

2.4. Results

2.4.1. Results for Iron Modified Biochar

2.4.1.1. Adsorption Isotherms

Several types of biochar were modified with 2% Fe and used in adsorption isotherm experiments to investigate their effectiveness in removing phosphorus (P) from simulated wastewater. The results, presented in Figure 6, show the amount of P adsorption in milligrams per kilogram of biochar versus the equilibrium concentration of P. All biochar types were tested in triplicate, and all replicates are shown.

For P concentrations at and below 10 mg/L, the replicates for all biochar types had small deviations, resulting in tight clusters amongst data points. However, as the concentrations increased, the replicates became more dispersed in general. Among the biochar types, BC Biocarbon showed the least adsorption, with an averaged maximum of 1578 mg/kg, while Wakefield Biochar exhibited the greatest adsorption, with an averaged maximum of 2751 mg/kg. Pacific Biochar performed second-best, with an average maximum of 2231 mg/kg. Based on these results, Pacific Biochar was selected for further experiments, as outlined in Section 2.5.1.1 of this thesis.

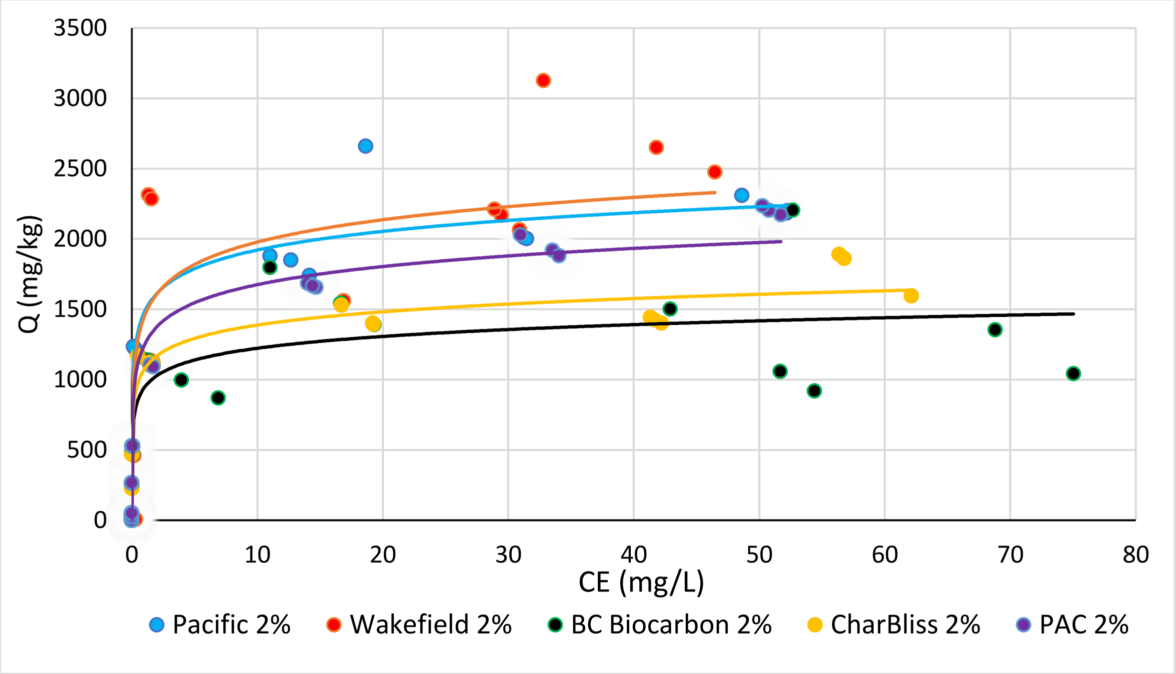

Figure 7. Biochar type and adsorption of P at 2% Fe-modification. (n=3)

After selecting Pacific Biochar for further experiments, an additional adsorption isotherm experiment was conducted to determine the optimal iron dosing percentage for removing phosphorus (P) from wastewater. Sub-samples of Pacific Biochar were modified with 2%, 4%, and 6% by weight Fe, and the results are presented as the amount of P adsorption in milligrams per kilogram of biochar versus the equilibrium concentration of P. The simulated wastewater concentrations for P were set at 0, 0.5, 1, 5, 10, 25, 50, 75, and 100 mg/L.

The three iron dosing levels performed similarly for the lower P concentrations. However, at higher concentrations (>25 mg/L P), the levels of adsorption began to vary. Specifically, the 2% Fe-modification had the lowest average maximum at 2231 mg/kg, while the 6% Fe-modification had the greatest average maximum at 4480 mg/kg for the 100 mg/L P concentration. The 2% and 4% treatments appear to have Langmuir adsorption curves, while higher concentrations would need to be further tested using higher P concentrations to determine the adsorption curve of the 6% treatment.

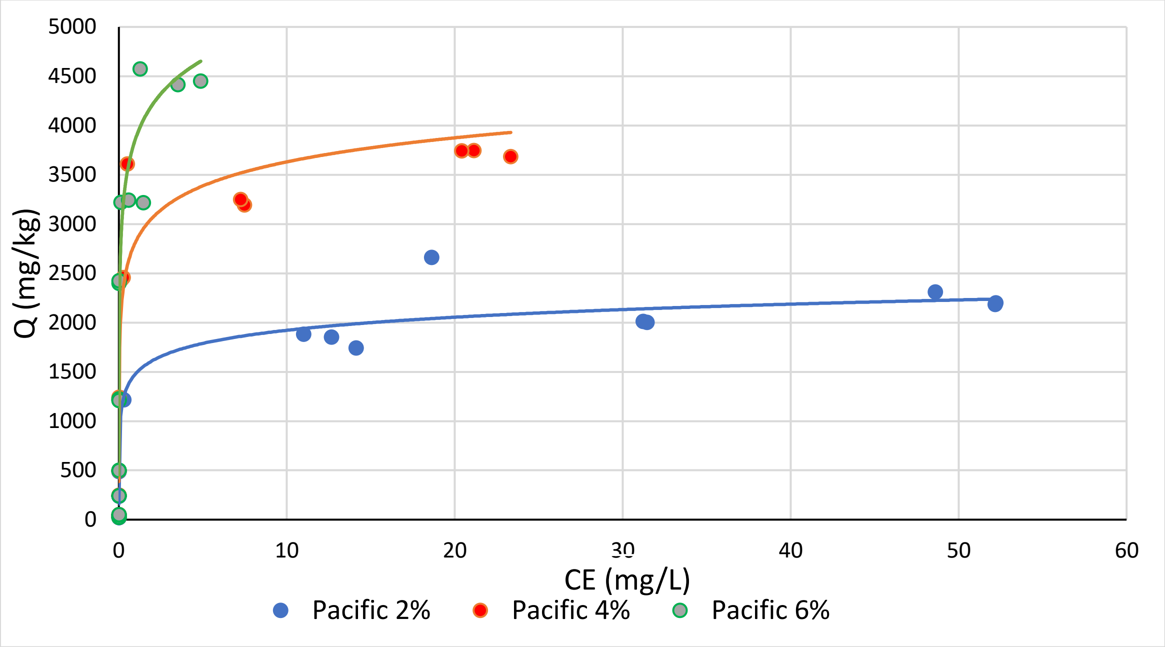

Figure 8. Adsorption of P at 2%, 4% and 6% Fe-modification for Pacific Biochar. (n=3)

4% Fe-biochar was deemed the optimal iron modification due to its' similar adsorption capacity as 6% Fe-biochar for most P concentrations that would likely be encountered in pilot scale testing. P concentrations of 75 and 100 mg/L were likely not to be encountered and the 4% Fe-biochar was cheaper to make than the 6% so it was selected. Two additional adsorption isotherm experiments were conducted to further investigate its performance. The first experiment involved testing the 4% Fe-biochar under a range of pH conditions that would likely be encountered during pilot-scale experiments. The results are presented as the amount of P adsorption in milligrams per kilogram of biochar versus the equilibrium concentration of P. The simulated wastewater concentration for P was fixed at 5 mg/L for all treatments, while the treatments were set up with different pH values ranging from 5.5 to 9.0 at 0.5 intervals. Each treatment was performed in triplicate, and the distribution of adsorption for each replicate is shown in Figure 8. Overall, the pH had no significant effect on the adsorption of P, with values ranging from 235 to 243 mg/kg. The adsorption showed no discernible trends within this pH range.

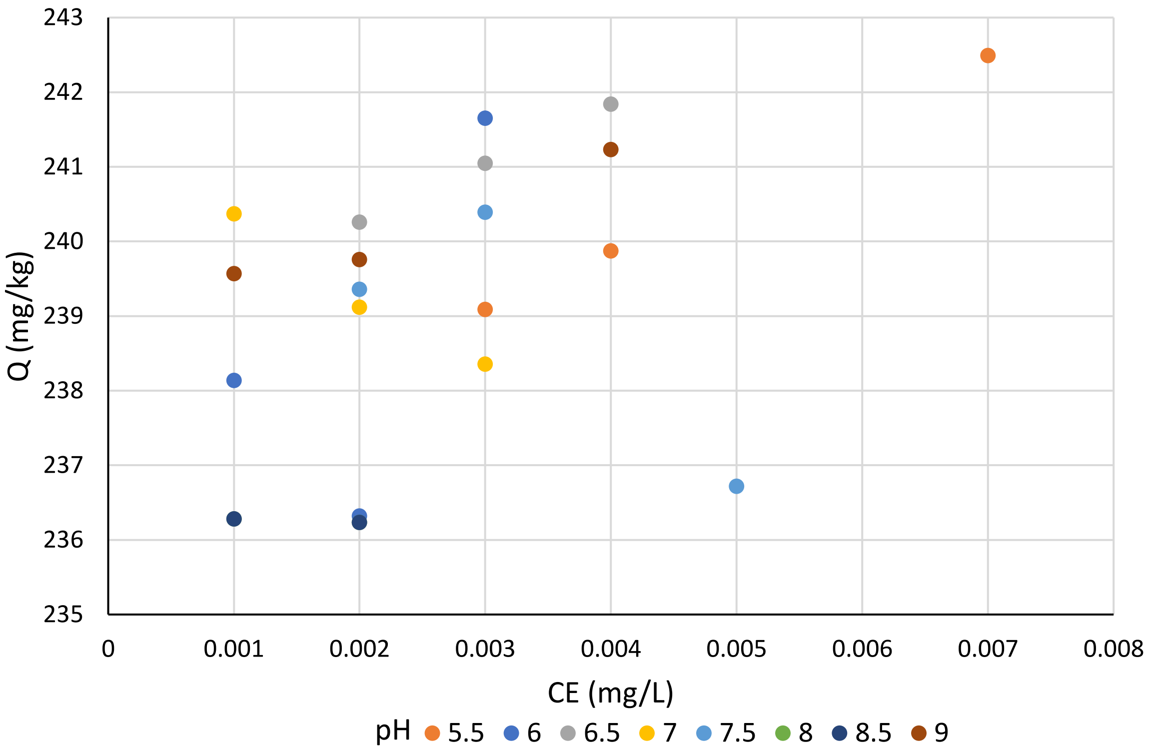

Figure 9. Pacific Biochar with 4% Fe-modification at pH 5.5-9 with initial P of 5 (mg/L). An outlier for pH 8.5 with a CE of 0.03 (mg/L) and an Q of 235 (mg/kg) is not shown. (n=3)

In the second adsorption isotherm experiment with 4% Fe-biochar, different solid-to-solution ratios were tested to determine the optimal ratio for P removal from wastewater. The results are presented as the amount of P adsorbed mg/kg vs the equilibrium concentration of P, with a concentration of 0.75 mg/L P in the simulated wastewater for all treatments. Replicates were performed in triplicate and solid-to-solution ratios ranged from 1:20 to 1:2000. Adsorption maximums were not reached at any solid-to-solution ratio with a concentration of 0.75 mg/L P. The equilibrium concentration of P mg/L was between 0.001 and 0.01 mg/L for most samples. As the solid-to-solution ratio decreased, adsorption increased. The highest adsorption maximum was 705 mg/kg for the 1:2000 ratio, and the lowest was 14 mg/kg for the 1:20 ratio.

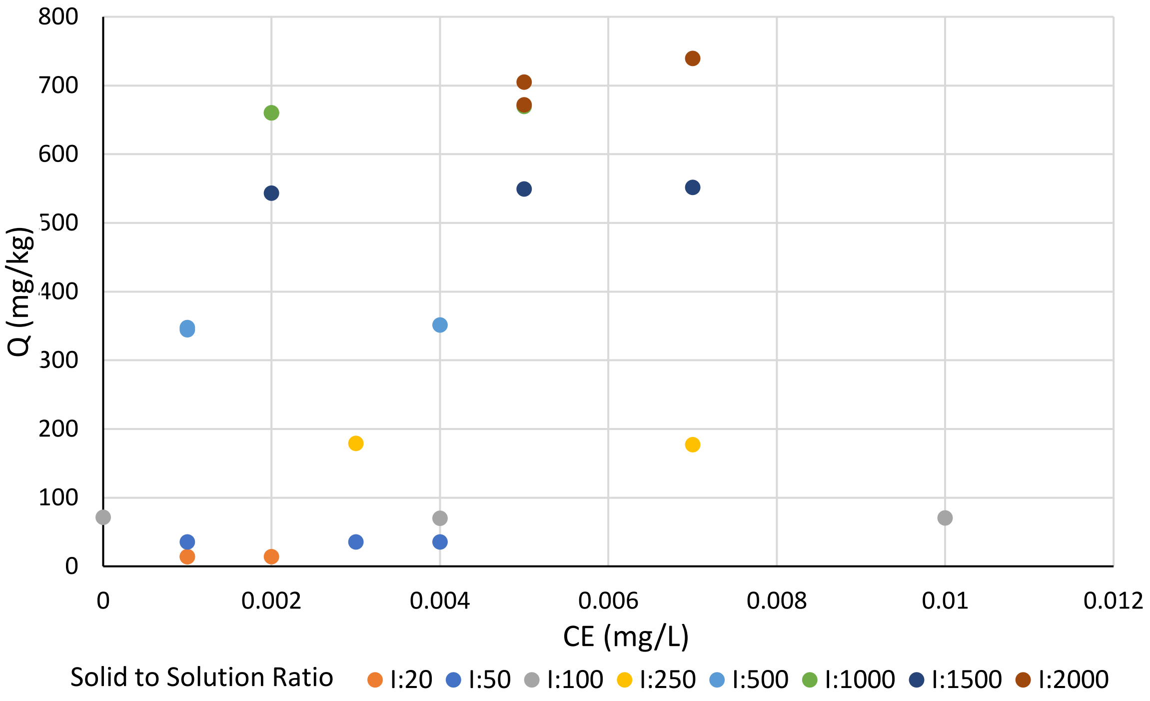

Figure 10. Pacific Biochar with 4% Fe-Modification at Various Solid to Solution Ratios with initial P of 0.75 (mg/L). An outlier for SS ratio 1:250 with a CE of 0.04 (mg/L) and an Q of 170 (mg/kg) is not shown. (n=3)

2.4.1.2. Total Elemental Digestion of Biochar and Nutrient Potential

Total elemental digestion was conducted on Pacific Biochar modified with 4% and 6% Fe. The results showed that Al, Ca, Mg, and P were similar between the two levels of modification. However, Fe, K, Mn, and Na were higher in the 6% modification compared to the 4%. Specifically, Na increased from an average of 1054 mg/kg to 2699 mg/kg, Mn increased from an average of 273 mg/kg to 464 mg/kg, and K increased from 1091 mg/kg to 1414 mg/kg. Fe was found to be the most abundant element tested, with 69,756 mg/kg in the 4% and 118,193 mg/kg in the 6% modification.

Furthermore, the nutrient potential of the 4% and 6% Fe-biochars were compared, showing an increase in Fe from 69,756 mg/kg in the 4% to 118,193 mg/kg in the 6%. The concentration of P remained almost the same, at 532 mg/kg and 527 mg/kg for the 4% and 6% modifications, respectively. These elements were highlighted because P is the main nutrient of concern, and Fe concentrations were important to analyze for the efficiency of Fe loading.

Table 4. Pacific Biochar 4% and 6% Fe-modified total element digestion.

Biochar Mod	**Al (mg/kg)**	**Ca (mg/kg)**	**Fe (mg/kg)**	**K (mg/kg)**	**Mg (mg/kg)**	**Mn (mg/kg)**	**Na (mg/kg)**	**P (mg/kg)**
4% Fe	1439	3085	72489	1032	993	280	1016	542
4% Fe	1471	3068	70005	1056	1000	268	1113	532
4% Fe	1437	3070	66776	1184	993	272	1032	520
6% Fe	1607	3398	121179	1396	1031	483	2698	543
6% Fe	1548	3350	117513	1364	985	464	2677	519
6% Fe	1478	3312	115888	1482	967	446	2722	518

2.4.2. Results for Calcium Modifications to Biochar

Based on the results of the adsorption isotherm for Ca-biochar (Figure 11), it appears that there is no relationship between P concentration levels and adsorption. In fact, all samples showed negative adsorption values (desorption), indicating that more P was released into the effluent samples rather than adsorbed onto the biochar. This was observed across all concentration levels of P. The least amount of P release occurred at the 75 mg/L P level, suggesting that higher P concentrations promoted formation of solid phases, such as Ca-P minerals, that had lower solubility. These maximum and minimum values did not follow any patterns observed in the other adsorption isotherm curves, which showed positive adsorption values and no trend in the amount of P released versus P concentration level. The pH of the samples ranged between the initial adjustment of 6.5 to as high as 8.0 for the equilibrium solution (complete data tables for pH are in the appendix of this thesis). Also, in most samples it was observed that Ca concentrations increased slightly for the equilibrium concentrations compared to the initial. This indicates that some Ca was leeched from the Ca-biochars into solution. In the lower concentrations 0.5 -5 mg/L the amount of Ca leached was more significant with about 6 mg/L and in the higher concentrations 5 – 50 mg/L the amount decreased to about 1 mg/L.

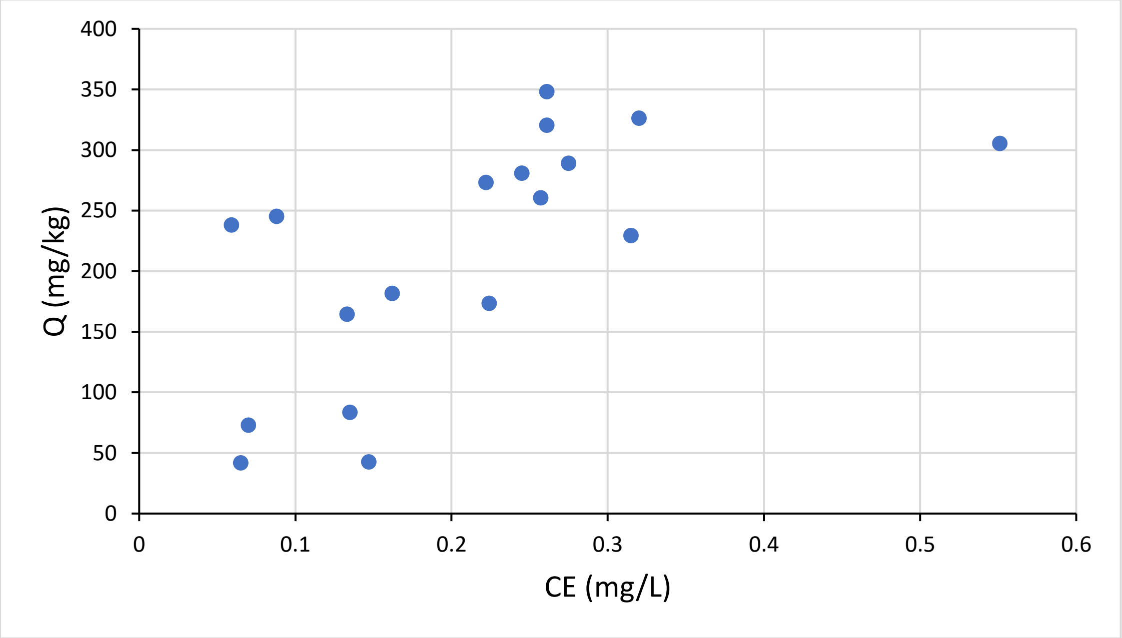

Figure 11. Phosphorus desorption on $CaCl_2$ modified Biochar Now (granular particle size). (n=3)

2.4.3. Calcium-Iron Modified Biochar Results

Ca-Fe-modified biochar treated with $CaCl_2$ showed a positive adsorption trend. The results are presented as the amount of P adsorbed mg/kg versus the equilibrium concentration of P. All concentrations were tested in triplicate, and all replicates are reported. The simulated wastewater had P concentrations of 0, 0.5, 1, 5, 10, 25, 50, 75, and 100 mg/L. The maximum adsorption mean was observed at the 100 mg/L P concentration level, with an average of 2225 mg/kg of P adsorbed. The 2% Fe Pacific Biochar adsorption isotherm data was included in Figure 12 for comparison.

