Evaluation of Pinyon-Juniper Biochar as a Media Amendment for Stormwater Treatment

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Executive Summary

Stormwater runoff affects the water quality of lakes, rivers and streams around the world, but many stormwater best management practices (BMPs) do not achieve adequate pollutant reductions, especially when receiving waters are very clean. Biochar, a product of controlled combustion under low oxygen conditions, has been used in agriculture for the improvement of soil fertility, water-holding capacity and nutrient retention. Recently, the Nevada Division of Forestry (NDF) has developed a biochar product from forest clearing and thinning of pinyon-juniper (P-J) landscapes. That biochar has been used on a trial basis to improve soil moistureholding capacity of rain-garden soils in the Tahoe Basin, and its physicochemical characteristics suggests that it may also improve the sequestration of nutrients from stormwater runoff. This study evaluated nutrient adsorption characteristics of NDF biochar using batch equilibrium tests and column experiments with mixtures of Washoe washed sand (WWS) and the P-J biochar. Results showed that biochar adsorption of dissolved inorganic nitrogen and phosphorus was most effective with the smaller size classes (125–250 microns) versus larger size classes (500–4000 μm). Batch equilibrium tests demonstrated significant improvements in phosphorus and nitrate removal with P-J biochar compared to WWS, and modest adsorption of ammonium relative to WWS, but also some leaching of phosphorus from biochar. Subsequent column adsorption-desorption experiments using a 30% biochar mixture in WWS with simulated stormwater showed a net retention of 11% for ammonium-N, 1.5% for orthophosphate-P, and negligible nitrate-N retention. Many studies on adsorptive media simply conduct batch adsorption tests on the media of interest, but we found that column adsorption-desorption experiments improved our interpretation of results and yielded better estimates of net nutrient retention. The 30% P-J biochar with WWS mixture retained 4.8 g m⁻³ dissolved inorganic phosphorus and 43 g m⁻³ of dissolved inorganic nitrogen. Subsequent batch equilibrium tests with iron-amended P-J biochar showed a much higher capacity for P adsorption than with P-J biochar, but also some potential ammonium leaching.

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Introduction

Stormwater runoff from urban and suburban areas continues to be a major source of pollution to receiving waters (U.S. EPA, 1999), despite point discharge permitting requirements established by the National Pollutant Discharge Elimination System (NPDES) in 1972. That is because widely distributed non-point sources of pollution, like stormwater runoff, are inherently more difficult to control than the typical point sources of pollution from industrial, agricultural or wastewater discharges addressed by NPDES.

The Impaired Waters and Total Maximum Daily Load (TMDL) Program was established in 1992 as part of the Clean Water Act to address cases where water bodies do not meet applicable water quality standards (WQS) for designated beneficial uses, such as recreation, water supply, aquatic life, or agriculture. The development of a TMDL is required for 303(d) listed impaired waters to identify all sources of point and non-point pollution within a watershed (source assessment), determine appropriate water quality targets to restore or maintain beneficial uses, and then establish load allocations to meet those targets.

Designated an Outstanding National Resource Water by California and as a water of extraordinary ecological value by Nevada (LRWQCB and NDEP, 2010), Lake Tahoe is afforded the highest level of protection, with no degradation allowed under the Clean Water Act (CWA) of 1972. Due to its long-term clarity loss the lake has qualified as an impaired water body under CWA section 303(d). The Lake Tahoe TMDL program was jointly developed by California and Nevada and was adopted in 2011 to address the nutrient and fine sediment loading reductions required to achieve numeric standards for open-water transparency (lake clarity) and nearshore clarity (turbidity).

Implementation of a TMDL plan to attain established targets can be difficult, however, when traditional stormwater best management practices (BMPs) do not

provide a sufficient level of treatment. This can be the case in watersheds that require extremely high levels of treatment prior to discharge to relatively pristine receiving waters, or simply because locations suitable for treatment facilities are limited and so higher demands are placed on the few sites available for installing structural BMPs. Urban areas in the Lake Tahoe basin contribute a significant portion of total nutrient and fine sediment loadings to the lake (LRWQCB and NDEP, 2010). Existing technology and available locations for BMP installation may not be sufficient to reverse the declining clarity in mid-lake and nearshore areas. Both the Tahoe TMDL and the Lake Tahoe Basin Science Plan (Hymanson and Collopy, 2009) have highlighted a need to identify new approaches that would enhance currently used BMPs and to develop and test advanced technologies.