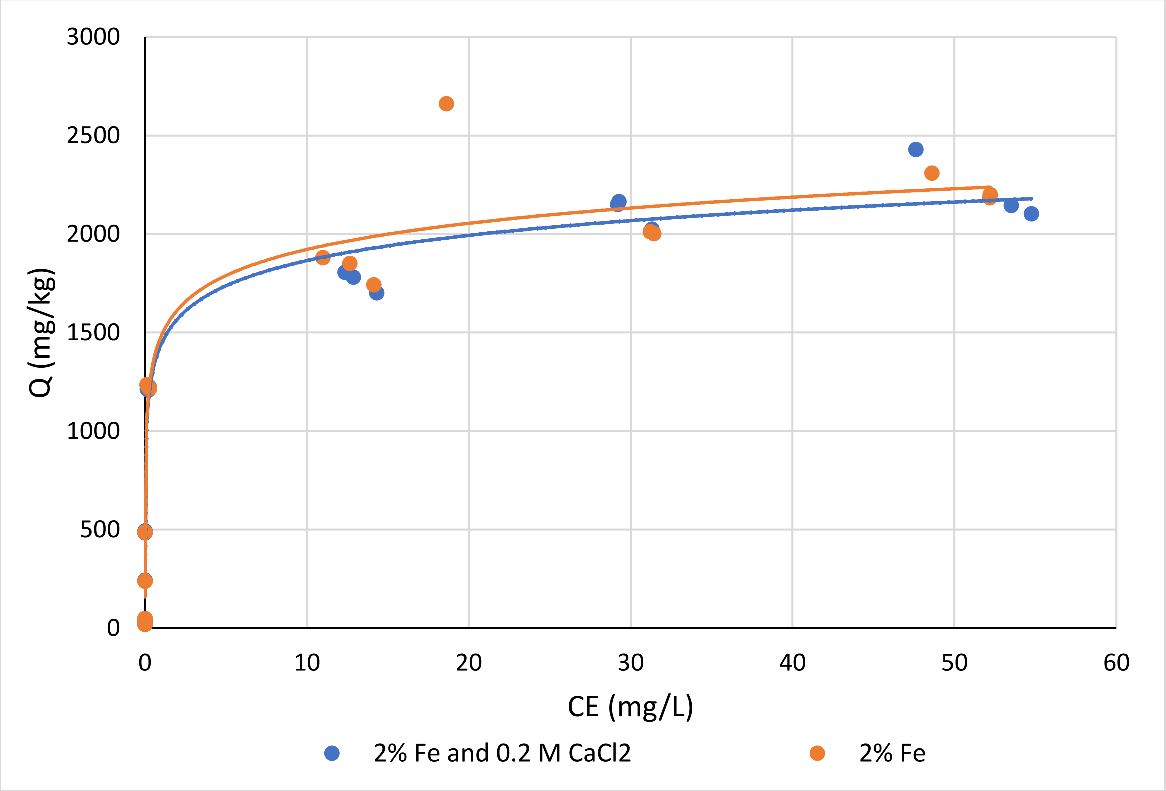

Figure 12. Phosphorus adsorption of Biochar Now (powdered particle size) modified with 2% Fe and 0.2 M $CaCl_2$. (n=3)

The Ca-Fe-modified biochar, which was modified from Aragonite instead of $CaCl_2$, exhibited positive adsorption. The results show the amount of P adsorbed mg/kg plotted against the equilibrium concentration of P, with all concentrations tested in triplicate. The simulated wastewater concentrations for P were 0, 0.5, 1, 5, 10, 25, 50, 75, and 100 mg/L. The initial pH of all samples was adjusted to about 6.5 and final pH ranged between 5.2 - 6.3. The maximum adsorption mean was 1399 mg/kg at the 100 mg/L P concentration level. The minimum adsorption mean was observed at a concentration of 0.5 mg/L, with an amount of 22 mg/kg. The 2% Fe Pacific Biochar adsorption isotherm data was included in Figure 13 for comparison.

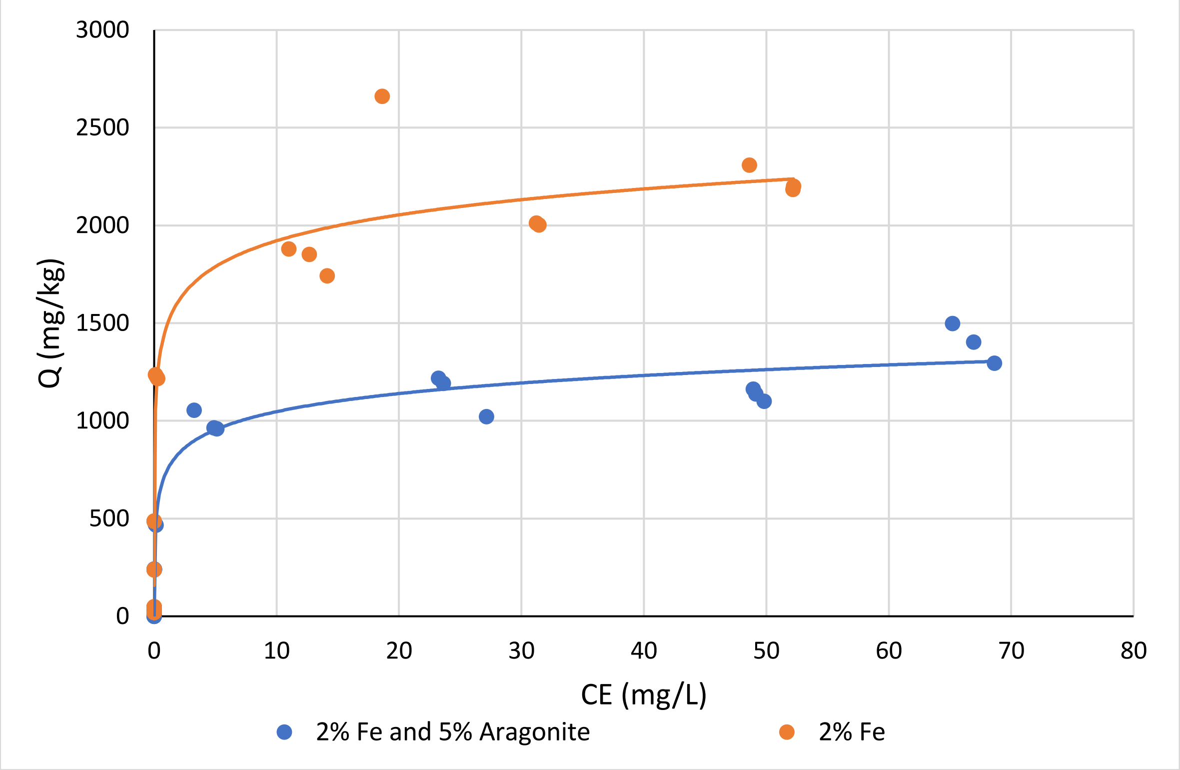

Figure 13. Adsorption of Pacific Biochar with 2% Fe and 5% aragonite-modification. (n=3)

2.4.4. Modification of Biochar with Magnesium Oxide to Precipitate Struvite

The precipitation of struvite requires a neutral to alkaline environment, so the pH of various treatments was adjusted and monitored. All final pH levels were alkaline after incubation times, except for Fe-Mod BC and Fe-Mod BC in just a P-bearing solution. The former had a final pH of 6.52, while the latter had a final pH of 4.98, which was the lowest final pH observed. Fe-Mod BC in P solution was used as a control to compare its performance with the struvite solution. In-situ Fe had the highest final pH of 11.74, which was 1.40 higher than the second-highest pH observed. All treatments involving MgO resulted in an increase in pH.

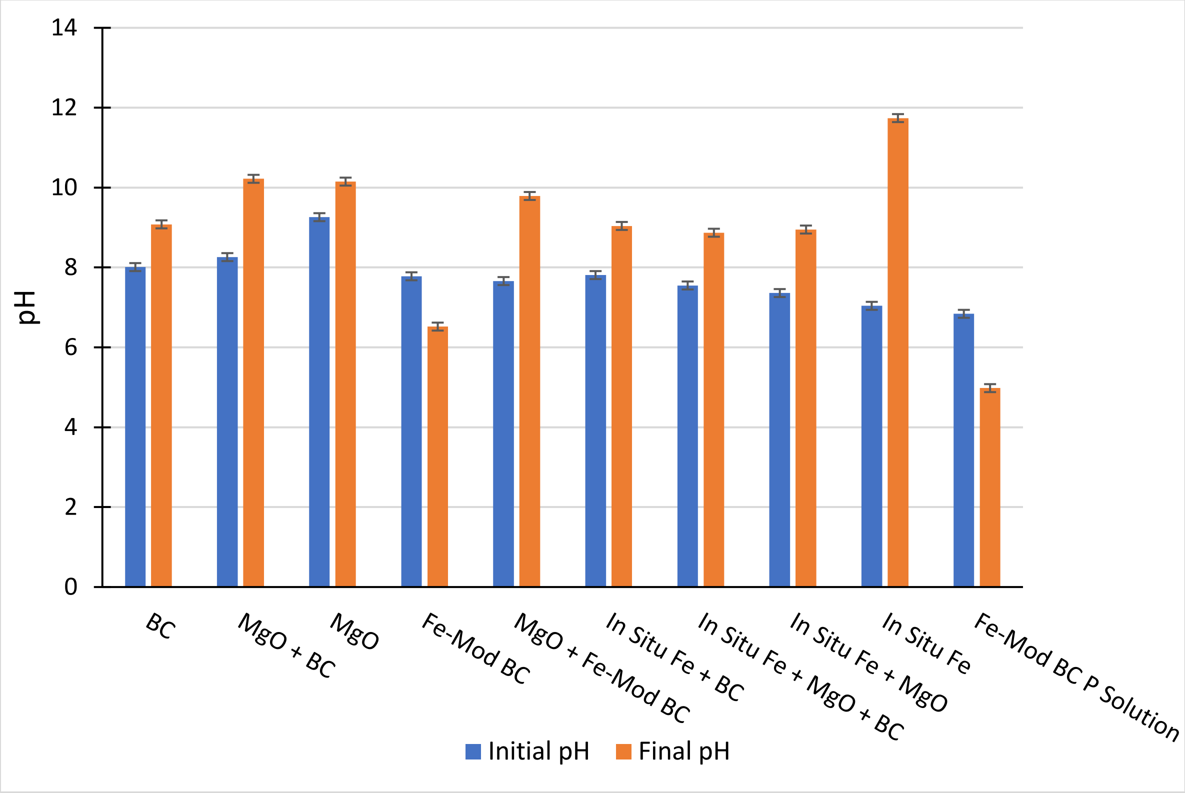

Figure 14. MgO modification and Pacific Biochar treatments vs. pH. (n=3)

Fe-Mod BC and In-situ Fe + MgO were the most effective treatments at removing P from solution, with both showing non-detect levels in the ICP-OES analysis (99.95% P removal). In contrast, unmodified biochar was the least effective, leaving 3.22 mg/L P in solution (67.80% P removal). All treatments were able to remove some level of P from the solution. The treatment with in-situ Fe + MgO + BC was the most effective after Fe-Mod BC, with a final P concentration of 0.010 (99.90% P removal), which is near the non-detect level. The treatment with in-situ Fe and BC had the highest relative standard deviation of 121 mg/L, due to one replicate having significantly less P than the other two. The cause of this discrepancy is unclear. MgO treatment also had a high RSD of 58.26, with variations among all replicates. All other treatments had RSD ranging from 4.9 to 13.5, with unmodified biochar having the lowest RSD at 4.897. Fe-Mod BC in P solution was used as a control to compare any differences with the struvite solution. The Fe-Mod BC in P solution was the same Fe-modified biochar as the rest of the experiment but instead of being exposed to the “struvite solution” it was only exposed to a P solution just like in the other adsorption experiments involving Fe-biochars. This was done to see the difference in adsorption from the addition of the Mg which was in the struvite solution. This control could also be compared to other isotherms which were done with the Fe-biochar and same P solution.

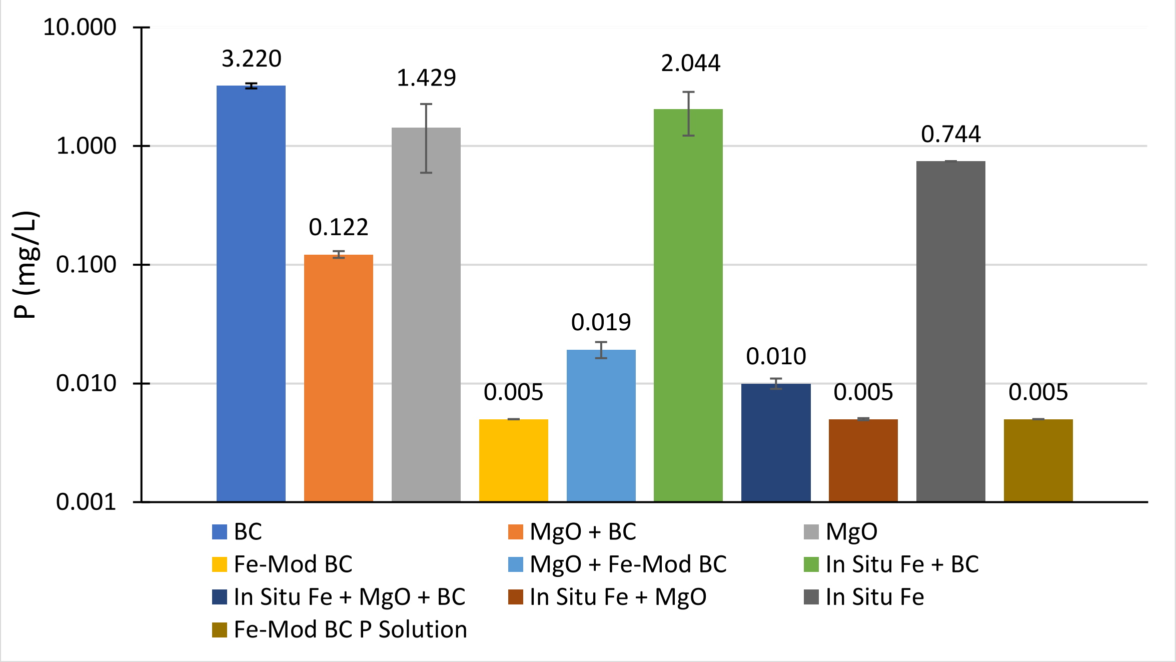

Figure 15. Mean effluent P concentration vs MgO modification and biochar treatment. (n=3)

2.4.5. Results of Modification to Biochar with Polydiallyldimethylammonium Chloride (pDADMAC)

The results show that Fe-modification plays a significant role in enhancing the adsorption of P onto biochar, with pDADMAC-Fe and Fe-biochar both performing significantly better than the treatments without Fe. The pDADMAC-Fe-modification showed a slightly lower P removal efficiency compared to Fe-biochar, but the difference was not significant. The adsorption capacity of pDADMAC-Fe BC and Fe-biochar was also very similar, suggesting that the addition of pDADMAC did not significantly affect the adsorption capacity of Fe-biochar for P. However, the pDADMAC-biochar and unmodified biochar showed very low adsorption capacity for P, indicating that the presence of Fe is crucial for effective P removal. Overall, the results suggest that Fe-modification, either alone or in combination with other modifications, is an effective method for enhancing the adsorption of P onto biochar.

Table 5. Single point isotherm pre-dose PDADMAC with influent concentration of 25 (mg/L) P.

Treatment	P Concentration (mg/L)	Percent Removal	SD
pDAD + UnMod BC	16.53	34.70	0.148
pDAD + Fe Mod BC	0.98	96.12	0.154
UnMod BC	21.43	15.34	0.049
Fe Mod BC	0.38	98.49	0.043
Water & Phosphorus	25.32	N/A	0.167
Water	0.01	N/A	0.002

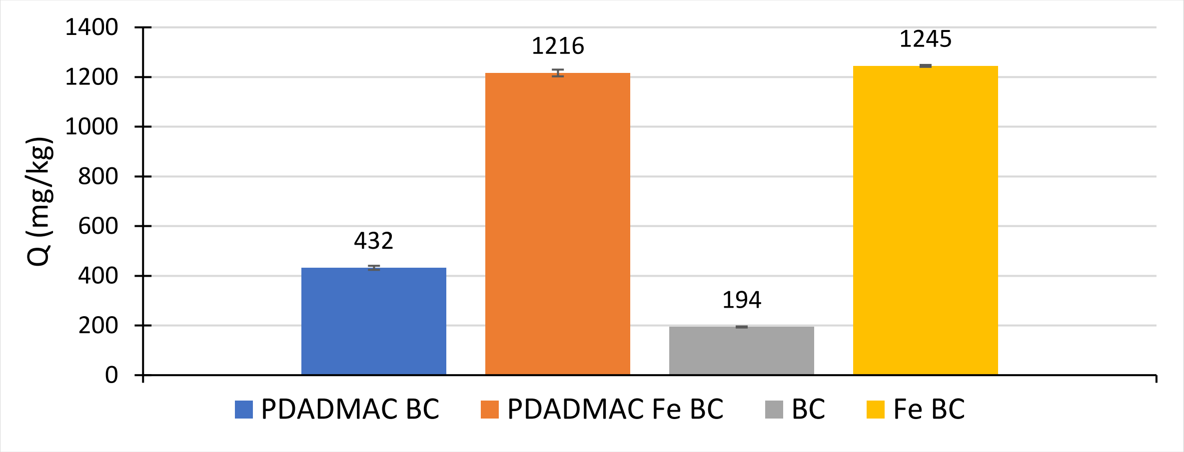

Figure 16. Adsorption of biochar type with/out pDADMAC pre-dose at 25(mg/L) P single point isotherm. (n=3)

2.5.6. Testing Iron Modified Biochar with Dairy Effluent Wastewater

After treatment with either Fe-biochar, P concentrations in the dairy effluent were reduced. The ICP-OES analyzed P decreased from 9.48 to 1.15 mg/L (87% P removal), ortho-phosphate decreased from 8.45 to 0.99 mg/L (99% P removal), and liquid digestion showed a decrease from 11.10 to 2.96 mg/L (73% P removal). Effluent pH slightly increased from 7.54 to 7.95. However, the electrical conductivity significantly increased from 1873 micro-siemens/cm to 2230 micro-siemens/cm. On the other hand, the alternative treatment using unmodified biochar did not work as well for removing P from wastewater. The ICP-analyzed P increased from 8.72 to 9.24 mg/L (6% P increase). Orthophosphate decreased from 8.68 to 8.02 mg/L (7% P removal), and liquid digestion showed a decrease from 10.64 to 8.99 mg/L (15% P removal). The pH increased from 7.76 to 8.23. Electric conductivity again significantly increased from 1910 micro-siemens/cm to 2030 micro-siemens/cm.

Table 6. P summary for liquid fraction of continuous dairy flow reactor.

	UnMod BC Slurry Solution	**SD**	**4% Fe BC Slurry Solution**	**SD**
Influent ICP P (mg/L)	8.72	0.26	9.48	0.31
Effluent ICP P (mg/L)	9.24	0.12	1.15	0.11
Influent Ortho P (mg/L)	8.68	0.19	8.45	0.27
Effluent Ortho P (mg/L)	8.02	0.09	0.99	0.05
Influent Liq. Dig. Total P (mg/L)	10.64	1.04	11.10	0.22
Effluent Liq. Dig. Total P (mg/L)	8.99	0.08	2.96	0.08
Influent pH	7.76	N/A	7.54	N/A
Effluent pH	8.23	N/A	7.95	N/A
Influent EC	1910 (µS/cm)	N/A	1873 (µS/cm)	N/A
Effluent EC	2030 (µS/cm)	N/A	2230 (µS/cm)	N/A

The solid fraction samples from both pre-treated material and post-treated filter cakes showed an increase in P for both treatments. The Fe-biochar treatment had a significant increase in plant available P from 27.16 to 138 mg/kg. However, this was still lower than the initial value of unmodified biochar which was 647 mg /kg and increased to 680 mg/kg after treatment. Total P was highest in the Fe-biochar post-treatment at 1224 mg/kg, while the unmodified biochar had a total P of 994 mg/kg. Both treatments had an increase in total P from 614 mg/kg and 725 mg/kg respectively.

The total carbon % decreased for the unmodified biochar from 85 to 81%, while the total nitrogen % increased from 0.07 to 0.45%. For the Fe-biochar, the total carbon % increased from 75 to 77%, and the total nitrogen % increased from 0.08 to 0.41%.

Table 7. P summary for solid fraction of continuous dairy flow reactor.

	UnMod Pacific BC	**UnMod BC Filter Cake**	**4% Fe Pacific BC**	**4% Fe Filter Cake**
Plant Available P (mg/kg)	646.79	680.35	27.16	138.33
SD of Plant Available P	18.53	88.56	1.52	9.24
Total P (mg/kg)	725.35	993.56	614.35	1224.16
SD of Total P	1.23	85.78	12.28	90.31
Total C %	84.55	80.88	75.16	77.22
SD of C%	0.26	0.19	1.16	1.08
Total N %	0.07	0.45	0.08	0.41
SD of N%	0.01	0.04	0.01	0.00

2.4.7. Scanning Electron Microscopy Images for Unmodified and Fe-Biochar

SEM images were used to analyze the distribution of Fe on unmodified and 4% Fe-modified biochar surfaces. Figures 17 and 18 depict the micro-textures and porosity of unmodified biochar, with the QBSD band used in Figure 18 to create a back scatter image that highlights elements with higher electron potential than carbon. The results in Table 8 indicate that the lighter particles in Figure 18 were mostly Si and Ca.

In contrast, Figure 19 displays a side-by-side comparison of a 4% Fe-modified biochar sample with the SE2 and QBSD bands. Na, Cl, and Fe are shown with higher contrast, indicating successful modification (Table 9). It is speculated that the initial Si and Ca washed off during the modification process and were replaced by Na, Cl, and Fe. However, the non-homogeneous distribution of Fe is evident from the Fe content of 6.64% at the spot shown in Figure 19 (Table 9), and speckled Fe in Figure 20 supports this observation. Nonetheless, there was an overall increase in Fe content during modification shown in the comparison from Table 8 to Table 9. The visible Fe in Figures 19 and 20 provide further evidence of the success of the Fe-modification process. The spectra graphs for Table 8 and 9 are included in the appendix of this thesis.

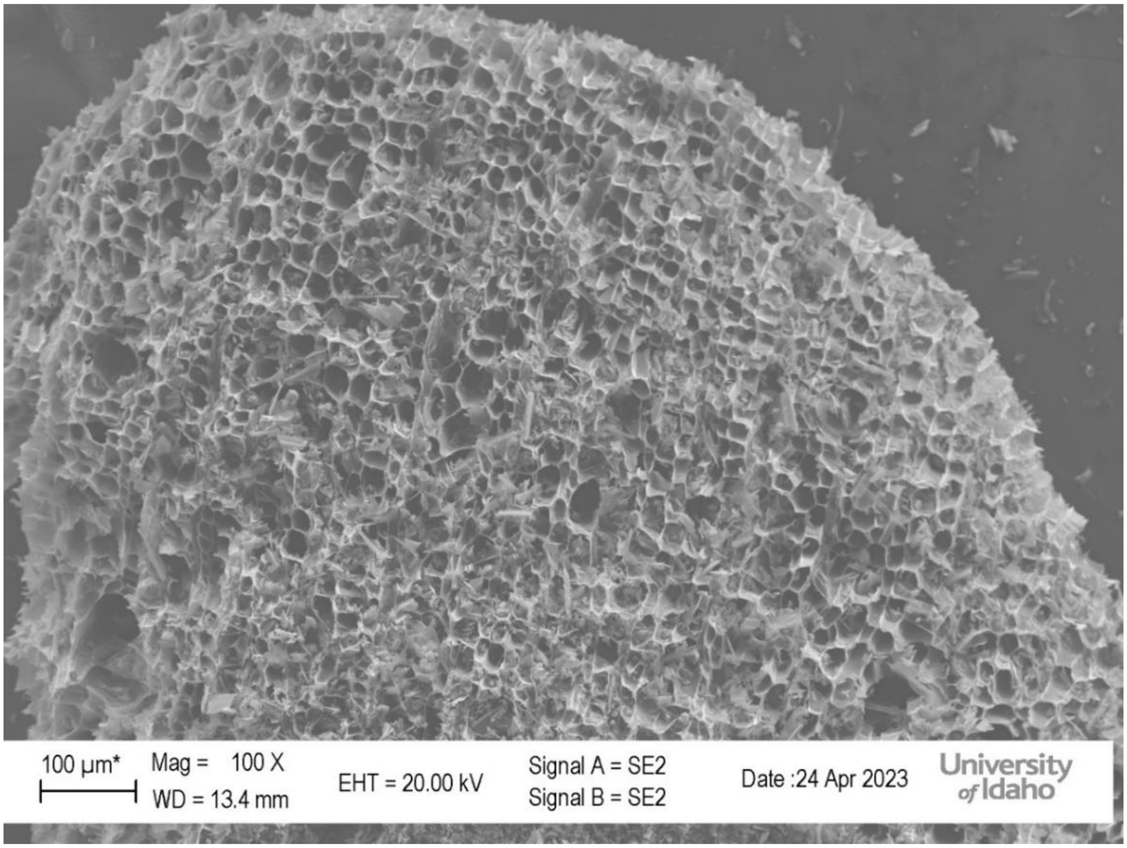

Figure 17. Unmodified Pacific Biochar in SE2 band showing micro-texture and porosity of biochar surface.

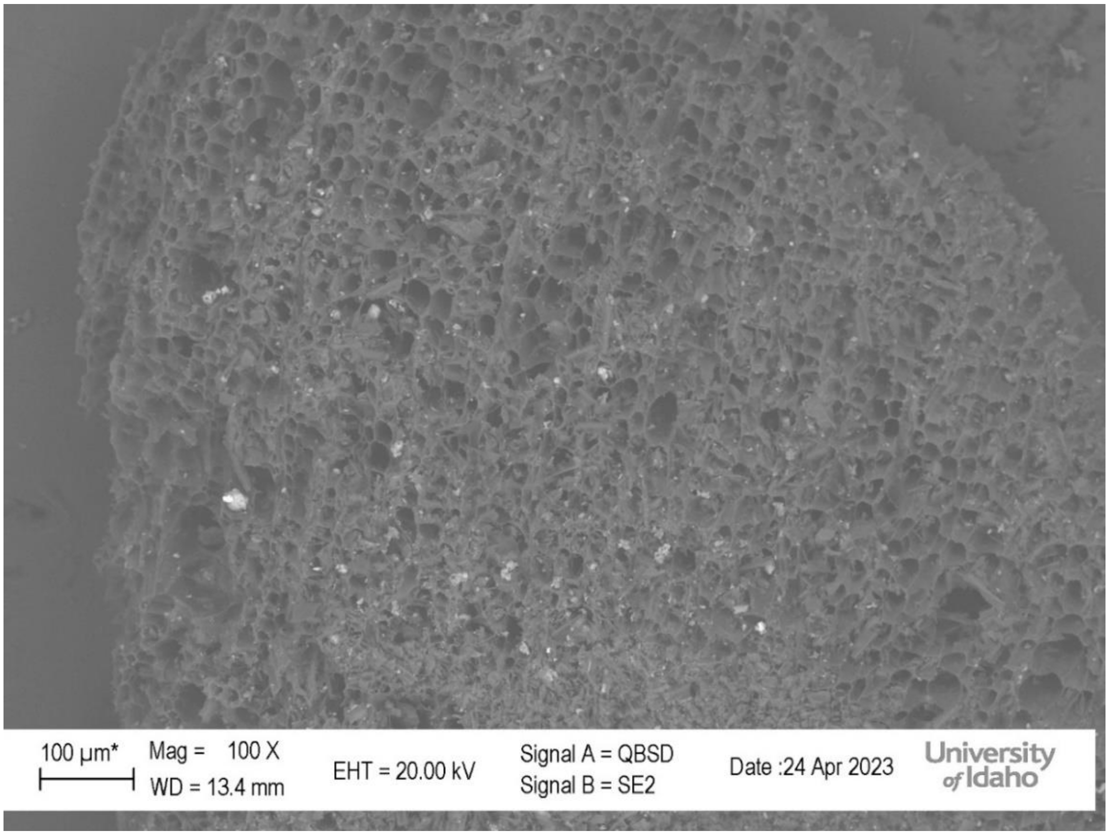

Figure 18. Unmodified Pacific Biochar in QBSD band highlighting Si and Ca in higher contrast.

Table 8. Elements detected on unmodified Pacific Biochar surface with SEM. Table corresponds to figures 17 and 18.

Element	**Net Counts**	**Int. Cps/nA**	**K-Ratio**	**ZAF**	**Weight %**	**Weight % Error**	**Atom %**	**Atom % Error**	**Formula**	**Compound %**
C	1613	98	0.24	4.18	38.37	± 1.19	53.93	± 3.34	C	38.37
O	2697	1634	0.09	7.97	27.63	± 0.83	29.15	± 1.75	O	27.63
Na	400	24	0.01	3.00	0.72	± 0.06	0.53	± 0.09	Na	0.72
Mg	481	29	0	2.07	0.40	± 0.04	0.27	± 0.06	Mg	0.40
Al	3521	214	0.04	1.66	2.47	± 0.10	1.55	± 0.12	Al	2.47
Si	11482	697	0.13	1.42	7.12	± 0.16	4.28	± 0.19	Si	7.12
Si	0	0	0	0	---	---	---	---	(null)	---
P	7227	439	0.1	1.44	5.32	± 0.13	2.9	± 0.14	P	5.32
P	0	0	0	0	---	---	---	---	(null)	---
K	1760	106	0.03	1.16	1.38	± 0.10	0.6	± 0.08	K	1.38
K	0	0	0	0	---	---	---	---	(null)	---
Ca	16711	1015	0.33	1.15	14.90	± 0.19	6.28	± 0.16	Ca	14.90
Ca	0	0	0	0	---	---	---	---	(null)	---
Fe	901	55	0.03	1.26	1.70	± 0.10	0.51	± 0.06	Fe	1.70
Fe	69	4	0	0	---	---	---	---	(null)	---
Total					100		100			100

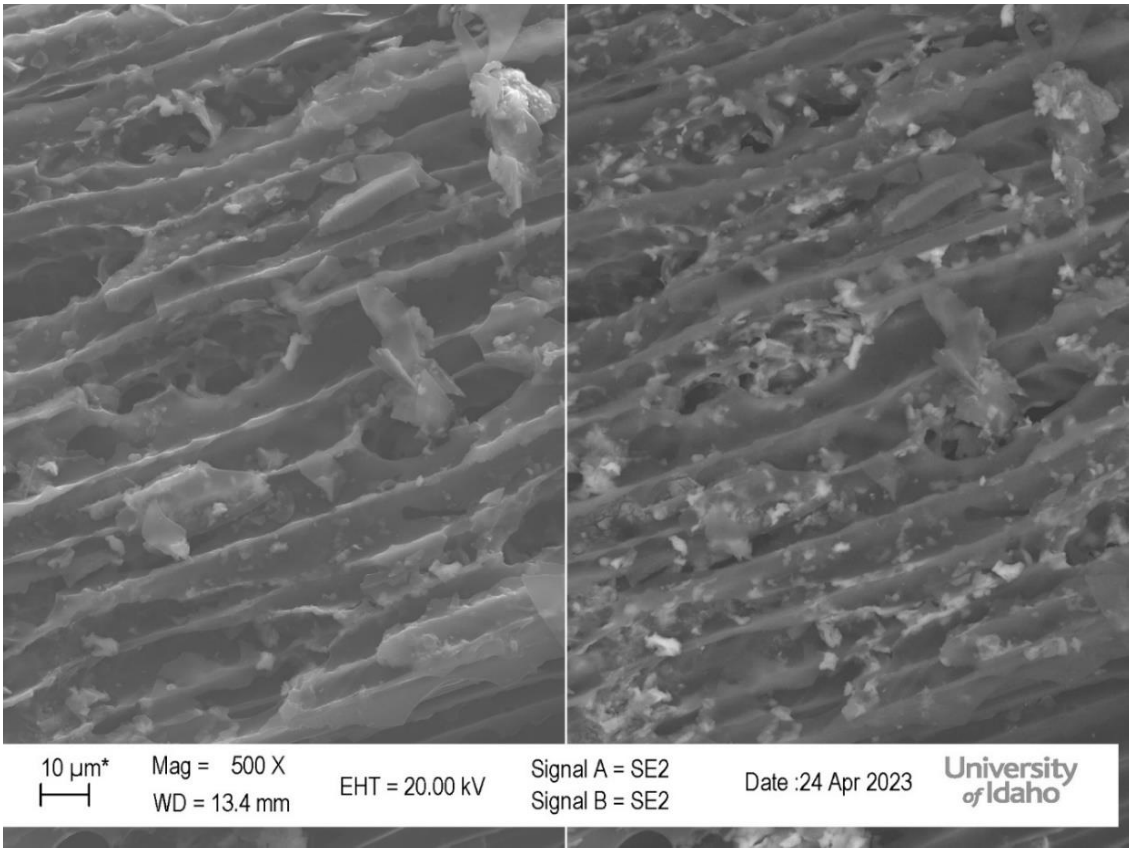

Figure 19. 4% Fe-modified Pacific Biochar. The left half of the image is in SE2 band showing micro-textures. The right half of the image is in QBSD band highlighting Fe, Cl, and Na in higher contrast.

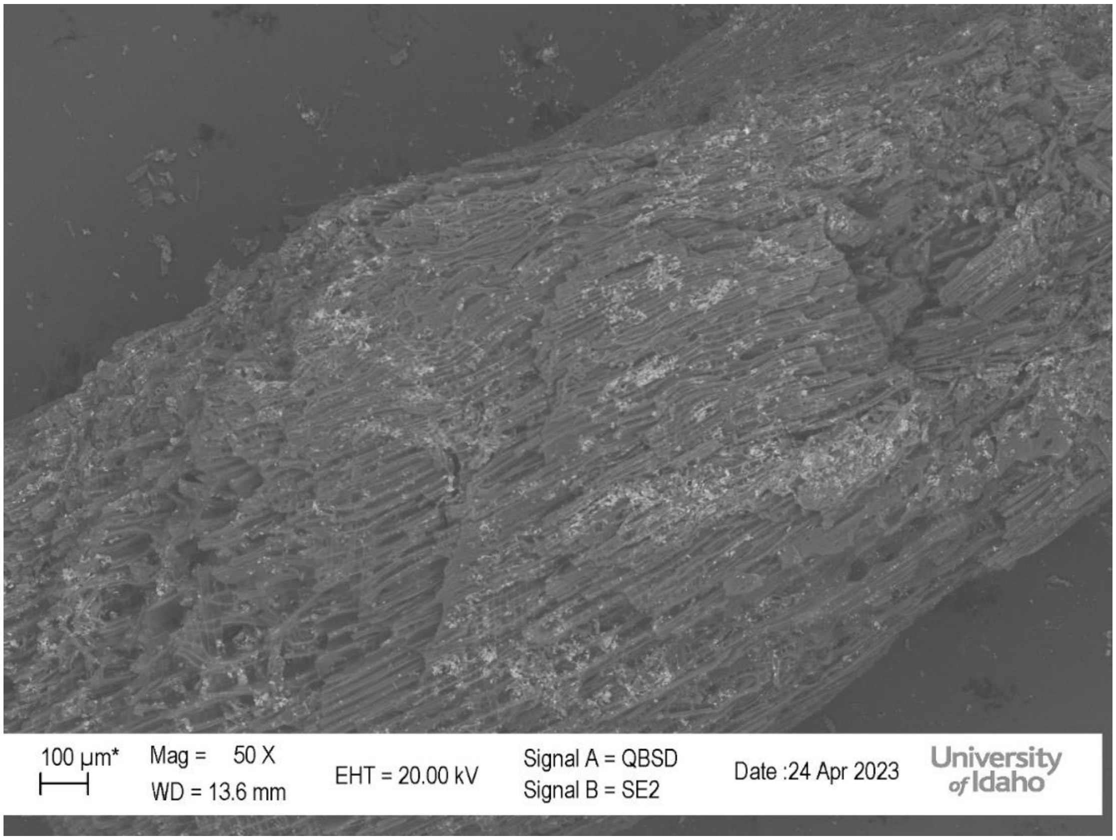

Figure 20. 4% Fe-modified Pacific Biochar in QBSD band showing the distribution of Fe across the biochar surface in higher contrast.

Table 9. Elements detected on 4% Fe-modified Pacific Biochar surface with SEM. Table corresponds to Figure 19.

Element	Net Counts	Int. Cps/nA	K-Ratio	ZAF	Weight %	Weight % Error	Atom %	Atom % Error	Formula	Compound %
C	6217	98.58	0.57	3.59	73.09	± 1.02	86.57	± 2.42	C	73.09
O	744	11.79	0.02	9.44	5.35	± 0.58	4.76	± 1.02	O	5.35
Na	4860	77.06	0.05	2.73	4.71	± 0.10	2.92	± 0.12	Na	4.71
Si	552	8.75	0	1.39	0.20	± 0.03	0.10	± 0.04	Si	0.20
Si	0	0	0	0	---	---	---	---	(null)	---
Cl	20709	328.37	0.2	1.19	8.79	± 0.10	3.53	± 0.08	Cl	8.79
Cl	170	2.69	0	0	---	---	---	---	(null)	---
K	876	13.89	0.01	1.21	0.42	± 0.06	0.15	± 0.04	K	0.42
K	0	0	0	0	---	---	---	---	(null)	---
Ca	1482	23.49	0.02	1.16	0.79	± 0.03	0.28	± 0.02	Ca	0.79
Ca	0	0	0	0	---	---	---	---	(null)	---
Fe	5956	94.44	0.14	1.26	6.64	± 0.19	1.69	± 0.09	Fe	6.64
Fe	729	11.55	0	0	---	---	---	---	(null)	---
Total					100		100			100

2.5. Discussion

2.5.1. Iron Modifications

2.5.1.1. Adsorption Isotherms for Biochar Type, Iron Dose, pH, and Solid to Solution Ratios

Pacific Biochar and Wakefield Biochar had similar results across the characterization experiments, but Pacific Biochar had less variation between replicates than Wakefield Biochar in the adsorption isotherm experiment. It was also easier to acquire larger amounts of the material from the manufacturer for future experiments. For these reasons it was selected as the “best” biochar to use in future modification experiments.

For the adsorption isotherm experiments comparing 2%, 4%, and 6% by weight Fe-modifications, it was decided that 4% Fe-modification would be used for future experiments because at concentrations of 75 mg/L P and lower, the adsorption of the 4% Fe treatment was nearly identical to the 6% Fe treatment. Although the 6% treatment performed the best overall, the 4% Fe treatment was deemed the "best" choice for removing P from wastewater. This decision was made because the concentration of 100 mg/L P is seldom seen in wastewater. The 4% Fe would perform the same as the 6% in most applications but cost less to produce due to the use of less Fe for modifying the biochar. Also, there is less pH adjustment needed to make the 4% Fe-biochar, which would also save costs in the modification process. Both the 2% Fe and 4% Fe treatments appear to have L-shaped adsorption curves, but the 4% is approximately 1500 mg/kg greater than the 2% Fe. So even though they performed equally at lower concentrations, the 4% has a much greater capacity for adsorption. This means it could be used longer and/or at lesser amounts than the 2%, which would also save on costs. For these reasons, the 4% Fe treatment was selected as the best Fe-Biochar modification.

This adsorption isotherm demonstrates that the 4% Fe-biochar can perform equally well at any pH level between 5.5 and 9. The equilibrium concentration measured was below 0.005 mg/L P, which falls below the detection limit of the ICP-OES used to measure the concentrations. This indicates that almost all P was adsorbed onto the biochar at all tested pH values. This isotherm confirms that iron oxide biochars possess the potential to operate efficiently across a wide range of pH levels in wastewater if they are utilized post-modification.

The data showed that the adsorption of P to biochar increased as the solid to solution ratio decreased. This meant that as there was less biochar available, more P was adsorbed to the available surface area, resulting in a higher adsorption value. Conversely, as more biochar was present, the adsorption decreased because all the available P had already been adsorbed. This trend ensured that the effluent P concentration was consistently below 0.01 mg/L for all treatments, as almost all P was adsorbed to the biochar. It was also observed that none of the treatments reached the maximum adsorption capacity, even at the lowest solid to solution ratio of 1:2000. This information was utilized to determine the optimal solid to solution ratio for the pilot-scale experiment.

2.5.1.2. Total Elemental Digestion of Fe-Biochar

The digestion data provided insights into the changes in nutrient composition of the biochar after the Fe-modification process. The Fe content increased from 4% to 6%, which was the intended goal of the modification process. In addition, the levels of K, Mn, and Na also increased in the 6% modified biochar, although it is not clear where the added K and Mn came from. The extra Na was most likely a result of the pH adjustment using NaOH during the modification process. However, the 6% modified biochar did not exhibit superior nutrient potential compared to the 4% modified biochar in terms of P concentration. As discussed earlier in section 2.5.1.1., the higher cost of producing the 6% modified biochar and its lack of improvement in P concentration made it an impractical choice. Overall, the Fe-modification process was successful in increasing the Fe content of the biochar.

2.5.2. Calcium Modified Biochar

Despite multiple attempts, the modification of biochar by Ca adsorption was not successful. Effluent samples showed that Ca was washing away from the biochar instead of binding to it. The adsorption isotherm supported this conclusion by showing negative P adsorption onto the biochar across all P concentration levels. This behavior was also exhibited by certain unmodified biochars, suggesting that the Ca was not adsorbed to the biochar and did not increase phosphate adsorption.

Previous experiments showed that P could be released into effluent waters, which was also observed in the case of the Ca-biochar. In fact, the Ca-biochar performed worse than unmodified Pacific Biochar, which had positive adsorption at low concentrations. Based on this information, the Ca-biochar was deemed unsuccessful and not utilized in further experimentation.

2.5.3. Calcium-Iron Modified Biochar

Based on the results, both types of Ca-Fe-biochar had positive adsorption isotherms indicating their potential in removing P from wastewater. However, when compared to an Fe-biochar at 2%, the P removal efficiency of these modifications was found to be the same or slightly worse. It is also possible that the Fe phosphate complexes were already optimized, and the addition of Ca did not provide any additional benefits. To simplify the process and reduce production costs, it was decided not to use Ca-Fe-biochar in future experiments.

2.5.4. MgO Modified Biochar with Struvite Precipitation

The test results indicated that Fe-Mod BC and In-situ Fe + MgO were the most effective treatments, resulting in nondetectable levels of P in both the "struvite solution" and phosphate solution, even when tested across a wide range of Mg and P concentrations. Fe-Mod BC showed equally good performance for both solutions. The effluent from Fe-Mod BC had a pH of around 6.5, while the effluent from In-situ Fe + MgO had a pH of around 9. In-situ Fe + MgO + BC was the next best treatment option after Fe-Mod BC that included biochar, but it resulted in an effluent pH of around 9. It should be noted that a pH of 9 may not be optimal for certain wastewater systems, and this should be considered in future experimentation.

Based on the test results, it seems that the addition of MgO to biochar did not provide significant benefits in terms of P removal compared to treatments with in-situ Fe. However, it does appear that biochar can be added to in-situ Fe and MgO treatments with only a slight reduction in efficiency, which may be sufficient for certain projects that wish to utilize biochar depending on their specific requirements. It is important to note that the MgO modifications require higher pH to work effectively, resulting in a narrower range of optimal pH compared to Fe-Mod BC.

It appears that Fe-Mod BC is a more effective and cost-efficient option for reducing P levels in wastewater compared to MgO modifications. Fe-Mod BC performed well over a wider range of pH without the need for additional MgO, which could potentially save on production costs. Additionally, Fe-Mod BC may be preferable for applications where maintaining a lower effluent pH is desired. Therefore, MgO modifications were not considered the best option for future experiments.

2.5.5. Modification to Biochar with Polydiallyldimethylammonium Chloride (pDADMAC)

Based on the results, it appears that pDADMAC did increase the efficiency of the biochar in adsorbing P from the solution but not as well as the Fe-biochar. Iron was found to be the common factor in both treatments that performed well. In fact, when pDADMAC was removed, the treatment with just Fe showed slight improvement, suggesting that pDADMAC may even reduce efficiency slightly by competing with other ions for a limited number of adsorption sites. Additionally, the use of pDADMAC would increase production costs. Therefore, Fe-biochar was deemed the best option for P recovery from wastewater in this experiment, and pDADMAC was not used in further experiments.

However, it should be noted that pDADMAC may have potential benefits that could be useful in other applications. For example, the treatment with pDADMAC-Fe-biochar showed much lower levels of Ca, K, Mg, and Na in the effluent solution compared to Fe-biochar alone. Thus, if an application requires the removal of these elements, the pDADMAC-Fe-biochar treatment could be more beneficial. Additionally, this could help mitigate the salinity increase associated with Fe-modified biochar, should it become an issue.