Infiltrating stormwater through alternative substrate materials and amended soils could improve BMP performance by enhancing infiltration properties, nutrient and sediment removal characteristics, moisture retention capacity, and vegetation vigor. This project was designed to evaluate the nutrient removal characteristics of pinyon-juniper biochar as a potential soil amendment. If proven effective, these biochar amendment practices would represent a low-cost approach to improve BMP performance, extend infiltration basin life cycles, and provide a useful retrofit option for BMP maintenance or restoration.

Background

Nutrient and sediment loadings generally increase with urbanization and the amount of associated impervious area (U.S. EPA, 1999). Principal nutrients of concern are nitrogen and phosphorus, which have been shown to increase algal production that leads to eutrophication and to depleted oxygen in aquatic systems and severe anoxia in some cases (Carpenter et al., 1998). Chemical species of nutrients are commonly designated by groups that distinguish between their dissolved and particulate forms. Analysis for total phosphorus represents both the particulate and the dissolved forms. While dissolved phosphorus includes both

inorganic and organic fractions, it is the inorganic (orthophosphate) fraction that is most commonly measured since it is readily available for algae growth. Analysis of soluble reactive phosphorus (SRP) is the typical analytical technique used to estimate orthophosphate concentrations. Soluble is operationally defined, in most cases, as that which passes through a 0.45 µm membrane filter. Nitrogen is also separated into particulate and soluble fractions by filtration. The dissolved inorganic nitrogen (DIN) fraction is represented by the combined concentrations of ammonium and nitrate (plus nitrite) ions, each analyzed separately. Total Kjeldahl nitrogen (TKN) analysis represents the particulate nitrogen fraction plus any dissolved ammonia. Total nitrogen is typically estimated as the sum of TKN plus nitrate and nitrite.

Both nitrogen and phosphorus composition and concentrations vary in stormwater runoff, based on land use types and hydrologic conditions (Flint and Davis, 2007; Li and Davis, 2014). On average, residential runoff to receiving waters is estimated to contribute 10–420 lbs/acre-yr of total suspended solids (TSS), 0.04–1 lbs/acre-yr of total phosphorus (TP), 0.03–4.2 lbs/acre-yr of nitrogen from ammonia, and 0.02–0.80 lbs/acre-yr of nitrogen from nitrate and nitrite (NO₃-N + NO₂-N), as well as loadings from many other contaminants (U.S. EPA, 1999).

Low impact development (LID) systems and practices that use or mimic natural processes are aimed at reducing runoff volumes and concentrations through infiltration, evapotranspiration, vegetative uptake, chemical adsorption, or by capture and beneficial use of stormwater (U.S. EPA, 2018). The LID approach focuses on reducing runoff volumes and peak flows by disconnecting impervious surface areas and increasing flow-paths, while preserving some of the more natural landscape characteristics and topography in an effort to reduce downstream pollution loading (Davis, 2008). Subsequent to these efforts, however, structural BMPs are often needed to help reduce pollutant concentrations prior to discharge into receiving waters.

Various types of structural BMPs are commonly used to mitigate the effects of increased development and land use within urbanized areas (Fry and Maxwell, 2017; Heyvaert et al., 2006; U.S. EPA, 1999). These configurations can include detention basins, retention ponds, media filtration or soil infiltration, treatment wetlands and bioretention systems. While each stormwater BMP may differ in treatment type or mechanisms of treatment, the overall treatment objective is to reduce urban stormwater runoff volumes or peak flows and to mitigate the associated contaminants commonly found in runoff flows.

Stormwater bioretention BMPs attempt to apply a combination of processes for more effective stormwater treatment. Traditional bioretention design has been shown to reduce TSS, TP, Cu, Pb, Zn, and nitrate-nitrogen (NO₃-N) as much as 47%, 76%, 57%, 83%, 62%, and 83% respectively (Davis, 2007). The cumulative areal footprint of a stormwater bioretention BMP generally accounts for 4–5% of the total drainage area (Hsieh et al., 2007). Currently, much of the material utilized in the construction of bioretention systems consists of either sandy-loam or loamy-sand amended with an organic layer such as topsoil, peat moss, or compost (Davis, 2008; Tian et al., 2016). The focus of this study is biochar, which could serve as an alternative organic material.

Pollutant removal in treatment areas occurs through a combination of physical and chemical mechanisms such as sedimentation, filtration, adsorption, ion exchange, precipitation, and biological uptake (Hatt et al., 2009; Hsieh et al., 2007; Li and Davis, 2014). Sedimentation is the primary pathway for removal of inorganic particulates, such as bound phosphorus, whereas sorption and redox processes typically regulate the amount of soluble constituents. Sorption mechanisms are kinetically driven reactions that have characteristic reaction times (Limousin et al., 2007), which are generally described mathematically through adsorption isotherm models (Appendix A).