These results agree with the literature, in that pDADMAC-modified biochars have an increased efficiency in phosphate adsorption compared to unmodified biochars though not at the same efficiency. Our data shows the pDADMAC-modified biochars were twice as efficient as the unmodified biochars. While a paper by Wang et al., (2020) showed that a pDADMAC-modified biochar tested by them was about 100 times more efficient than unmodified biochar. It is unclear why our pDADMAC-modified biochar was significantly less adsorbent than that produced by Wang et al., (2020). One possible difference was the biochar produced by Wang et al., (2020) was derived from both soft and hard woods while ours was from just soft wood. The biochar produced by Wang et al., (2020) was also ground to pass through a 0.5 mm sieve where ours only passed through a 2 mm sieve. This smaller particle size would have increased biochar surface area leading to an improved adsorption.

The modification process was essentially the same for both sets of material. A further study to identify this difference would prove beneficial in expanding knowledge. Another paper by Zhou et al., (2021) showed that pDADMAC-modified fly ash was 1.5 times more efficient at removing phosphate from water than activated carbon.

2.5.6. Testing Iron Modified Biochar with Dairy Effluent Wastewater

The results indicate that Fe-biochar is a more effective material for removing P from wastewater compared to unmodified biochar. The efficiency of Fe-biochar at removing P from dairy effluent wastewater was 77%, which is lower than the 98% removal seen in simulated P wastewater. This reduction in efficiency could be due to changes in pH and competing ions present in the dairy effluent wastewater. However, the pH did not change significantly during the treatment with Fe-biochar, indicating that it is a stable material that does not release or consume H^+ during its reaction with wastewater. On the other hand, unmodified biochar had a slight increase in pH, indicating it may be less stable. Both Fe-biochar and unmodified biochar showed an increase in electrical conductivity (EC), which should be taken into consideration if salinity additions become an issue for the application.

The data for the filter cake showed that the initial plant available P is reduced compared to the unmodified biochar. The plant available P is most likely stripped from the biochar during the Fe-modification process. This means that Fe-biochar is more effective at removing P from wastewater, but unmodified biochar could be better for use as a soil amendment due to its greater plant available P and faster release rates. The Fe-biochar could be beneficial as a soil amendment if slow releasing P is desirable. The total P values were higher for Fe-biochar, but it is possible that phosphate complexes could be harder to break by organic acids, leading to a reduced amount of plant available P. The total nitrogen percent for both treatments was close to equal, indicating that the Fe does not affect N adsorption, and a separate mechanism related to the biochar is most likely the cause. Both treatments saw an increase in the total nitrogen percent with 0.07 to 0.45 mg/kg for the unmodified and 0.08 to 0.41 mg/kg for the Fe-biochar. Overall, the Fe-biochar was deemed the best material to use in further experiments.

2.5.7. Selection of 4% Fe Pacific Biochar for Pilot Study

Based on the effectiveness of the 4% Fe Pacific Biochar compared to the other modifications in removing P from both simulated and dairy effluent wastewaters, it was chosen for further pilot scale experimentation. To serve as a control, unmodified biochar will also be included in the pilot scale testing.

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Chapter 3: Removal and Recovery of Phosphorus from Groundwater using Biochar: Case Study at a Hops Farm in Northern Idaho

3.1. Abstract

Agricultural practices occurring in areas with shallow groundwater are a source of nutrient loading to surface waters. In this chapter, results from a pilot study conducted at Elk Mountain Farms, Idaho, were analyzed to assess the effectiveness of Fe-modified biochar in removing phosphorus (P) from groundwater impacted by agriculture. The study aimed to quantify the performance of Fe-modified biochar in real-world applications beyond the laboratory setting. The University of Idaho Clean Water Machine, which utilizes reactive filtration technology, was used to remove and recover P from groundwater. Both unmodified and 4% Fe-modified biochars were employed in the experiment. The study took place from July 17th to July 26th, 2022, and comprehensive analysis of biochar, water, and surrounding soils was performed to quantify the results. The water samples revealed that the 4% Fe-modified Pacific Biochar treatment resulted in a decrease in total P concentration from 0.166 mg/L in the influent to 0.019 mg/L in the effluent samples. Similarly, ortho-phosphate concentration decreased from 0.102 mg/L to 0.008 mg/L. The unmodified biochar also exhibited reductions in total P and ortho-phosphate concentrations, with total P dropping from 0.091 mg/L to 0.025 mg/L and ortho-phosphate decreasing from 0.049 mg/L to 0.003 mg/L between the influent and effluent samples. Analysis of soil samples indicated that total P content ranged from 400 to 800 mg/kg across all sites and depths. Plant available P in soil samples estimated using formic acid extraction was highest in the surface samples and decreased with depth, likely because of surface enrichment from fertilizer applications. Both the unmodified and Fe-modified biochar solids demonstrated increased total P content after being utilized in the Clean Water Machine. The initial P amount for unused unmodified biochar was 725 mg/kg, which increased to 1108 mg/kg after water treatment. The Fe-modified biochar initially contained 614 mg/kg of P, which increased to 995 mg/kg after water treatment. Overall, both biochar treatments effectively removed P from groundwater through adsorption, with the Fe-modified biochar exhibiting a higher P removal efficiency for total P. However, the unmodified biochars contained a higher amount of total P after the treatment process.

3.2. Introduction

3.2.1. Recycling Used Biochar as P Soil Amendment

In recent years, biochar has gained popularity as a soil amendment in agricultural production, with growing interest in its potential benefits (Jung et al., 2016). Recent meta-analyses of published literature have shown that biochar can enhance plant-available phosphorus (P) (Bakshi et al., 2021). Typically, biochar is applied to soils by broadcasting it on the soil surface and tilling it in, or it can be incorporated using no-till drilling methods (Bakshi et al., 2021). Subsurface banding is also an efficient method for biochar application (Gelardi and Parikh, 2021). The incorporation of biochar into soils has been shown to increase crop yields, soil fertility, water retention, microbial biomass, and microbial activity, while also shifting the microbial community composition towards a more fungal-dominated profile (Gelardi and Parikh, 2021).

In addition to improving soil fertility and crop yield, biochar is beneficial for saline and sodic soils because it sorbs sodium onto available exchange sites and releases non-sodium base cations, thus reducing exchangeable sodium (Ye et al., 2020). It is recommended to use biochar in conjunction with synthetic fertilizers, compost, or manure, rather than as a substitute for these materials (Ye et al., 2020).

Biochar persists in soil for a long time, reducing the need for frequent application, and it has been suggested that applying biochar every three years can optimize its potential benefits (Oladele, 2019). This recommendation was based on a three-year field trial conducted on acidic soils, where the effect of rice husk biochar on select soil qualities was tested (Oladele, 2019). One of the main applications of biochar as a soil amendment is to release plant-available phosphorus (P). Iron-modified biochar, which is a common modification, as well as unmodified biochar, has been shown to desorb P in significant amounts (Bakshi et al., 2021). If biochar is applied at a rate of 1% in soil (equivalent to 10 tons/acre), this would provide approximately 45 mg/kg of soil with iron-modified biochar and 8 mg/kg of soil with unmodified biochar (Bakshi et al., 2021). Considering that typical soils in the Midwestern US, where a large portion of US agriculture is based, require around 22 mg/kg of P annually, a 1% application rate of iron-modified biochar could fulfill soil P needs, whereas unmodified biochar would require a higher application rate of 3% (Oladele, 2019). Oladele (2019) observed that biochar application rates of 6-12 tons/acre to acidic Alfisols provided sufficient P. Explicit recommendations based on a literature review and greenhouse trials suggested that concentrations of 2-5% by weight for wood and crop residue-derived biochars, and 1-3% for manure-derived biochars may be effective, though these recommendations were for unmodified biochars (Guo, 2020).

Although there is strong evidence supporting the potential of biochar as a soil amendment, studies have shown mixed results regarding its effectiveness in increasing crop water use efficiency and mitigating drought conditions in soils (Jones et al., 2012). These discrepancies can be attributed to variations in soil types and textures across studies (Gelardi and Parikh, 2021). Nevertheless, biochar has been found to bring reliable agronomic benefits in environments where soils require conditioning or remediation, including acidic and sandy soils.

Using biochar as a soil amendment can also create possible new revenue streams. Analyses of pyrolysis biorefineries have projected positive net profit values for biochar production, assuming a value for biochar of $50−$100 per metric ton (Bakshi et al., 2021). This will allow the production of biochar to be a profitable business. Having a stable supply of biochar will then allow it to be a reliable source for agricultural soil amendments.

Biochar has the potential to be a sustainable product as it can be made from bio waste materials and used as a soil amendment. However, as interest in biochar as a soil amendment grows, it becomes imperative to better understand its potential consequences for water and air quality, as well as its impact on human health and the environment. Currently, the potential adverse effects of biochar on human health, agricultural workers, neighboring farm communities, livestock, and wildlife remain understudied (Gelardi and Parikh, 2021). To achieve long-term sustainability, it is crucial to address these questions.

Some studies have indicated potential risks associated with the application of biochar. For instance, studies have shown that polycyclic aromatic hydrocarbons (PAHs), which are carcinogens, may form during the production of biochar through pyrolysis, posing a risk to human health (Liu et al., 2019). These findings were based on simulated lung fluid experiments under "worst case scenario" exposure conditions. However, it has also been shown that the potential toxicity from biochar decreases with time, suggesting that the threat may be short-term and manageable as the biochar ages.

3.2.2. Pilot Study at Elk Mountain Farms to Test Fe-Modified Biochar for P Recovery and use as a Soil Amendment

This pilot study aimed to explore the potential of using biochar to remove excess phosphorus from shallow groundwater in agricultural fields, such as those at Elk Mountain Farms. This could help mitigate phosphorus runoff into drain tiles and ultimately into the surrounding groundwater and surface waters, which can have negative impacts on water quality and ecosystem health.

Elk Mountain Farms, located in the northern Idaho region, is the largest contiguous hop farm in the United States. It is situated just ten miles south of the Canadian border and is nestled between the Selkirk Mountains in the Kootenay River Valley. The farm spans over 1,700 acres and has been owned and operated by Anheuser-Busch since 1987. The farm cultivates a variety of hops, including Cascade, Centennial, Chinook, and Willamette, which are widely used in the brewing industry for their distinct flavors and aromas. As the largest hop farm in the country, Elk Mountain Farms plays a significant role in the production of hops for Anheuser-Busch, one of the largest brewing companies in the world. Elk Mountain Farms is a key player in the brewing industry and an important part of the local economy in the Idaho panhandle region.

The University of Idaho conducted a pilot study at field 70 of Elk Mountain Farms to quantify the amount of phosphorus (P) removed from groundwater using 4% iron-modified Pacific biochar and unmodified biochar during a reactive filtration trial. The study utilized the University of Idaho Clean Water Machine, which is a dual filter moving bed reactive filter that uses iron amendment to achieve P removal. The pilot filter inflow was taken from an access well for drain tiles. The general setup of the experiment involved pumping water from the well into a contact tank that contained the 4% iron-modified biochar or unmodified biochar. In the contact tank, the biochar adsorbed the phosphorus from the water. After a brief contact time, the water and biochar in suspension were then pumped through reactive filtration sand filters to further clean the water. After the sand filters, bag filters were used to collect the biochar particles, while the cleaned water was deposited back into the well. The collected biochar was then analyzed to determine the amount of phosphorus adsorbed.

The pilot study at Elk Mountain Farms ran from July 17th to July 26th, 2022, and both unmodified and 4% iron-modified biochars were tested. To assess the effectiveness of the biochar treatments, water samples were collected before and after treatment to quantify changes in phosphorus levels. Additionally, soil samples from the surrounding field were collected to characterize the groundwater in the area. The two biochar treatments, unmodified and 4% iron-modified, were also analyzed before and after treatment for total elemental digestion, plant available phosphorus, and CNS (carbon, nitrogen, sulfur) analysis.

Figure 21. Pilot study site location in field 70 at the drain tile well, Elk Mountain Farms Idaho.

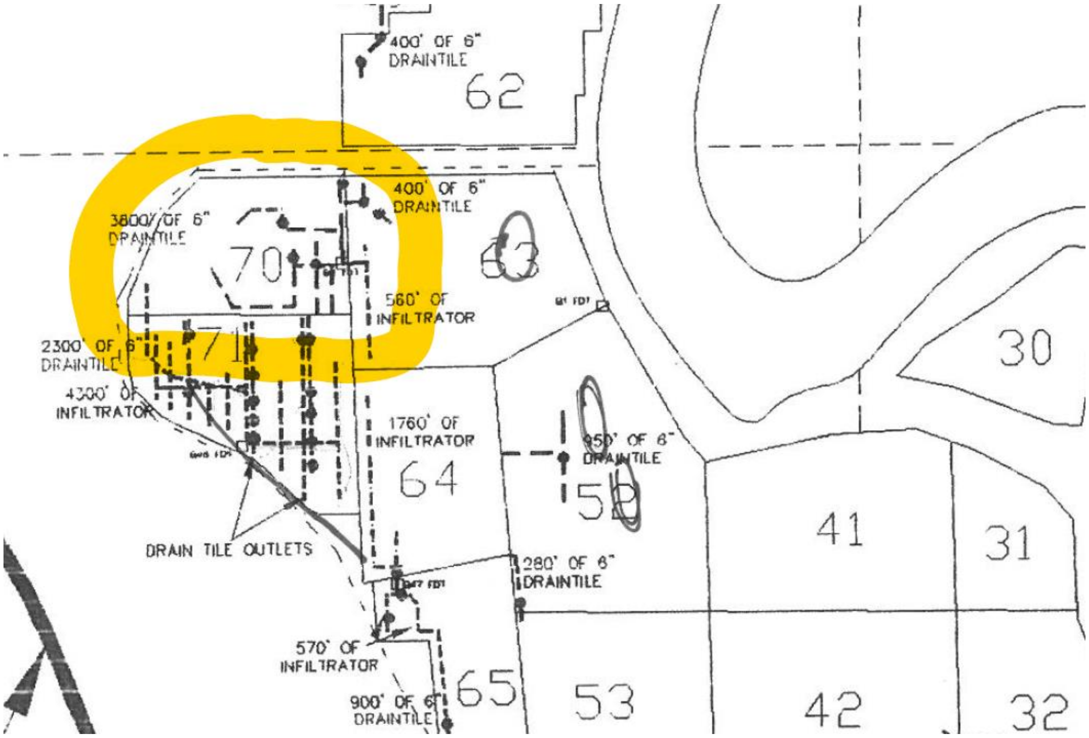

Figure 22. Diagram of Elk Mountain Farms tile drain system, field 70 where the test site was is circled.

3.3 Methods

3.3.1. Iron-Modified Biochar Production

The biochar modification process for the pilot scale differed from that used in the lab scale experiments. Initially, approximately 1 kg of biochar was slowly added to 5 gallons of ultrapure water in a HDPE mixer at room temperature, with continuous stirring at 30 RPM. The slurry was mixed at this speed for the entire length of the modification process. Next, the pH of the slurry was adjusted to around 3 using a syringe and muriatic acid. A pH probe calibrated with pH 4, 7, and 10 buffer standards was used for pH measurement. While the slurry was being stirred, the desired volume of $FeCl_3$ was added to make the biochar 4% Fe by weight, using Equation 3 from Chapter 2 of the thesis for calculation. The $FeCl_3$ solution used was sourced from PVS Technologies Inc. and had a density of 1.10 g/mL at 25 °C, with a Fe content of 12.94% by weight.

Following Fe addition to the biochar, the pH was checked, and 18 M NaOH was added using a syringe while monitoring the pH until it reached the range of approximately 6.5 – 7.0. The pH adjustment was done slowly to allow for adequate coating of biochar particles with HFO.

Subsequently, the slurry was poured into a large HDPE container, and careful decantation was performed to retain as much biochar as possible. The remaining biochar was then poured through mesh filter bags to remove the remaining water while retaining the biochar. The biochar material was transferred to a tarp and allowed to air dry for 48-72 hours, with efforts made to spread it out for increased drying efficiency. Finally, the dried biochar material was stored in a HDPE container with a sealed lid to prevent rehydration, and it was later used in the pilot study.

Figure 23. Picture of pilot scale Fe-modified biochar drying after modification process.

3.3.2. Reactive filtration set up and use with 4% Fe-Modified Biochar

The Clean Water Machine with its reactive filtration system was set up at the access well to the drain tile system in field 70 at Elk Mountain Farms. The system was designed to operate continuously, circulating water through the filters and back into the well. All hoses used in the system were 2" Kanaflex hoses. The water treatment process started by lowering a suction line into the well, and the water was then pumped into the system using two primary pumps, which were 1/3 HP Dayton pumps with stainless steel innards. The water then entered a large contactor tank made of HDPE with a capacity of 100 gallons. Inside the contactor tank, the pH was adjusted using peristaltic dosing pumps (Masterflex L S Variable Speed Drive w/ Remote I O 600 rpm) to add 50% w/wt% sodium hydroxide. This pH adjustment was necessary because the influent water had a pH close to 6, and the adsorption process performs better at a neutral or slightly alkaline pH. Thus, sodium hydroxide was continuously dosed to maintain the pH around 7. Simultaneously with the pH adjustment, the biochar treatments were added to the contactor tank using a dual screw-feed auger (Acrison - Model BDF-1-B/2). The dosing rate of the biochar was continuous at a rate of 0.47 g/L. This allowed for consistent and continuous treatment of the water with the modified biochar in the system.

After the biochar/water slurry passed through the contactor tank, it was pumped through an additional 40-foot-long hose to allow for extended contact time between the biochar and groundwater, promoting the adsorption reaction. The slurry then entered sand filters (CentraFlo CF-3) containing HFO-coated sand particles for further water purification. $FeCl_3$ was dosed into the system at a concentration of 13-15%, equivalent to 7.3-8.4 mg/L, to create the HFO coating on the sand particles. Following the sand filters, the slurry passed through a second sand filter before entering a bag filter assembly consisting of an Eaton stainless (SS-301) housing and Eaton NMO-100-P02S-50 Nylon monofilament filter bags with a 100-micron mesh. The purpose of the bag filter assembly was to capture biochar particles as they were pumped through. Once a filter bag was filled with biochar, it was replaced with a fresh one. In the case of the 4% Fe-biochar treatment, the filled bags were removed from the assembly and hung up to dry. As the bags hung, the water in them slowly percolated through the filter cake that had formed. When the bags were completely dry and all the water had drained through the filter cake, they were taken down and the biochar was recovered. For the unmodified biochar treatment, any reject water from the assembly was collected in a 65-gallon stock tank and pumped back into the contactor using a 1/2 horsepower sump pump. This step was implemented to capture any biochar particles that might have bypassed the initial pass through the 100-micron screen, maximizing the recovery of biochar for future testing. The reason the collection method was changed for the unmodified biochar compared to the 4% Fe-biochar treatment was to save time and establish a continuous process instead of a batch system. After the biochar was collected using either process, the effluent water from the bag filter assembly was spread onto the surrounding field. The biochar was then removed from the filter bags and spread out to dry in a child's plastic swimming pool made of HDPE plastic. Once dry, the biochar was stored in a 5-gallon bucket and sealed with a locking lid, ensuring its readiness for future analysis or other applications.

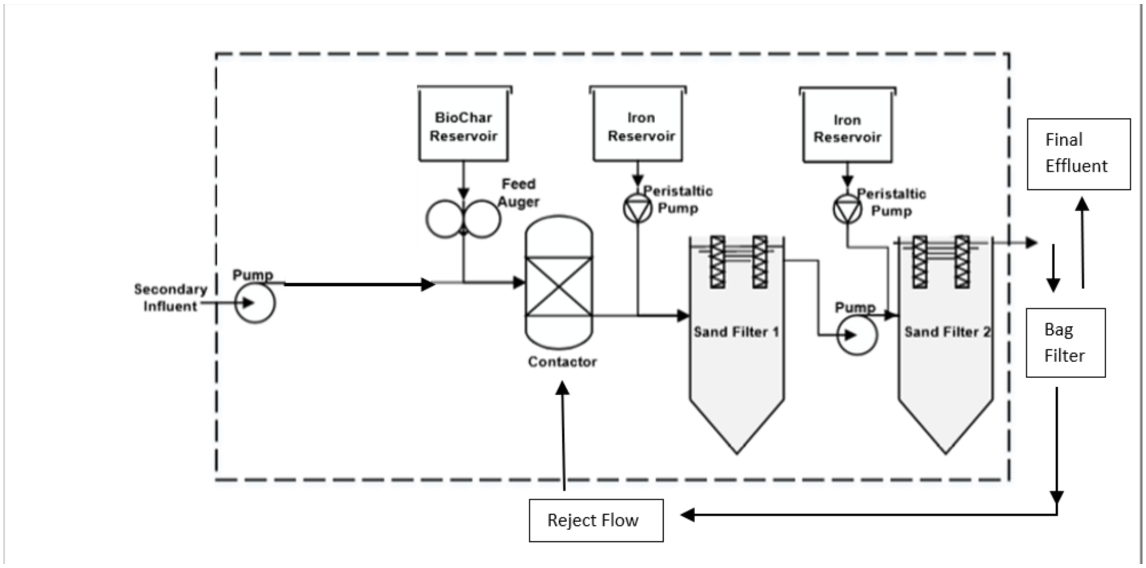

Figure 24. Conceptual diagram of clean water machine P removal process, courtesy of Martin Baker.

Figure 25. Picture of Clean Water Machine on-site at Elk Mountain Farms.

3.3.3. Laboratory Analysis on Samples

To quantitatively measure the chemistry of the process, water samples were systematically collected during the experiment from influent and effluent ports, specifically installed for this purpose. The collection of samples followed the methods outlined in pages 102-109 by Haygarth et al. in "Methods of Phosphorus Analysis" (2009). All on-site water testing also followed the protocols listed in the QAQC plan written by Martin Baker (team engineer). In brief, water sampling entailed filling 50 mL HDPE containers from designated sampling ports. Water samples collected for ortho phosphorus (OP) analysis were preserved with ~0.1 mL of 2.5 M H_2SO_4 and filtered with 0.45 µm screens. Samples for TP were not filtered but were preserved with ~0.1 mL of 2.5 M H_2SO_4. Samples collected for dissolved metals were preserved with ~0.1 mL of 1 M HNO_3. On-site testing included pH, temperature, alkalinity, turbidity, Fe concentration, electric conductivity, and ortho-phosphorus concentrations (Table 10). Water samples were collected in 50 mL HDPE sample bottles and temperature, electric conductivity, and pH were all measured with their respective probes following the protocols described in Singh et al. (2017). Other on-site testing methods for analyzing the water included:

- Alkalinity – HACH Method 8203 – Digital Titrator
- Iron Concentration – HACH Iron Test Kit IR-18 (146400)
- Phosphate Concentration – HACH Total Phosphate Test Kit PO-24 (225001)
- Turbidity – Thermo Scientific Orion AQUAfast AQ4500 Turbidity Meter, EPA Method 180.1: Determination of Turbidity by Nephelometry, calibrated with 1, 10, and 20 NTU standards

Water samples were collected, preserved if needed, and stored in coolers with ice for transportation to the lab. Samples were collected each day with duplicate “grab samples” from their respective sample ports. Samples that were taken on the same day were taken approximately one hour apart from each other. Water samples for the 4% Fe-modified Pacific Biochar were collected over a period of three days, from July 21st to July 23rd , 2022 with a total of eight samples. Water samples for the unmodified biochar were collected on July 25th and 26th, 2022 with a total of 6 samples. All samples were sent to the University of Idaho Analytical Sciences Laboratory for analysis (conforms with applicable standards of ISO 17025 (General Requirements for the Competence of Testing and Calibration Laboratories) https://www.uidaho.edu/cals/analytical-sciences-laboratory/quality-assurance). The water samples were analyzed for concentrations of:

- Total Phosphorus (TP) – SM 4500 PF – Removal Efficiency
- Ortho-phosphorus (OP) – SM 4500 P-B1, E
- Metals by IC – EPA 200.7
- Anions by IC – SM 4110
- Filterable Residue (TDS) – Mass Balance
- Nitrogen and Ammonia - GC

This data was then used to compare the changes in water chemistry before and after treatment using the filtration process with biochar as well as the chemistry in the contact tank. The findings were reported in graphical form to facilitate easier interpretation of the results (complete data tables for all tests are in the appendix of this thesis).

A QAQC plan to collect soil samples was prepared by Alex Crump. Soil samples were collected in the method described in the QAQC, which is described below: Soil samples were collected from three designated sites and the approximate location of each site is shown below in Figure 26. Site locations were captured using Google Maps screenshots of sampler position with an accuracy of 30 meters. These sites were carefully selected as they were expected to represent the soil that directly impacts the shallow groundwater that drains into the tiles. Samples were collected using a hand auger at 15 centimeters intervals at each site, with a depth of 152 centimeters for site 1 and 122 centimeters for sites 2 and 3. Following collection, the soil samples were placed in polyethylene plastic bags and sealed. Subsequently, the samples were sent to Ward Laboratories Inc. in Nebraska for comprehensive analysis (https://www.wardlab.com/about-us/). The properties analyzed and methods used included:

- Soil pH - p. 199-223. In A. L. Page et al. (ed.), Methods of Soil Analysis
- Organic Matter % - Combs, S. M. and M. V Nathan. 2011 Soil Organic Matter. p. 53-58.
- Total Carbon % - Carbon/Nitrogen in Soil and Plant Tissue. Form No. 203-821-437
- Total N % - Total Nitrogen in Botanical Materials - Automated Combustion Method. p. 106-107
- Nitrate – Geldeman, R. H. and D. Beegle. 1998. Nitrate-Nitrogen, p. 17-20
- Total P % - AOAC Method No. 965.17
- Plant Available P – Frank, K., D. Beegle and J. Denning. 1998. Phosphorus p. 21-29
- Total K % - Peters, J; Combs, S. 2003. Recommended Methods of Manure Analysis, Pg 35-38.
- Plant Available K – Haby, V.A., M.P. Russelle, and Earl O. Skoley. 1990. Testing Soils for Potassium, Calcium, and Magnesium. p. 181-227.
- Total Fe % - AOAC Method 984.27 Modified
- Plant Available Fe – Warncke, D. and J. R. Brown J. R. 1998. Potassium and Other Basic Cations p. 31-33
- Plant Available Na – Warncke, D. and J. R. Brown J. R. 1998. Potassium and Other Basic Cations p. 31-33

Figure 26. Soil sample locations for Elk Mountain Farms Idaho.

The biochar samples collected for analysis included both unmodified and 4% Fe-modified biochar at both pre and post water treatment levels, resulting in a total of four sample types. The pre-treatment samples (unused biochar) were stored in the laboratory for analysis as they were not needed on site. The post-treatment samples (used biochar) were collected from bag filters, as detailed in section 3.2.2., and were then spread out to dry in a child's plastic swimming pool made of HDPE plastic. Once the post-treatment biochar was dry, it was stored in a 5-gallon bucket and sealed with a locking lid for transportation back to the University of Idaho's Soil Chemistry Lab. All four sample types were subsequently analyzed for pH, CNS, total elemental digestion, and plant available phosphorus (2% formic acid extraction) using the same methods outlined in Chapters 1 and 2 of this thesis.

3.3.4. CNS Data Protocols

KCl extractions and CNS combustion analysis were performed to acquire information about total nitrogen. The KCl extractions were done following the method outlined on page 1130 in Extraction of Exchangeable Ammonium and Nitrate and Nitrite (Sparks et al., 1996) with a Latchat Quickchem 8500. The CNS analysis was performed using an Elementar Vario Max Cube following the method outlined on pages 41-43 in Biochar: A Guide to Analytical Methods (Singh et al., 2017).

3.4. Results

3.4.1. Water Samples

Water sample data collected from field measurements between July 17th and July 26th are listed in Table 10. No field data was collected on the 24th. The other data included comes from the samples that were sent in for analytical testing in the University of Idaho Analytical Sciences Laboratory.

Table 10. Water sample data collected on-site during pilot study. Sample data is from the last test of each day when the process was the most stable.

Date	Sample Port	pH	Temperature (°C)	OP (mg/L)	Conductivity (µS/cm)	Fe (mg/L)	Turbidity (NTU)	Alkalinity (ppm CO_3)
7/17/2022	Influent	5.95		8	410			
7/18/2022	Influent	6.75		11	390	> 5.0	7.03	64
	Filter 2	6.83		10	450	3.8	12.30	
7/19/2022	Influent	6.79	13.2					
7/20/2022	Influent	6.80	13.5	10	380	>5.0	5.24	62
	Filter 2	7.68		0.3				
7/21/2022	Influent	5.89	14.0	10	380		4.42	79
	Filter 2	6.99	19.0	1	650	0.1	0.20	218
7/22/2022	Influent	6.00	14.6	10	360	>5.0	2.95	79
	Filter 2	7.13	20.4	2	670	0.2	0.51	251
7/23/2022	Influent	5.97	16.1	8	370		3.19	84
	Filter 2	7.06	20.2	2	660	0.6	2.15	241
7/25/2022	Influent	7.68	15.5	8	440	2.9	2.28	122
	Filter 2	7.20	19.7	0	710	0.2	0.62	290
7/26/2022	Influent	6.14	17.1	6	570	2.2	2.66	146
	Filter 2	7.20	23.9	1	800	0.4	0.33	287

Water samples treated with 4% Fe Pacific Biochar demonstrated effective removal of P from groundwater, as evidenced by a decrease in total filterable P and ortho-phosphate concentrations (Figure 27, Table B.14, and Table B.15). Values are reported as the mean for all the samples across all days they were collected. The error bars shown represent the standard deviation across the samples. Specifically, total P dropped from 0.17 mg/L to 0.02 mg/L between the influent and effluent samples for a removal efficiency of 89%. Orthophosphate decreased from 0.10 mg/L to 0.01 mg/L between the influent and effluent samples for a removal efficiency of 92% (Table B.22. in appendix). Orthophosphate in the contact tank was also analyzed, and it was below the detection limit of 0.006 mg/L for all the days the 4% Fe Pacific Biochar was tested.

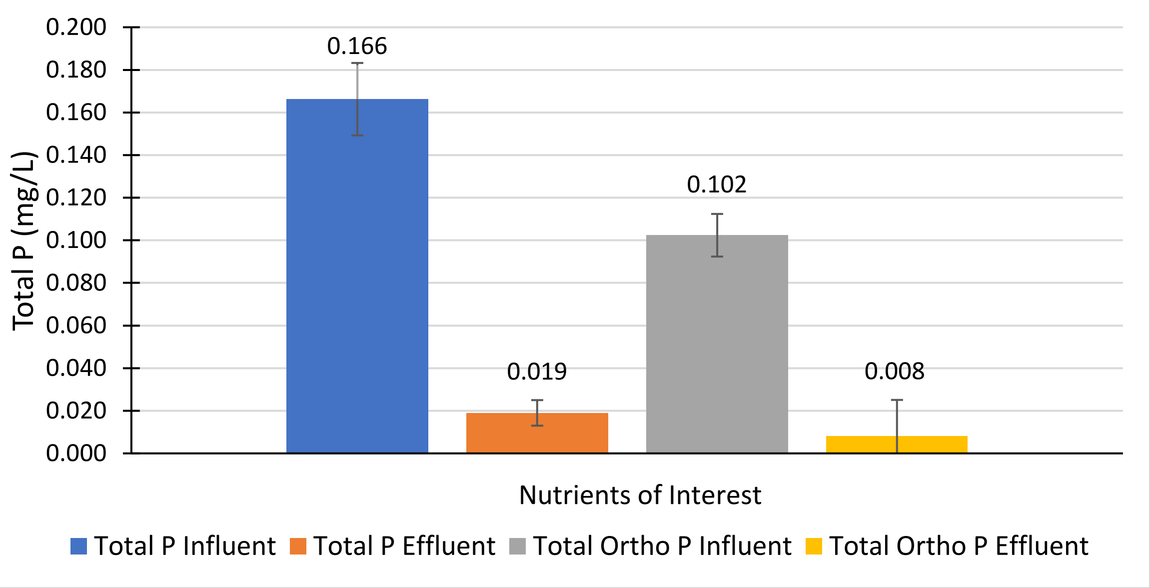

Figure 27. Influent vs effluent total P water concentrations for 4% Fe-modified Pacific Biochar (n=16).

Similar analysis was performed for water samples treated with unmodified biochar. Values are reported as the mean for all the samples across all days they were collected. The error bars shown represent the standard deviation across the samples. The unmodified biochar also showed reductions in total and ortho-phosphate concentrations as (Figure 28). Total P dropped from 0.09 mg/L to 0.03 mg/L between the influent and effluent samples for a removal efficiency of 73%. Orthophosphate decreased from 0.05 mg/L to 0.003 mg/L between the influent and effluent samples for a removal efficiency of 94% (Table B.22. in appendix). Orthophosphate in the contact tank was also analyzed, and it was below the detection limit of 0.006 mg/L for all the days the unmodified Pacific Biochar was tested except on June 26th when it was 0.01 mg/L.

Overall, the Fe-modified treatment demonstrated better performance in terms of final concentrations of total P, while both treatments were comparable in terms of ortho-phosphate concentrations. The Fe-modified treatment initially had higher P concentrations, suggesting that it removed more total P and ortho-P from the groundwater compared to the unmodified biochar treatment.

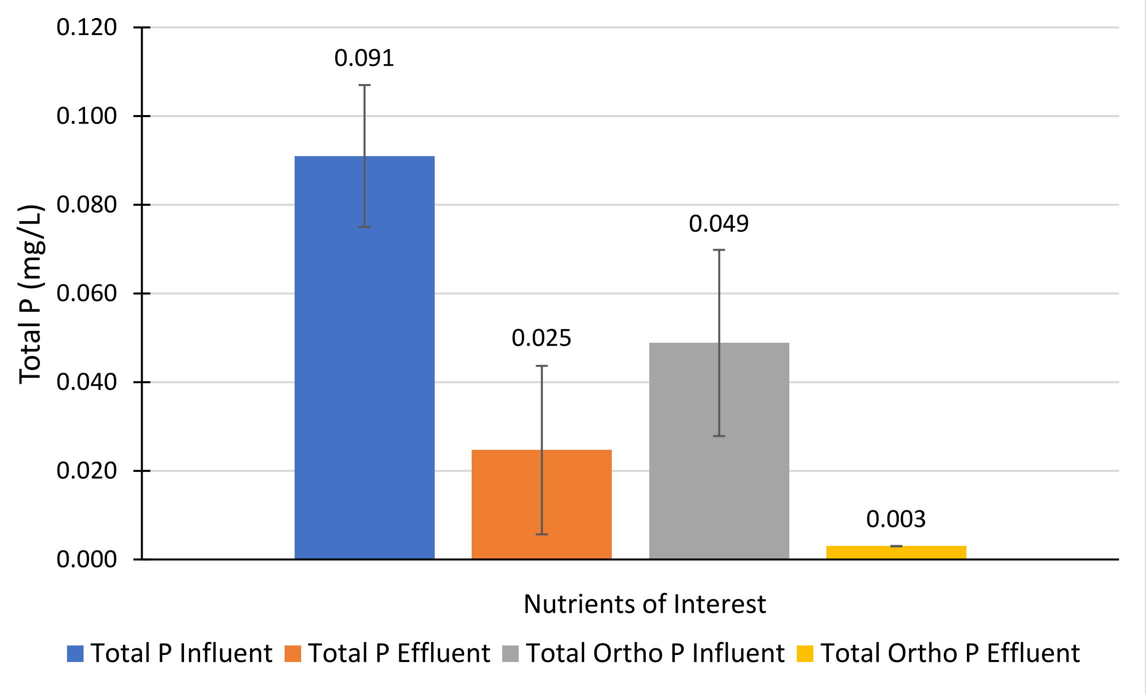

Figure 28. Influent vs effluent P water concentrations for unmodified Pacific Biochar (n=16).

Water samples from both the 4% Fe Pacific Biochar and unmodified biochar treatments were also analyzed for elements that could potentially impact water quality or soil when the biochar is reused as a soil amendment. The concentrations of Na, Fe, and Cl were measured in mg/L. Values are reported as the mean for all the samples across all days they were collected. The error bars shown represent the standard deviation across the samples. For the 4% Fe Pacific Biochar treatment (Figure 26), influent Na concentrations were 11.76 mg/L, and after treatment, the effluent concentrations increased to 128.75 mg/L. Iron concentrations decreased from 9.91 mg/L to 0.29 mg/L for influent and effluent, respectively. Chloride had the greatest variance between samples, as indicated by the range in standard deviation. The Cl concentration in the influent was 116.25 mg/L, and it increased to 124.63 mg/L in the effluent water. Similarly, for the unmodified biochar treatment (Figure 30), influent Na concentrations were 11.17 mg/L, and after treatment, the effluent concentrations increased to 115.00 mg/L. Fe concentration decreased from 3.63 mg/L to 0.13 mg/L for influent and effluent, respectively. Both treatments showed similar trends with all three elements (Na, Fe, and Cl) that were tested. It is important to monitor and understand the potential impacts of these elements on water quality and soil when considering the reuse of biochar as a soil amendment after groundwater treatment.

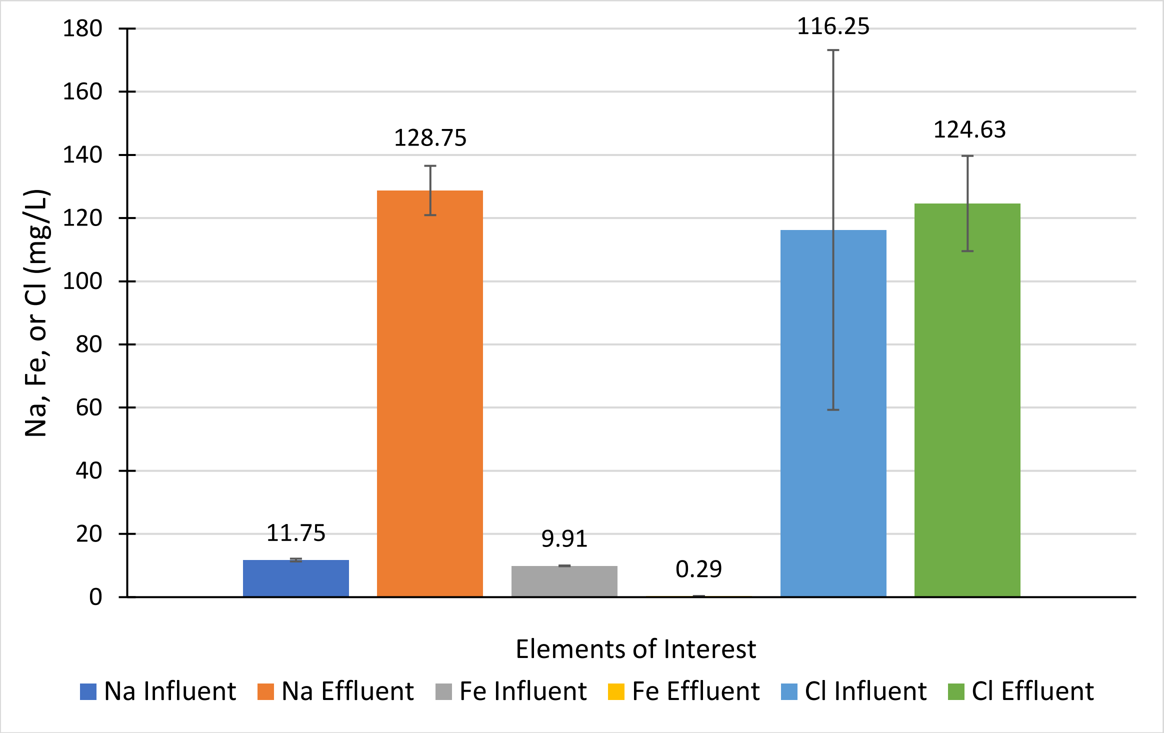

Figure 29. Na, Cl and Fe water concentrations in the 4% Fe-modified Pacific Biochar trial (n=16).

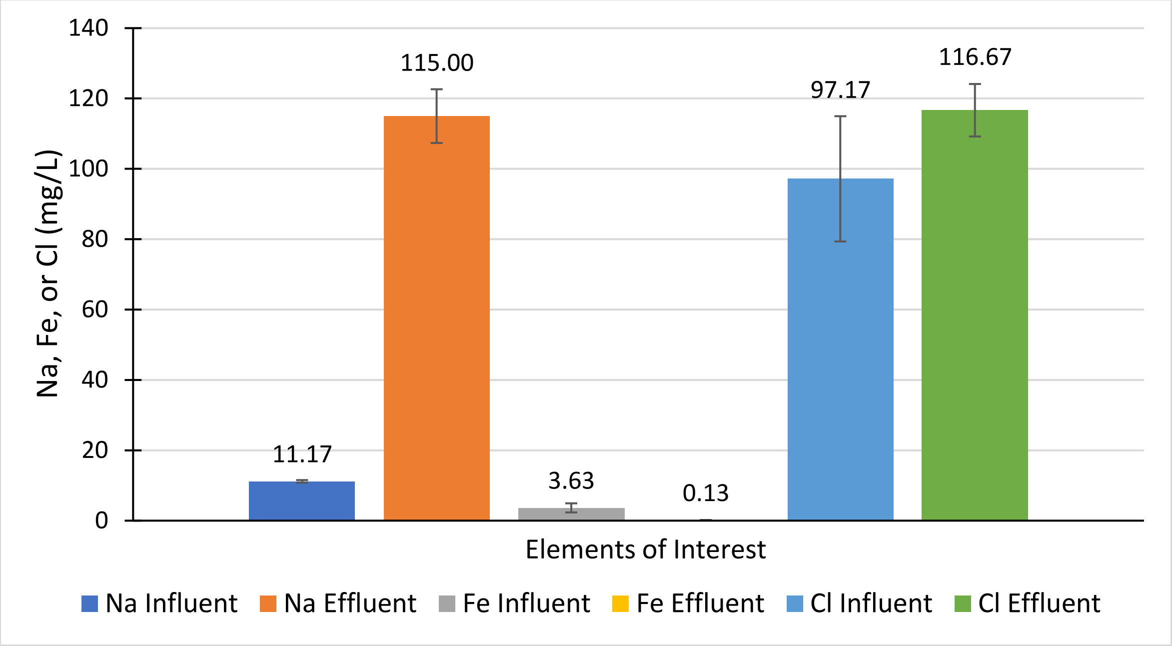

Figure 30. Na, Cl and Fe water concentrations in the unmodified Pacific Biochar trial (n=16).

3.4.2. Soil Samples

Table 11 displays soil sample data collected from three sites across the study area, which were representative of the entire field that infiltrated into the drain tiles. The soil pH ranged from 6.3 to 7.5 for sites 1 and 2, while site 3 was more acidic with a pH of 5.1 to 5.6. Organic matter content in the soil showed wide variability across depths and did not appear to be related to the site location. Total carbon content in the soil ranged from 0.59% to 6.28%, while total nitrogen content was less variable with a range of 0.04% to 0.48%. Nitrate concentrations were relatively low across the soil samples, except in site 3 at depths of 15-30 and 30-45 centimeters, which had concentrations of 125 mg/L and 40 mg/L, respectively.

Total phosphorus content varied from 0.04% to 0.08% (400 to 800 mg/kg) across all sites and depths. Plant available phosphorus was highest in the surface soil samples and declined with depth at all sites, which is likely due to fertilizer applications. Similarly, plant available potassium showed a similar trend with increased concentrations near the surface of the soils, also likely resulting from fertilizer applications. The initial 0-15 centimeters of soil had the highest levels of potassium, with a significant decrease observed after 30 centimeters of depth. Plant available iron varied across all depths and sites, with no discernible trend to indicate that iron was applied to the fields. Site 3 had much higher iron concentrations compared to the other two sites. Lastly, plant available sodium concentrations were relatively low, ranging from 11 mg/L to 29 mg/L.

Table 11. Chemical profile of AB pilot study soils at three sampling sites.

ID	Depth (cm)	pH	Org Mat. %	T C %	T N %	Nitrate (mg/L)	T P %	Plant Ava. P (mg/L)	T K %	Plant Ava. K (mg/L)	T Fe %	Plant Ava. Fe (mg/L)	Plant Ava. Na (mg/L)
Site 1	0-15	6.9	6.5	3.88	0.37	1.4	0.08	78.2	0.18	390	1.08	95	22
Site 1	15-30	7.1	6.0	3.60	0.33	2.1	0.08	52.3	0.19	160	1.31	107	25
Site 1	30-46	6.8	9.6	5.28	0.45	2.3	0.08	18.1	0.17	63	1.31	164	25
Site 1	46-61	6.6	9.7	4.91	0.42	8.4	0.06	12.6	0.16	60	1.17	148	22
Site 1	61-92	6.6	7.8	4.34	0.35	8.3	0.06	18.2	0.17	89	1.16	140	16
Site 1	92-122	6.5	10.1	6.04	0.48	3.8	0.06	12.8	0.14	25	1.21	155	20
Site 1	122-152	7.5	2.8	2.89	0.13	0.9	0.06	8.9	0.09	24	1.31	101	16
Site 2	0-15	6.8	6.0	3.49	0.33	4.3	0.06	34.6	0.18	147	1.13	86	22
Site 2	15-30	7.1	6.1	3.33	0.31	3.0	0.05	21.0	0.14	48	1.04	83	29
Site 2	30-46	7.0	6.9	4.88	0.35	11.1	0.06	11.4	0.15	19	0.95	83	27

Table 11 Continued.

Site 2	46-61	7.1	1.3	0.59	0.04	5.2	0.07	7.2	0.16	12	0.80	29	14
Site 2	61-92	6.8	1.5	0.75	0.04	3.1	0.08	7.9	0.22	13	0.96	34	16
Site 2	92-122	6.3	9.3	6.28	0.40	3.4	0.06	10.4	0.18	18	1.12	144	26
Site 3	0-15	5.1	6.3	3.34	0.29	0.2	0.06	54.2	0.18	260	1.03	316	11
Site 3	15-30	5.6	6.9	3.5	0.29	125.0	0.05	19.1	0.17	119	1.15	295	15
Site 3	30-46	5.6	8.5	4.33	0.36	39.6	0.05	14.9	0.15	41	1.05	277	20
Site 3	46-61	5.3	13.0	6.25	0.48	3.5	0.06	17.6	0.24	21	1.26	313	21
Site 3	61-92	5.3	8.2	LS	LS	3.8	0.05	13.3	0.18	34	1.17	271	24
Site 3	92-122	5.4	3.1	LS	LS	3.6	0.04	9.4	0.14	38	0.82	220	21

3.4.3. Total Elemental Digestion on Biochars

The loading of P onto the biochar through adsorption of P-bearing groundwater was assessed by total elemental digestion. Samples were analyzed in the lab in triplicate, and the error bars shown represent the standard deviation for each sample. Both the unmodified biochar and the Fe-modified treatment showed an increase in total P after the reactive filtration process. The unused unmodified biochar had an initial P amount of 725 mg/kg, which increased to 1109 mg/kg after water treatment. The Fe-modified biochar treatment had an initial P amount of 614 mg/kg, which increased to 996 mg/k after water treatment (Figure 31).

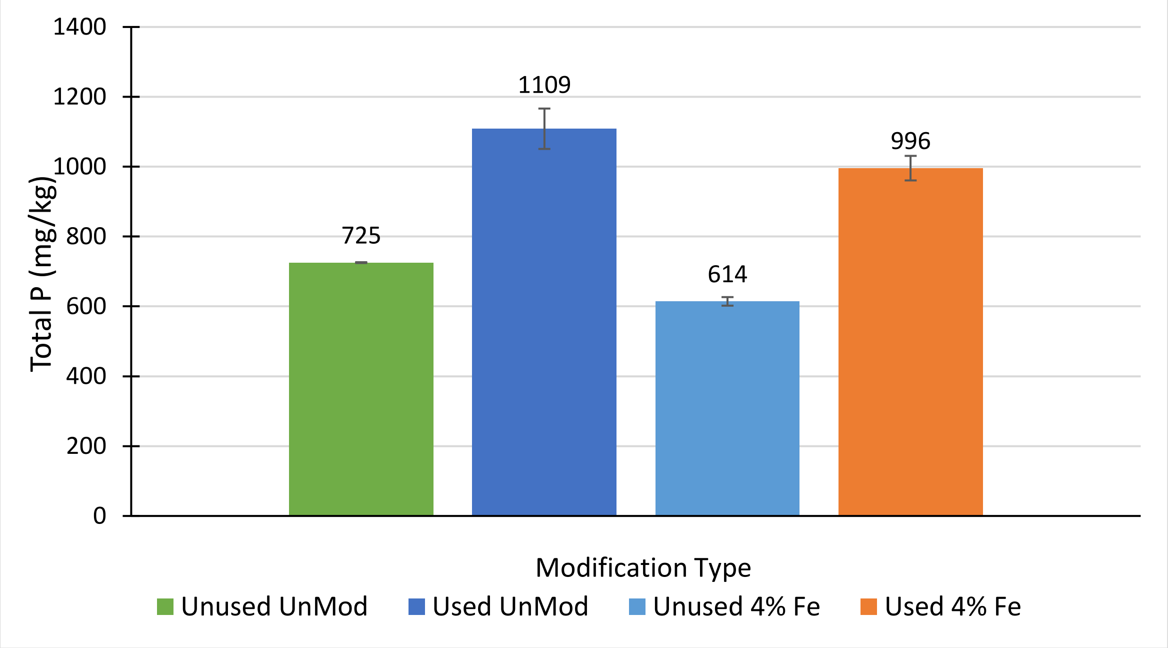

Figure 31. Biochar total P content from Elk Mountain Farms pilot study. (n=3)

Iron concentrations in the unmodified biochar started off at 1928 mg/kg but after being used in the reactive filtration process increased up to 61,945 mg/kg (Figure 32). As expected, the 4% Fe-modified biochar had a higher initial Fe concentration of 25,513 mg/kg and saw an increase up to 71,020 mg/kg. The Fe content of the 4% Fe-modified biochar was less than 4%, suggesting some iron loss occurred in the production process: likely during the rinsing step. The increased iron in the biochar after treatment indicates that both biochar treatments had the potential to uptake Fe from the tested groundwater. However, it is unclear if it was the biochar or a combination of the biochar and filtration process that contributed to this increase. The unmodified biochar samples most likely saw an increase in Fe due to precipitation of Fe from the groundwater as the pH increased (NaOH addition) and potential oxidation of the ferrous Fe to less soluble ferric Fe occurred. The concentrations of Fe and all other elements that were measured during the analysis are included in the appendix.

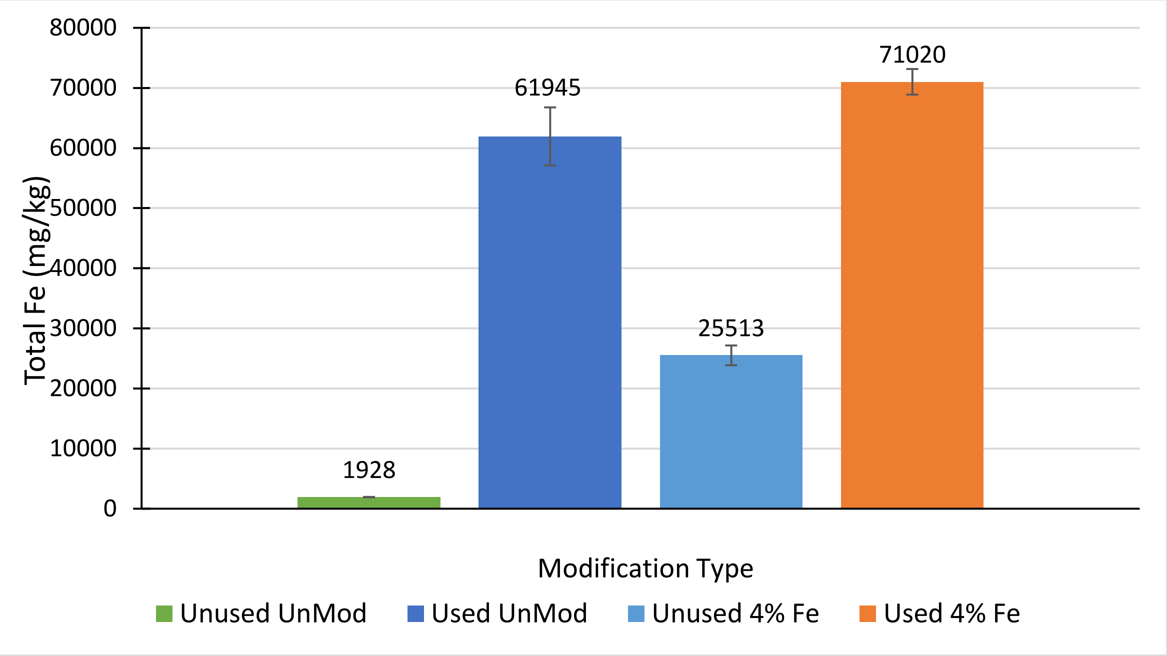

Figure 32. Biochar total Fe content from Elk Mountain Farms pilot study. (n=3)

3.4.4. Plant Available Phosphorus

Formic acid extractions were performed on the biochar samples collected (Figure 33), including both unmodified and 4% Fe-modified biochar, at both pre- and post-water treatment levels. This resulted in four sample types that were analyzed, with samples analyzed in triplicate and error bars representing the standard deviation for each sample. The unused unmodified biochar, which was the regular Pacific Biochar not used in the groundwater treatment, had the highest amount of plant available P, with 647 mg/kg. However, after water treatment, the used unmodified biochar's plant available P decreased significantly to 91 mg/kg. The 4% Fe-modified biochar showed a small increase in plant available P, from 27 mg/kg to 39 mg/kg for the unused 4% Fe and used 4% Fe, respectively. Despite this small increase, both Fe-modified types had considerably less plant available P compared to the unmodified biochar. By comparing total P with plant available P (as shown in Figure 34), the percentage of plant available P was determined. The unused unmodified biochar had a significantly higher percentage of plant available P at 89%. However, after being used in the groundwater treatment, this percentage dropped down to only 8%. The two Fe-modified treatments had even lower percentages, with only 4.4% and 3.9% of plant available P for unused 4% Fe-modified biochar and the used 4% Fe-modified biochar, respectively.

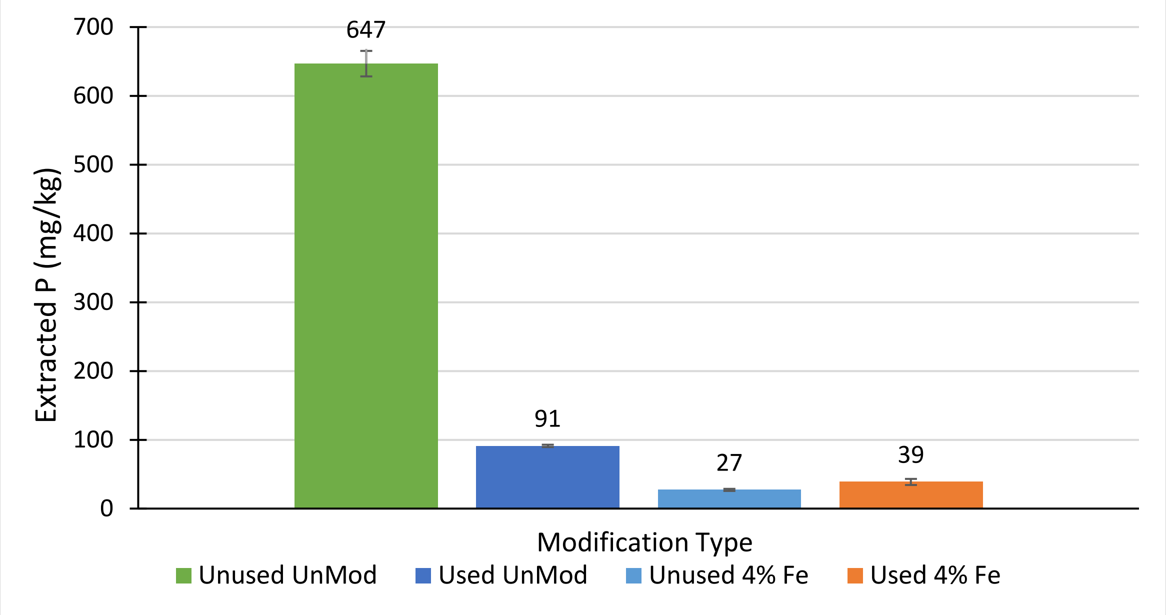

Figure 33. Plant available P from 2% formic acid extraction in biochar from Elk Mountain Farms pilot study. (n=3)

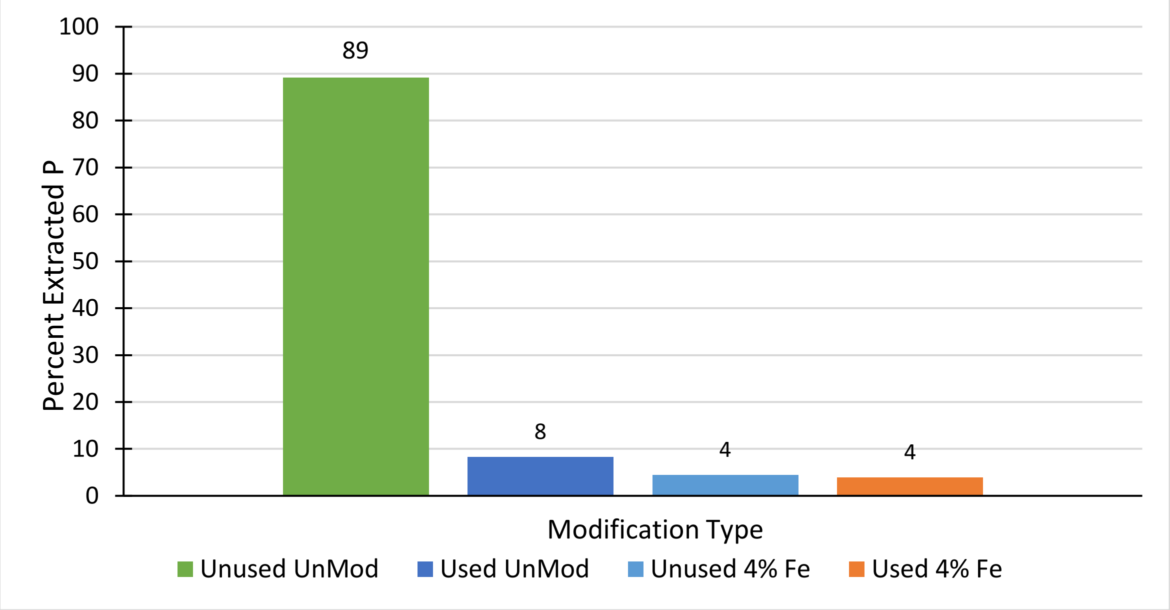

Figure 34. Percent plant available P in biochar used for Elk Mountain Farms pilot study. (n=3)

3.4.5. Nitrogen Data

Potassium chloride (KCl) extractions and CNS analysis were performed on the biochar samples to determine the amount of total nitrogen, inorganic nitrogen and organic nitrogen were present in each sample. The data obtained from the CNS analysis provided the amount of total N in mg/kg. The KCl extractions were done to determine the amount of inorganic N present in each sample, which was then subtracted from the total N obtained from CNS analysis to calculate the amount of inorganic and organic nitrogen in each sample (as shown in Figure 35). The samples contained significantly more organic N compared to inorganic N. The used unmodified biochar had the highest amount of N, with 2935 mg/kg of organic N and 145 mg/kg of inorganic N. The unused unmodified biochar had the least amount of N, with 1842 mg/kg of organic N and 38 mg/kg of inorganic N. Both the unmodified and 4% Fe treatments showed increases in N after being exposed to the groundwater.

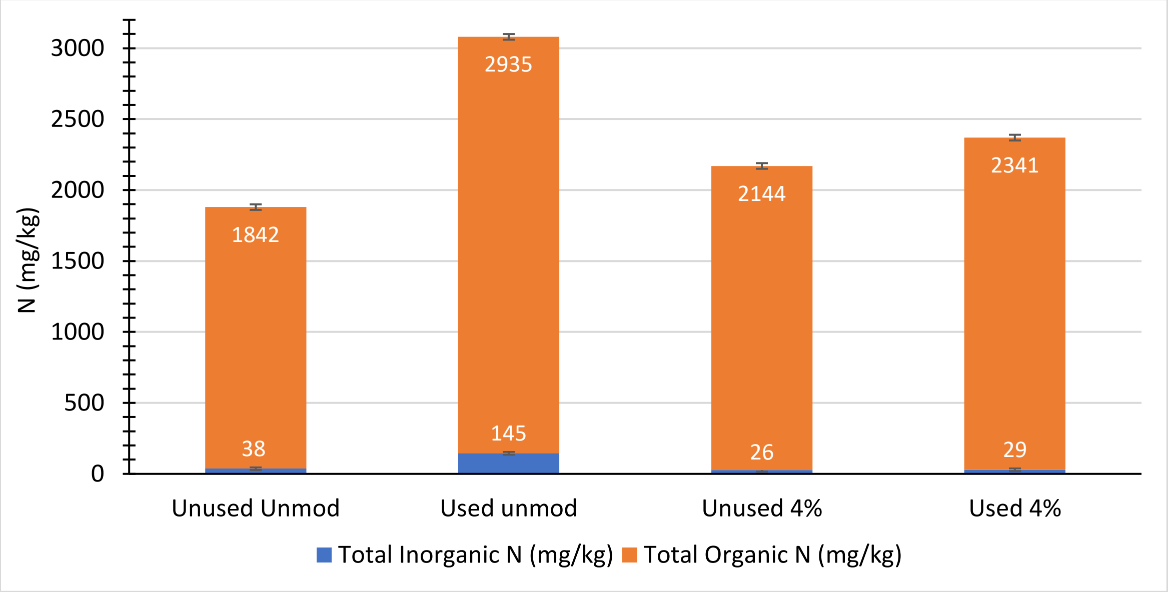

Figure 35. KCl extracted N for 4% Fe and unmodified Pacific Biochar used in Elk Mountain Farms pilot study. (n=3)

3.5 Discussion

3.5.1. Water Samples

The results of the study show that both the unmodified and 4% Fe-modified biochars were effective at removing phosphorus (P) from the tile drain water. However, the Fe-modified performed better overall, with lower effluent concentrations of P compared to the unmodified-biochar. The Fe-modified also removed more total P, even when the initial P concentration in the influent water was higher. The influent P concentrations showed variability from day to day, likely due to fluctuations in groundwater levels and water percolation in the field (Table 10) (Tables B.14, B.15, B.19, and B.20 of the appendix). The influent P concentrations were averaged over the run times for each sample treatment to account for this variability. The range of influent P concentrations was lower overall during the unmodified biochar trial, possibly because it was tested a week later and the water levels in the well had dropped during that time, thus reducing groundwater-soil particle interactions in the surface soils where the concentrations of P were higher.

The performance of the unmodified biochar in the field study was better than expected based on laboratory trials. In the laboratory trials, the unmodified biochar showed only slight adsorption of P at 16 mg/kg at 25 mg/L P, while the 4% Fe-modified biochar had much higher adsorption of P at 1229 mg/kg. Although the laboratory test used higher initial P concentrations than the pilot study, it was expected that the trend would be similar for lower influent concentrations encountered in the pilot study. One possible explanation for the better performance of the unmodified biochar in the field study could be the lower initial P concentrations in the influent water compared to the laboratory trial. The pilot study observed P concentrations ranging from 0.17 to 0.09 mg/L, which are considerably lower than the 25 mg/L used in the laboratory trial. These lower concentrations could have been within the adsorption capacity of the unmodified biochar, resulting in reduced P concentrations in the effluent.

Another important difference that contributed to the increased performance of the unmodified biochar is the Fe present in the groundwater. The ground water on-site fluctuated between the detection limit of <0.10 mg/L to as high as 10 mg/L (Table B.13 and B.18 in the appendix). It is important to note that the highest Fe concentrations occurred during the Fe-modified testing and that concentrations during the unmodified-biochar only got as high as 3.2 mg/L. The Fe in the influent water could have interacted with the biochar, mimicking a similar reaction as the Fe-modified and resulting in more Fe-phosphate bonds in the unmodified-biochar than predicted. Additionally, Fe-coated sands from the Clean Water Machine reactive filters could be a potential source of added Fe in the system, interacting with the unmodified-biochar and increasing its adsorption capacity, like the extra Fe in the groundwater.

Sodium and chlorine concentrations in the effluent water increased in both treatments, indicating that Na and Cl were introduced to the system. Additions of concentrated NaOH to the system to adjust the pH added Na to the system. $FeCl_3$ amendment of the sand columns also added Cl to the system. In addition, the 4% Fe-modified biochar treatment contained slightly more Na and Cl compared to the unmodified biochar treatment. This slight increase likely came from the biochar that released Na and Cl added during the modification process that used $FeCl_3$ and NaOH. Even after rinsing and decantation of the modified biochar residue, Na and Cl were still present in the biochar, potentially contributing to the higher levels in the water samples (Table B.17 in the appendix). Fe concentrations in the water samples, on the other hand, decreased in both treatments. The sand-coated filters used in the study could have adsorbed the extra Fe in solution as the water passed through them, resulting in lower Fe concentrations in the effluent water. It is important to note that the Fe-modified treatment had higher initial Fe levels due to the modification process.

Additional studies of the groundwater iron content are required to better understand how it impacts the biochar and water treatment process. The original intent of the study was to collect these groundwater samples for analysis, but the well had already gone dry for the water year by the time the samples were to be collected.

The efficiency of biochar reactive filtration used in this pilot study was compared to similar approaches in removing P from water. The results demonstrated that the 4% Fe Pacific Biochar effectively removed P from groundwater, with a removal efficiency of 89% for total P and 92% for ortho-phosphate. The unmodified biochar performance was not as efficient, with a total P removal efficiency of 73% and ortho-phosphate removal efficiency of 94%. In a study by He et al. (2017) that also used HFO-modified biochars, they were able to remove 95% of total P from biogas slurry at the bench scale. Similarly, in a study by Liu et al. (2015), Fe-modified biochar was able to remove 99% of total P in a filtration column that required two hours to filter. Although both studies achieved better efficiencies for P removal, they were conducted at a smaller scale and over longer periods of time. The biochar reactive filtration in this pilot study demonstrated competitive P removal at the field scale without significant wait times, highlighting its effectiveness. In comparison to other field-scale studies, such as the one conducted by Bryant et al. (2012) using FGD gypsum in a filter in a field ditch, which removed approximately 65% of the total dissolved P load over 3 years, and the study by Penn et al. (2012) using a P removal structure filled with steel slag in a drainage ditch, which removed around 25% of the total dissolved P load during a 5-month study, the biochar reactive filtration showed promising results. To further evaluate the long-term efficiency of biochar reactive filtration, conducting studies of longer duration (greater than 9 days) in comparison to these and other similar studies would be beneficial. Nevertheless, the current results indicate that biochar reactive filtration technology has the potential to be a viable option for effective P removal from water in the future.

3.5.2. Soil Samples

The soil samples taken from field 70 showed that the Fe content in this field had a mean of 1.11%. The relatively high Fe content in field 70 was also reflected in the water samples, which posed challenges for the Clean Water Machine process and required corrective measures. One of the main corrective measures was adjusting the pH of the water. The mean pH of the soil in field 70 was 6.39, which was higher than the groundwater samples, which ranged from 5.8 to 6.0. Adjusting the pH of the water up to pH 7 allowed the Clean Water Machine process to work more efficiently. The evidence of fertilizer application was also apparent in the soil samples, with increased concentrations of P and K at the surface, indicating that fertilizers were applied to the field. However, the infiltration of P and K concentrations in the deeper soils was much less, suggesting limited downward movement of these nutrients. The P appears to instead follow runoff patterns similar to those modeled by Vadas et al., (2008), where the P is moving offsite within surface waters and via drain tiles under the fields. It is important to consider these soil characteristics, such as Fe content, pH, and fertilizer application, when interpreting the results of the biochar treatment in the pilot study, as they could have influenced the performance of the biochar in the system and its interaction with the groundwater.

The texture of the soils in the study area was primarily silts and clays, with a reduction in these finer particles at depths greater than 61 cm. There were also sand lenses observed, indicating that historically the riverbed had meandered over the area where field 70 currently resides. This was supported by the presence of preserved reed bits and an overall increase in organic matter at specific depths, such as 91-122 cm for site 1 and 46-61 cm for site 3, suggesting that the river's edge had shifted over time. The depth of increased organic matter indicated that the river's edge may have been at least as far west as site 3, which could have influenced the soil texture and chemistry observed in the samples.

Unfortunately, during the analysis process, the laboratory accidentally discarded samples, resulting in incomplete analysis for certain depths, marked as "lost samples (LS)". These limitations in sample collection and analysis should be taken into consideration when interpreting the results of the study.

3.5.3. Biochar Samples

The digestion of the biochar samples revealed that both treatments had higher final Fe concentrations compared to their initial concentrations, which was expected as the biochar was designed to adsorb P from groundwater onto its surface. However, it was unexpected that the unmodified-biochar would gain so much Fe that it would be similar to the Fe-modified biochar (figure 32). This contradicts the initial hypothesis that the Fe-modified, with additional Fe added during the modification process for better performance in removing P (Newcombe et al., 2008), would have significantly higher Fe concentrations. The reasons for this unexpected result could be the presence of additional Fe in the groundwater, which could have coated the unmodified biochar (Abdel-Ghani et al., 2015). Additionally, the effects of iron-coated sand filters on the biochar are unknown at this point, and further laboratory analysis involving Fe-coated sands and biochar could be beneficial in explaining this discrepancy. Further research and analysis are needed to fully understand the interactions between Fe, biochar, and other ions in the groundwater, as well as the effects of iron-coated sand filters on the biochar's performance. These findings highlight the need for continued investigation and experimentation to elucidate the underlying mechanisms and optimize the use of biochar for groundwater treatment and nutrient removal.

The analysis of the biochar samples revealed that despite the higher concentrations of total P in the biochar, the plant available P decreased for the unmodified biochar after exposure to water. Initially, the unmodified biochar had 647 (mg/kg) of plant available P, but this dropped to 91 (mg/kg) after exposure to the groundwater. One possible explanation for this decrease in plant available P is that it was washed away during the treatment process, and other species of P that are not available to plants were adsorbed to the biochar, leading to an overall increase in total P. Another possibility is the Fe in the groundwater that created Fe-modified biochar in-situ, which increases Fe-P bonds that are difficult for formic acid to cleave creating a quasi-Fe-modified biochar from the unmodified biochar.

The Fe-modified biochar behaved as expected, based on laboratory trials, with low plant available P before use due to the modification process, which strips the biochar of its initial P. This is likely due to the strong acids used during the modification process to adsorb Fe to the biochar. The Fe can also tightly sequester the P as adsorbed or precipitated P, further reducing the plant available P. The plant available P may even be buried below the Fe mineral coating that forms during the modification process.

The strong Fe-phosphate bonds that were formed during the modification process are resistant to cleavage by formic acid (Camps-Arbestain et al., 2017 from Biochar: A Guide to Analytical Methods). These strong Fe-phosphate bonds could also be a possible explanation for the decrease in plant available P observed in the unmodified-biochar. If the unmodified-biochar is being exposed to Fe in-situ during the process, which could explain its increased efficiency at absorbing P, it is possible that the Fe-phosphate bonds formed are too strong to be cleaved by formic acid, leading to a reduction in plant available P. This could provide insights into the underlying mechanisms of P adsorption and release in biochar, and further research is needed to fully understand the interactions between Fe, biochar, and plant available P, as well as the effects of the modification process on biochar's P availability.

Further studies focusing on the interactions between biochar, Fe-coated sand, and P adsorption could provide valuable insights into the observed unexpected performance of unmodified biochar. Additionally, conducting tests to determine the Fe-modification method on biochar properties could provide a better understanding of the efficiency of modified biochar in adsorbing P. Currently, the modification process is done at a pH lower than 3, before being titrated up to 6.5, but studying the modification at higher pH levels and evaluating the performance of the resulting modified biochar in terms of P adsorption could shed light on the unexpected performance of unmodified-biochar. Different species of Fe could also be analyzed for their effects on biochar, as different forms of Fe could have varying impacts on biochar properties and P adsorption capacity (Zhang et al., 2018). These experiments could help determine if and to what extent biochar is modified at higher pH levels with different species of Fe, which could have occurred in the pilot study. By conducting further research on these aspects, a better understanding of the underlying mechanisms of biochar modification, Fe-coated sand interactions, and their impacts on P adsorption can be achieved.

The primary aim of the pilot study was to determine the efficiency of biochar in adsorbing P from groundwater and its potential as a soil amendment. The results of the greenhouse study, which is currently being conducted, will provide insights into the effectiveness of biochar as a soil amendment. However, the observed reduction in plant-available P could pose challenges for the soil amendment application, as finding a balance between increased P adsorption from groundwater and P release back into the soil may be challenging. Further studies, including greenhouse experiments and future research, could help to address these questions and solve the problems associated with biochar as a soil amendment. Understanding the impacts of Fe-modification on biochar properties, as well as its effects on P adsorption and plant-available P will be crucial in finding the right balance between P removal from groundwater and P availability in the soil for optimal soil amendment applications. Continued research and experimentation will provide valuable insights into the potential use of biochar as a sustainable solution for groundwater treatment, soil amendments and to help to address challenges associated with its application.

3.5.4. Limitations of Study

Location and water type were the two primary factors that are important for selecting a study site. For the Clean Water Machine deployment, a suitable site had to fulfill certain criteria: accessibility by road, flat terrain, and availability of power hookups for machine deployment. Unfortunately, other potential locations that could have been good candidates for reactive filtration using modified biochars had to be excluded due to their failure to meet these qualifications. Another significant criteria in site selection is the water chemistry. Groundwater and agricultural runoff water can exhibit substantial differences depending on underlying geology and the types of fertilizers used in crop production. The variability in influent water poses efficiency issues for the reactive filtration process, necessitating individualized adjustments at each potential location. For instance, in this pilot study, the drain tile water had relatively high pH and iron content requiring pH adjustments to be made in the field to improve water treatment efficiency.

Another consideration for water treatment and nutrient recovery on biochar is the presence of potential hazards in the treated water. If the treated water contains substances that are harmful to agricultural production, reuse of the recovered biochar for nutrient recycling is not possible. Consequently, this could result in the generation of contaminated "waste" biochar, which would require additional treatment before disposal. This risk of contamination becomes even more pronounced when using modified biochars in wastewater treatment facilities. To address this potential contamination, it would be necessary to implement further treatment alongside modified biochar reactive filtration.

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Appendix A. Supplemental Table and Figures for Chapter 2

Fe Desorption Experiment

Methods for Desorption of Phosphorus from Fe Modified Biochar Using Deionized Water

The method used for the water desorption of Fe modified biochar was the same method used for the unmodified biochar. Refer to section 1.3.5. of this thesis for a detailed explanation of that method.

Results for Desorption of Phosphorus from Fe Modified Biochar Using Deionized Water

The water desorption experiment was performed twice and labeled as trials 1 and 2, where the concentration of phosphorus was measured in mg/L or (mg/L) over a period of 120 minutes. Trials 1 and 2 were conducted with distinct batches of 2% PAC Biochar that were produced at different times. The biochar used in Trial 1 had been stored for approximately 6 months, while the material for Trial 2 was manufactured one week before the experiment. As the biochar for Trial 1 had been depleted, it was necessary to create a new batch for Trial 2. Both trials showed similar trends in P release from exposure to water, with P concentrations increasing rapidly within the first 16 minutes. Trial 2 released more P than trial 1, with a maximum concentration of 0.033 (mg/L), while trial 1 had a maximum of 0.023 (mg/L). Trial 1 reached its peak at 26 minutes and then steadily decreased to a concentration of 0.008 (mg/L) at 120 minutes. Similarly, trial 2 reached its maximum at 34 minutes and then steadily decreased to a concentration of 0.015 (mg/L) at 120 minutes. Although it is possible that the biochar could have continued to release leached P beyond 120 minutes, the experiment was terminated at this point. The initial data point in trial 2 is likely incorrect due to contamination in the hose during the priming process. As a result, the initial decrease seen in the graph should instead follow the upward trend shown in trial 1.

Discussion of Water Desorption of Fe-Biochar

The water desorption experiment provided valuable information on the ability of the modified biochar to release the adsorbed phosphorus back into solution. While it did not determine the species or plant availability of the released phosphorus, it did demonstrate that the phosphorus could be released from the biochar using just water. This is an important step in determining the soil nutrient potential of the modified biochar, as it indicates that phosphorus can be made available to plants. The experiment also provided insight into the timing of phosphorus release, which led to the subsequent kinetic experiments that were conducted.

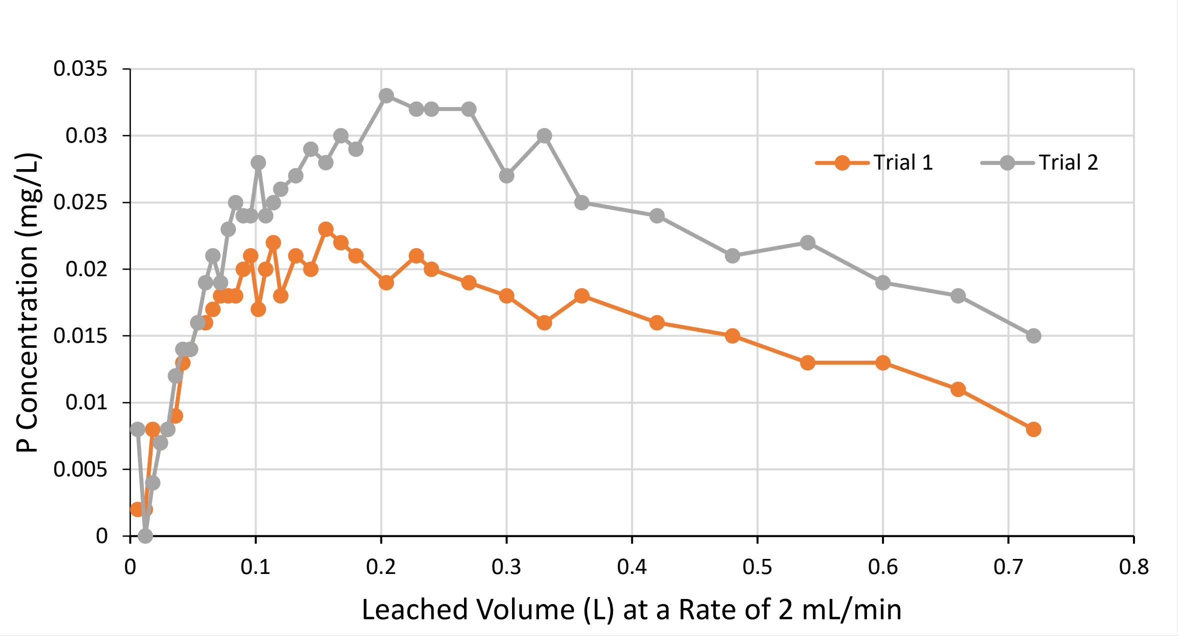

Figure A.36. PAC biochar water desorption with 2% Fe modification loaded with 10 (mg/L) P, analyzed with ICP-OES.

Kinetics Experiment

Methods for Kinetic Experiments on Fe Modified Biochar

In this experiment, the kinetics of phosphorus adsorption and desorption onto 2% Fe modified biochar were studied by taking sub-samples at timed intervals. A 1:50 ratio of biochar to solution was prepared by adding 8 grams of biochar to 400 mL of pH-adjusted 18 megohm DI water, with the pH adjusted to 6.5 using 1 M HCl or 1 M NaOH depending on the initial pH of the biochar. A method blank and water blank were also set up along with the samples taken in triplicate. A 20 (mg/L) P solution was prepared from a 1000 (mg/L) NaPo4 * 7H2O stock solution and DI water using Equation 4. The P solution was then added to the biochar and pH-adjusted water to obtain a final concentration of 20 (mg/L) P. The solution was covered to prevent light from reaching it and shaken in a Glas-Col end-over-end shaker between samplings. During sample taking, the solution was transferred from the shaker and placed on a stir plate to ensure the solution was homogenous. The stir plate was set to a speed that ensured mixing without forming a vortex. After a sample was taken, the batch was transferred back to the end of the shaker.

Sub-samples were taken at specific time intervals of 1 min, 5 min, 10 min, 20 min, 30 min, 1 hr, 1.5 hr, 2 hr, 4 hr, 8 hr, 16 hr, 24 hr, 36 hr, 48 hr, and 72 hr. 8 ml sub-samples were taken in triplicate, filtered using a 0.45-micron filter PES membrane filter syringe, and then acidified with one drop of 1 M nitric acid. pH was also recorded during the sampling times using a Denver Instrument Model 250 pH probe that was calibrated using pH 4, 7, and 10 buffer standards. Phosphorus concentrations were then analyzed using ICP-OES (Agilent 5110, Santa Clara, California) after all samples were collected. Effluent P, Mg, Fe, and Ca concentrations were compared to the initial P concentration to determine the amount of desorption. Desorption vs time was plotted to obtain the kinetics curve. Equation 1 was used with the effluent P concentrations to calculate adsorption values for the sample intervals. Adsorption was then plotted vs time to obtain the kinetics curve.

Results of Kinetic Experiment of Fe-Biochar

To assess the kinetics of the adsorption reaction to biochar, the equilibrium concentration of simulated P wastewater was analyzed over 144 hours. All samples were taken from the same batch in duplicate. The pH of the slurry mix remained mostly constant between 6.41 to 6.68. During the experiment, trace amounts of Fe and Mg were released from the biochar. Larger amounts of Ca were released, with a maximum concentration of 1.158 (mg/L) at 144 hours, where the initial concentration was 0.237 (mg/L). Concentrations of P decreased throughout the experiment, with an initial concentration of 5.982 (mg/L) decreasing to a final concentration of 0.956 (mg/L). The first sample was taken at 0.03 hours, and by comparing the initial P concentrations, it was calculated that 70.54% of P was removed from the solution in the first 0.03 hours. At the end of 144 hours, 95.29% of P had been removed from the solution. Adsorption to the biochar increased from 17.876 (mg/kg) to 24.149 (mg/kg) from the start to the finish, respectively. Adsorption data shows a Langmuir adsorption curve, with a maximum adsorption being reached, causing the curve to flatten.

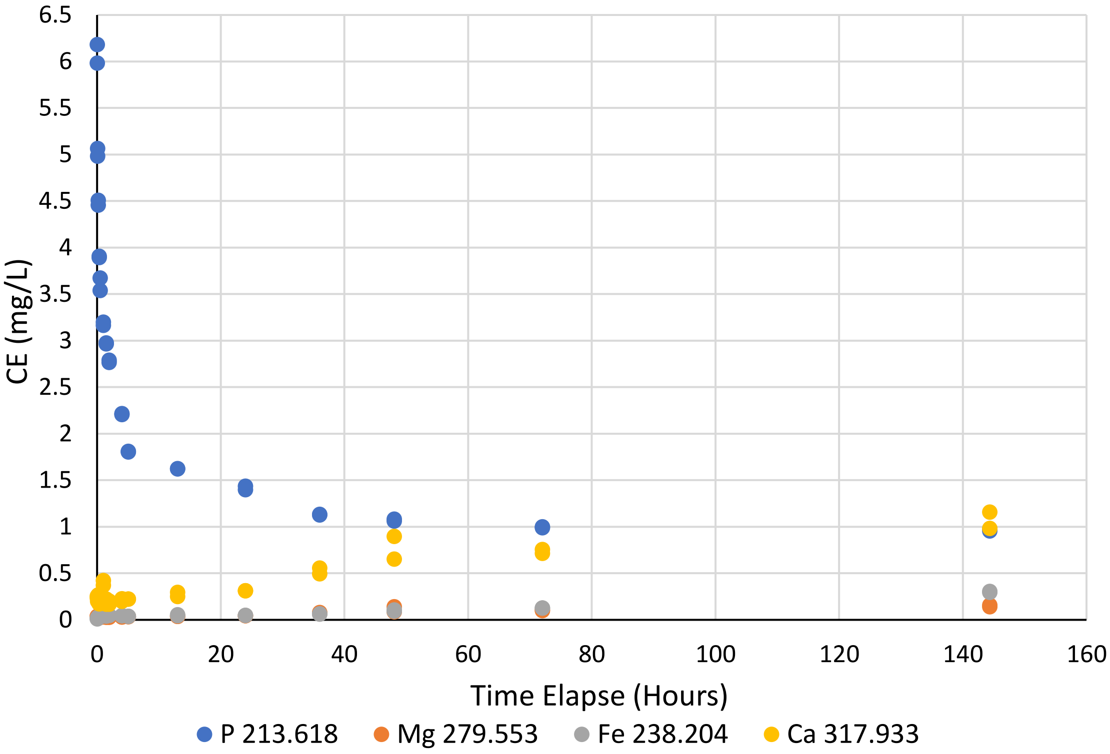

Figure A.37. Elemental concentration by time of effluent PAC 2% Fe modification loaded with 20 (mg/L) P.

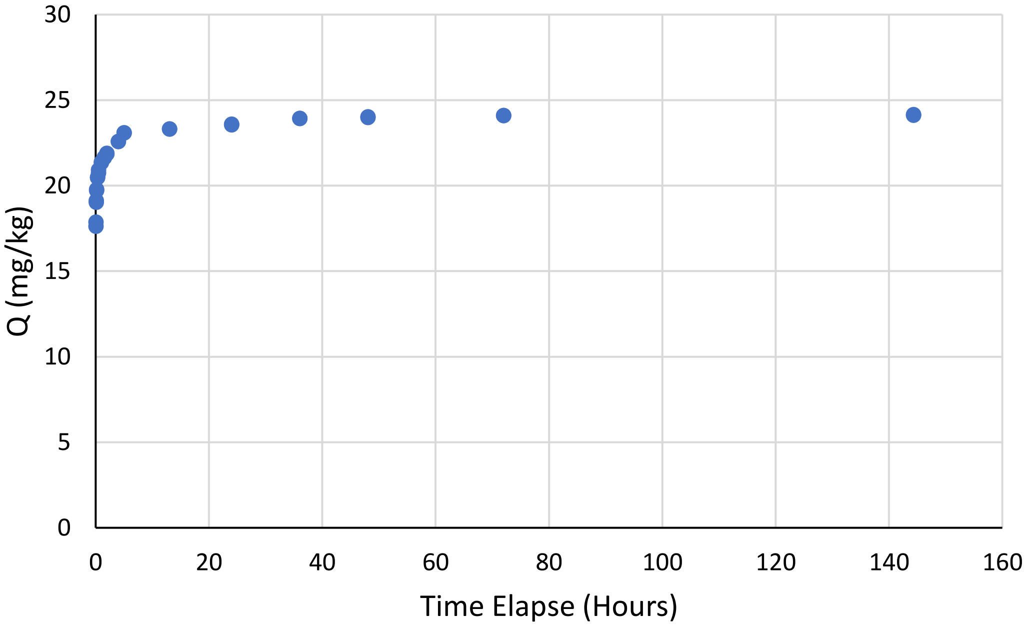

Figure A.38. Adsorption by time of 2% Fe modified PAC loaded with 20 (mg/L) P.

Discussion of Kinetic Experiment for P Adsorption to Fe-Biochar

Based on the kinetics experiment, it was found that over 90% of P removal occurred within the first 24 hours, with 93% of the P being removed. Subsequently, the rate of P removal per unit time decreased significantly, indicating that 24 hours was sufficient for achieving the desired level of efficiency. Moreover, the experiment demonstrated that most of the P adsorption occurred rapidly, within the first 0.03 hours. This finding was useful in designing the pilot study, where predicting the incubation time was challenging. Although increasing the incubation time resulted in increased P adsorption, achieving a 144-hour incubation period would be difficult in most cases. Comparing the adsorption curve with the P concentration curve, it can be inferred that the P removed from the solution was adsorbed to the biochar. The curves were inverse, suggesting that the biochar absorbed the P. To confirm this, total elemental digestion was performed on the biochar and solution later using similar material. The results confirmed that the P concentrations increased in the biochar as concentrations decreased in the solution.

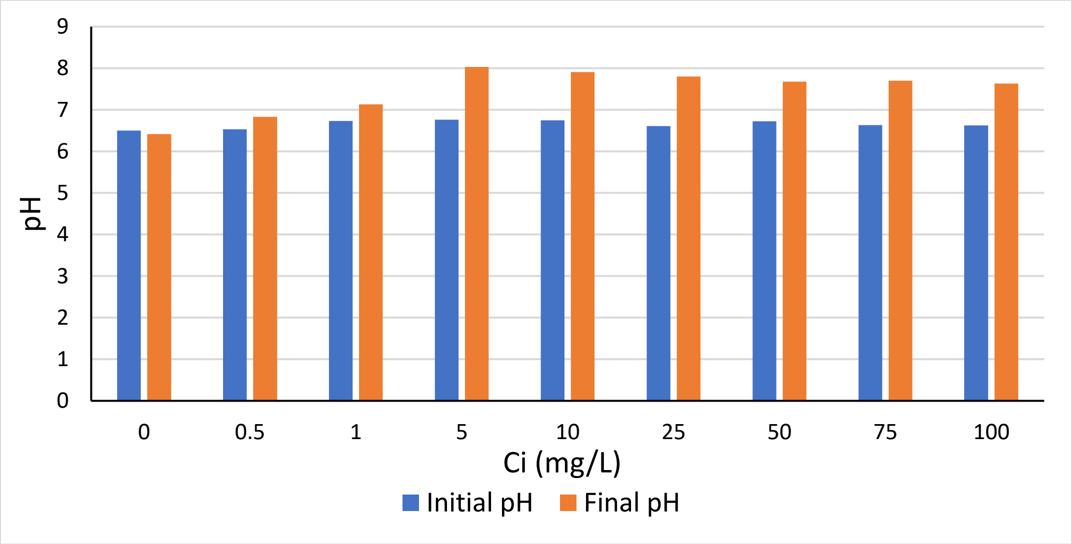

Figure A.39. Initial and final pH of Ca modified Biochar Now (granular particle size) for adsorption isotherm experiment.

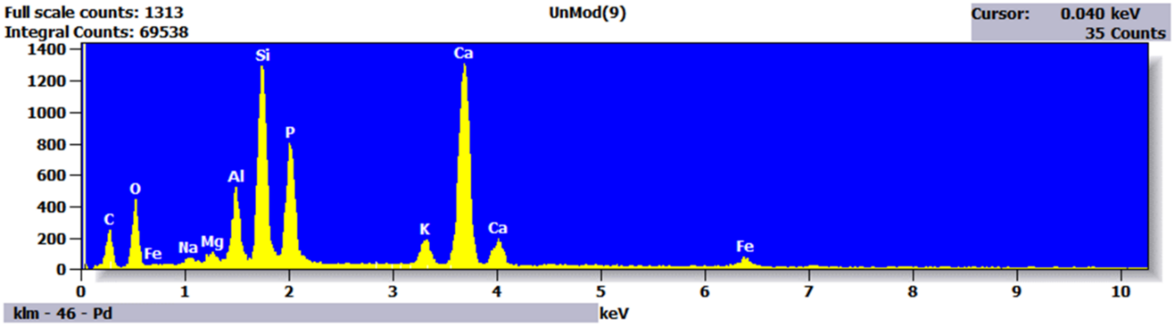

Figure A.40. Spectra graph of unmodified-biochar from SEM analysis; corresponds with Table 8 in Chapter 2.

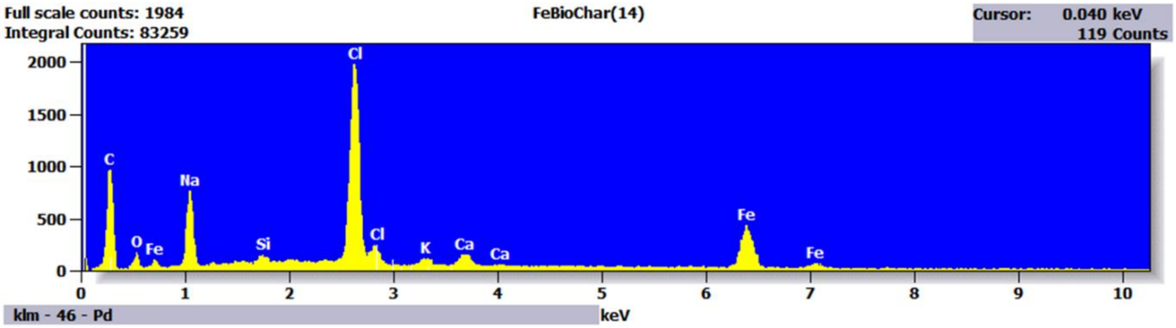

Figure A.41. Spectra graph of 4% Fe-biochar from SEM analysis; corresponds with Table 9 in Chapter 2.

Appendix B. Supplemental Tables and Figures for Chapter 3

Table B.12. Anion analysis for 4% Fe-modified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Bromide	Chloride	Fluoride	Nitrate-N	Nitrite-N	O-Phosphate -P	Sulfate	PORT
21-Jul-22	A1	< 0.10	240	< 0.10	0.2	< 0.10	< 0.10	130	Influent
21-Jul-22	A2	< 0.10	70	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
21-Jul-22	A5	< 0.10	87	< 0.10	< 0.10	< 0.10	< 0.10	43	Effluent
21-Jul-22	A6	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
22-Jul-22	A7	< 0.10	170	< 0.10	< 0.10	< 0.10	< 0.10	130	Influent
22-Jul-22	A8	< 0.10	83	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
22-Jul-22	A9	< 0.10	140	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
22-Jul-22	A10	< 0.10	130	0.16	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A11	< 0.10	130	< 0.10	0.12	< 0.10	< 0.10	120	Influent
23-Jul-22	A12	< 0.10	89	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
23-Jul-22	A13	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A14	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A15	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.20	BLANK
23-Jul-22	A16	< 0.10	74	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
23-Jul-22	A17	< 0.10	74	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
23-Jul-22	A18	< 0.10	120	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A19	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent

Table B.13. Metal analysis for 4% Fe-modified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	ID	Ba	Cd	Ca	Cr	Co	Cu	Fe	Mg	Mn	Mo	Ni	K	Na	V	Zn	As	PORT
21-Jul-22	C1	0.11	< 0.02	82	< 0.05	< 0.01	< 0.02	10	19	0.36	< 0.25	< 0.05	4.3	12	< 0.02	< 0.02		Influent
21-Jul-22	C2	0.11	< 0.02	80	< 0.05	< 0.01	< 0.02	9.8	18	0.35	< 0.25	< 0.05	4.2	12	< 0.02	< 0.02		Influent
21-Jul-22	C5	0.074	< 0.02	78	< 0.05	< 0.01	< 0.02	< 0.10	18	0.38	< 0.25	< 0.05	5.8	140	< 0.02	< 0.02		Effluent
21-Jul-22	C6	0.072	< 0.02	74	< 0.05	< 0.01	< 0.02	< 0.10	17	0.36	< 0.25	< 0.05	5.6	140	< 0.02	< 0.02		Effluent
22-Jul-22	C7	0.11	< 0.02	77	< 0.05	< 0.01	< 0.02	10	18	0.37	< 0.25	< 0.05	4.1	12	< 0.02	< 0.02		Influent
22-Jul-22	C8	0.11	< 0.02	74	< 0.05	< 0.01	< 0.02	9.8	17	0.35	< 0.25	< 0.05	4	11	< 0.02	< 0.02		Influent
22-Jul-22	C9	0.071	< 0.02	76	< 0.05	< 0.01	< 0.02	< 0.10	17	0.37	< 0.25	< 0.05	6.2	130	< 0.02	< 0.02		Effluent
22-Jul-22	C10	0.073	< 0.02	73	< 0.05	< 0.01	< 0.02	< 0.10	17	0.37	< 0.25	< 0.05	6.1	130	< 0.02	< 0.02		Effluent
23-Jul-22	C11	0.11	< 0.02	79	< 0.05	< 0.01	< 0.02	10	18	0.39	< 0.25	< 0.05	4.3	12	< 0.02	< 0.02	< 1.0	Influent
23-Jul-22	C12	0.11	< 0.02	78	< 0.05	< 0.01	< 0.02	10	18	0.38	< 0.25	< 0.05	4.1	12	< 0.02	< 0.02	< 1.0	Influent

Table B.13. Continued.

23-Jul-22	C13	0.079	< 0.02	77	< 0.05	< 0.01	< 0.02	< 0.10	18	0.42	< 0.25	< 0.05	6.7	120	< 0.02	< 0.02	< 1.0	Effluent
23-Jul-22	C14	0.085	< 0.02	77	< 0.05	< 0.01	< 0.02	< 0.10	18	0.43	< 0.25	< 0.05	6.6	120	< 0.02	< 0.02	< 1.0	Effluent
23-Jul-22	C15	< 0.020	< 0.02	< 0.10	< 0.05	< 0.01	< 0.02	< 0.10	< 0.05	< 0.005	< 0.25	< 0.05	< 1.0	< 10	< 0.02	< 0.02		BLANK
23-Jul-22	C16	0.11	< 0.02	77	< 0.05	< 0.01	< 0.02	10	18	0.37	< 0.25	< 0.05	4.1	12	< 0.02	< 0.02		Influent
23-Jul-22	C17	0.11	< 0.02	74	< 0.05	< 0.01	< 0.02	9.7	17	0.35	< 0.25	< 0.05	4	11	< 0.02	< 0.02		Influent
23-Jul-22	C18	0.075	< 0.02	75	< 0.05	< 0.01	< 0.02	0.29	17	0.4	< 0.25	< 0.05	6	120	< 0.02	< 0.02		Effluent
23-Jul-22	C19	0.075	< 0.02	74	< 0.05	< 0.01	< 0.02	0.29	17	0.4	< 0.25	< 0.05	6.1	130	< 0.02	< 0.02		Effluent

Table B.14. Total P analysis for 4% Fe-modified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Total Phosphorus	PORT
21-Jul-22	T1	0.16	Influent
21-Jul-22	T2	0.21	Influent
21-Jul-22	T5	0.027	Effluent
21-Jul-22	T6	0.031	Effluent
22-Jul-22	T7	0.16	Influent
22-Jul-22	T8	0.16	Influent
22-Jul-22	T9	0.015	Effluent
22-Jul-22	T10	0.016	Effluent
23-Jul-22	T11	0.16	Influent
23-Jul-22	T12	0.17	Influent
23-Jul-22	T13	0.02	Effluent
23-Jul-22	T14	0.012	Effluent
23-Jul-22	T15	0.012	BLANK
23-Jul-22	T16	0.15	Influent
23-Jul-22	T17	0.16	Influent
23-Jul-22	T18	0.016	Effluent
23-Jul-22	T19	0.015	Effluent

Table B.15. Ortho-P analysis for 4% Fe-modified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Ortho Phosphorus	PORT
21-Jul-22	O1	0.1	Influent
21-Jul-22	O2	0.096	Influent
21-Jul-22	O3	< 0.0060	Contact
21-Jul-22	O4	< 0.0060	Contact
21-Jul-22	O5	0.04	Effluent
21-Jul-22	O6	0.0067	Effluent
22-Jul-22	O7	0.1	Influent
22-Jul-22	O8	0.11	Influent
22-Jul-22	O9	< 0.0060	Contact
22-Jul-22	O10	< 0.0060	Contact
22-Jul-22	O11	< 0.0060	Effluent
22-Jul-22	O12	< 0.0060	Effluent
23-Jul-22	O13	0.12	Influent
23-Jul-22	O14	0.11	Influent
23-Jul-22	O15	< 0.0060	Contact
23-Jul-22	O16	< 0.0060	Contact
23-Jul-22	O17	< 0.0060	Effluent

Table B.16. Nitrogen and Ammonia analysis for 4% Fe-modified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Ammonia - N	Nitrate-N + Nitrite-N	PORT
21-Jul-22	N1	1.9	< 0.10	Influent
21-Jul-22	N2	2.1	< 0.10	Influent
21-Jul-22	N5	2.1	< 0.10	Effluent
21-Jul-22	N6	2.2	< 0.10	Effluent
22-Jul-22	N7	2	< 0.10	Influent
22-Jul-22	N8	2.1	< 0.10	Influent
22-Jul-22	N9	2.2	120	Effluent
22-Jul-22	N10	2.2	140	Effluent
23-Jul-22	N11	2.2	< 0.10	Influent
23-Jul-22	N12	2.1	< 0.10	Influent
23-Jul-22	N13	2.3	0.13	Effluent
23-Jul-22	N14	2.2	< 0.10	Effluent
23-Jul-22	N15	< 0.10	< 0.10	BLANK
23-Jul-22	N16	2.1	< 0.10	Influent
23-Jul-22	N17	2.1	< 0.10	Influent
23-Jul-22	N18	2.2	< 0.10	Effluent
23-Jul-22	N19	2.2	< 0.10	Effluent

Table B.17. Anion analysis for unmodified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Bromide	Chloride	Fluoride	Nitrate	Nitrite	O-Phosphate P	Sulfate	PORT
21-Jul-22	A1	< 0.10	240	< 0.10	0.2	< 0.10	< 0.10	130	Influent
21-Jul-22	A2	< 0.10	70	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
21-Jul-22	A5	< 0.10	87	< 0.10	< 0.10	< 0.10	< 0.10	43	Effluent
21-Jul-22	A6	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
22-Jul-22	A7	< 0.10	170	< 0.10	< 0.10	< 0.10	< 0.10	130	Influent
22-Jul-22	A8	< 0.10	83	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
22-Jul-22	A9	< 0.10	140	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
22-Jul-22	A10	< 0.10	130	0.16	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A11	< 0.10	130	< 0.10	0.12	< 0.10	< 0.10	120	Influent
23-Jul-22	A12	< 0.10	89	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
23-Jul-22	A13	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A14	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A15	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.20	BLANK
23-Jul-22	A16	< 0.10	74	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
23-Jul-22	A17	< 0.10	74	< 0.10	< 0.10	< 0.10	< 0.10	120	Influent
23-Jul-22	A18	< 0.10	120	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent
23-Jul-22	A19	< 0.10	130	< 0.10	< 0.10	< 0.10	< 0.10	120	Effluent

Table B.18. Metal analysis for unmodified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	ID	Ba	Cd	Ca	Cr	Co	Cu	Fe	Mg	Mn	Mo	Ni	K	Na	V	Zn	PORT
25-Jul-22	C1	0.09	< 0.02	100	< 0.05	< 0.010	< 0.02	0.16	19	0.4	< 0.25	< 0.05	5	120	< 0.02	< 0.02	Influent
25-Jul-22	C2	0.13	< 0.02	100	< 0.05	< 0.010	< 0.02	5.2	19	0.4	< 0.25	< 0.05	4	11	< 0.02	< 0.02	Influent
25-Jul-22	C3	0.14	< 0.02	110	< 0.05	0.011	< 0.02	5.6	21	0.4	< 0.25	< 0.05	4	12	< 0.02	< 0.02	Influent
25-Jul-22	C28	0.08	< 0.02	100	< 0.05	< 0.010	< 0.02	< 0.10	20	0.4	< 0.25	< 0.05	5	120	< 0.02	< 0.02	Effluent
26-Jul-22	C20	0.16	< 0.02	140	< 0.05	< 0.010	< 0.02	2.8	24	0.4	< 0.25	< 0.05	4	11	< 0.02	< 0.02	Influent
26-Jul-22	C21	0.16	< 0.02	140	< 0.05	< 0.010	< 0.02	2.1	24	0.4	< 0.25	< 0.05	4	11	< 0.02	< 0.02	Influent
26-Jul-22	C22	0.1	< 0.02	120	< 0.05	< 0.010	< 0.02	< 0.10	22	0.4	< 0.25	< 0.05	5	100	< 0.02	< 0.02	Effluent
26-Jul-22	C23	0.1	< 0.02	120	< 0.05	< 0.010	< 0.02	< 0.10	22	0.4	< 0.25	< 0.05	5	110	< 0.02	< 0.02	Effluent
26-Jul-22	C24	0.15	< 0.02	140	< 0.05	< 0.010	< 0.02	2.9	23	0.3	< 0.25	< 0.05	3	11	< 0.02	< 0.02	Influent
26-Jul-22	C25	0.15	< 0.02	140	< 0.05	< 0.010	< 0.02	3.2	24	0.3	< 0.25	< 0.05	4	11	< 0.02	< 0.02	Influent
26-Jul-22	C26	0.11	< 0.02	140	< 0.05	< 0.010	< 0.02	0.1	24	0.3	< 0.25	< 0.05	5	120	< 0.02	< 0.02	Effluent
26-Jul-22	C27	0.11	< 0.02	140	< 0.05	< 0.010	< 0.02	< 0.10	23	0.3	< 0.25	< 0.05	5	120	< 0.02	< 0.02	Effluent

Table B.19. Total P analysis for unmodified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Total Phosphorus	PORT
25-Jul-22	T1	0.11	Influent
25-Jul-22	T28	0.011	Effluent
25-Jul-22	T29	0.011	Effluent
25-Jul-22	T30	0.11	Influent
26-Jul-22	T20	0.071	Influent
26-Jul-22	T21	0.072	Influent
26-Jul-22	T22	0.025	Effluent
26-Jul-22	T23	0.023	Effluent
26-Jul-22	T24	0.093	Influent
26-Jul-22	T25	0.09	Influent
26-Jul-22	T26	0.066	Effluent
26-Jul-22	T27	0.012	Effluent

Table B.20. Ortho-P analysis for unmodified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Ortho Phosphorus	PORT
25-Jul-22	O8	< 0.0060	Effluent
25-Jul-22	O9	< 0.0060	Effluent
25-Jul-22	O10	< 0.0060	Contact
25-Jul-22	O11	< 0.0060	Contact
25-Jul-22	O12	0.071	Influent
25-Jul-22	O13	0.074	Influent
26-Jul-22	O1	< 0.0060	Effluent
26-Jul-22	O2	0.035	Influent
26-Jul-22	O3	0.063	Influent
26-Jul-22	O4	< 0.0060	Contact
26-Jul-22	O5	< 0.0060	Contact
26-Jul-22	O6	< 0.0060	Effluent
26-Jul-22	O7	< 0.0060	Effluent
26-Jul-22	O26	0.023	Influent
26-Jul-22	O27	0.027	Influent
26-Jul-22	O28	< 0.0060	Contact
26-Jul-22	O29	0.0096	Contact
26-Jul-22	O30	< 0.0060	Effluent

Table B.21. Nitrogen and Ammonia analysis for unmodified Pacific Biochar water samples, reporting units are (mg/L).

Collection Date	Sample ID	Ammonia - N	Nitrate-N + Nitrite-N	PORT
25-Jul-22	N1	1.6	4.7	Influent
25-Jul-22	N2	1.5	64	Effluent
25-Jul-22	N3	2.8	44	Effluent
25-Jul-22	N28	2.2	4.7	Influent
26-Jul-22	N20	1.9	11	Influent
26-Jul-22	N21	1.6	11	Influent
26-Jul-22	N22	1.8	8.7	Effluent
26-Jul-22	N23	1.7	8.6	Effluent
26-Jul-22	N24	1.9	12	Influent
26-Jul-22	N25	1.7	13	Influent
26-Jul-22	N26	1.5	13	Effluent
26-Jul-22	N27	1.4	14	Effluent

Table B.22. Percent phosphorus removed during reactive filtration with modified and unmodified biochars.

Treatment	Total P Removed	Ortho-P Removed
4% Fe-modified Pacific Biochar	89%	92%
Unmodified Pacific Biochar	73%	94%

Table B.23. Additional chemical profile of AB pilot study soils at 3 sampling sites.

Sample ID	Depth (cm)	T Ca %	T Mg %	T S %	T Zn (mg/L)	T Mn (mg/L)	T Cu (mg/L)	T B (mg/L)	T Mo (mg/L)
Site 1	0-15	0.524	0.59	0.057	62	134	33.5	20.3	0.29
Site 1	15-30	0.711	0.75	0.067	70	155	32.9	27	0.09
Site 1	30-46	0.722	0.74	0.125	56	122	26.2	26.3	0.53
Site 1	46-61	0.598	0.71	0.102	58	100	20.8	22.1	0.22
Site 1	61-92	0.526	0.68	0.076	55	115	22.7	22.2	0.36
Site 1	92-122	0.567	0.7	0.124	65	102	23.8	23.4	0.52
Site 1	122-152	2.237	1.38	0.061	62	151	17.3	24.6	0.06
Site 2	0-15	0.479	0.62	0.057	62	149	29.4	23.4	0.3
Site 2	15-30	0.416	0.54	0.044	45	121	20.5	20.2	0.32
Site 2	30-46	0.508	0.53	0.064	35	121	16.6	19	0.27
Site 2	46-61	0.33	0.35	0.019	25	126	5.9	13.7	0.07
Site 2	61-92	0.373	0.43	0.026	33	158	7.6	16.7	0.11
Site 2	92-122	0.501	0.56	0.092	47	143	17.5	20.8	0.42
Site 3	0-15	0.218	0.42	0.034	44	127	23.8	18.8	0.36
Site 3	15-30	0.264	0.49	0.047	43	126	19.9	21.5	0.33
Site 3	30-46	0.294	0.47	0.069	36	105	20.2	20	0.53
Site 3	46-61	0.376	0.61	0.126	43	142	25.5	24.3	1.04
Site 3	61-92	0.282	0.62	0.064	50	123	17.8	21.7	0.36
Site 3	92-122	0.211	0.5	0.027	38	70	10	15.6	0.13

Table B.24. Total digestion with dry ash method of 4% Fe-modified biochar and unmodified biochar from AB pilot study. Reported values are sample means from triplicate samples; reporting units are (mg/kg).

Treatment	**Al**	**Ca**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**P**
Unused UnMod	1853	10238	1928	6553	1606	343	929	725
Used UnMod	3136	15732	61945	2137	2204	446	1454	1109
Unused 4% Fe	2213	6835	25513	4407	1316	326	14104	614
Used 4% Fe	3116	7466	71020	1754	1645	398	1406	996