Media Filtration and Engineered Adsorbents

Media filtration is designed to capture particles and remove contaminants through surface adsorption. Austin sand filters are a common type of BMP used around the country for stormwater clarification and pollutant removal. Washoe washed sand is an example of locally sourced septic sand that has been used for stormwater treatment within the Tahoe Basin (Russell Wigart, pers. comm.). The grain size of filtration media affects hydraulic condcutivity, where coarser particles increase flow-through rates while the finer grain sizes decrease flow-through rates but are more effective at removing suspended sediments.

Some soil types are effective at contaminant sorption, while others are less effective. Because sand is a relatively inert silica-type material, for example, the removal of soluble nutrients such as nitrate and phosphorus is usually minimal. In some cases the concentrations of soluble constituents like nitrate can increase from media leaching during treatment (Jiang et al., 2015). Other types of media materials incorporate minerals like bauxite, dolomite and zeolite that have naturally high concentrations of aluminum, iron, calcium or magnesium, which can increase the surface adsorption of phosphorus and similar constituents (Vohla et al., 2011). Engineered materials that help increase media adsorptive capacity have been gaining more attention recently.

Engineered adsorbents often are proprietary blends designed for treatment of specific contaminants. These proprietary blends can be a complex mixture of natural materials or modified substances (Vohla et al., 2011; Duranceau and Biscardi, 2015), but are usually derived from iron or aluminum (e.g., Bauxol), or they are mineral clays high in magnesium and calcium that are treated at extremely high temperatures (e.g., Filtralite), or they can include mixtures of sand, clay, lime and other materials like tire crumbs (e.g., Bold and Gold). The main function of engineered absorbents is to: (1) increase surface area, thus creating more available binding sites; and (2) add elements that bond strongly with contaminants of

concern (Yan et al., 2016). While many of these commercially available products show high removal efficiencies (Duranceau and Biscardi, 2015; Vohla et al., 2011), they are costly to implement on a large scale and may only target one or two specific pollutants. For this reason, there is increasing interest in the potential efficacy of biochar as an amendment to improve soils and remove contaminants.

Biochar

Biochar is an organic carbon that results from the incomplete combustion of organic feedstocks under low oxygen conditions (Morales et al., 2015). It is produced through partial thermal degradation (pyrolysis) of the organic material combusted at temperatures between 350–800°C (Schmidt, 2014). The resulting product is a highly recalcitrant material that resembles activated carbon with a high porosity, increased surface area, and more ionic charge.

The physiochemical properties of biochar are influenced by feedstock type, overall production temperatures, and the highest treatment temperature applied, among other factors. Feedstock can consist of biological organic materials such as sugarcane, corn, or poultry waste, and forest trimmings such as pinyon pine (*Pinus monophylla*) or juniper (*Juniperus osteosperma*). Production temperatures create unique physicochemical properties in the final product (Figure 1), where high temperature biochars develop a more uniform molecular structure while low temperature biochars exhibit properties more reminiscent of the non-combusted organic matter. Chemical composition is largely a function of feedstock type, which affects the functional groups present and overall surface charge.

Resulting changes in the physicochemical properties yield chemical differences in pH, cation exchange capacity (CEC), and anion exchange capacity (AEC), along with structural differences such as increased porosity and surface area (Gray et al., 2014; Hollister et al., 2013; Silber et al., 2010). Surface area was shown to increase by more than 30 times when comparing biochar production at temperatures between 450°C and 600°C (Sun et al., 2014). Heterogeneity of both surface area and average

pore size showed medium to strong dependence on both feedstock types and pyrolysis temperatures (Zhao et al., 2013). Increasing production temperature increases total carbon content (Freitas et al., 1997; Sun et al., 2014). Biochars derived from ligno-cellulosic feedstock produced at high temperatures ($\geq 600^{\circ}$ C) tend to possess low nutrient contents (Gul et al., 2015), while biochars produced at lower temperatures may have increased oxygen-containing functional groups, such as carboxylates, which contribute to ammonium adsorption (Takaya et al., 2016).

The unique physicochemical properties of biochar have long been recognized for enhancing soil properties. Addition of biochar to agricultural soils has contributed to improved nutrient-holding capacity for elements such as phosphorus, nitrogen, calcium and potassium, as well as higher soil moisture-holding capacity (Glaser et al., 2001). Furthermore, biochar amended soils have been shown to improve cation exchange capacity (CEC) (Hollister et al., 2013; Libra et al., 2014; Paramashivam et al., 2016; Silber et al., 2010; Takaya et al., 2016; Zhao et al., 2013), and to decrease nutrient leaching from amended soils (Dunisch et al., 2007; Knowles et al., 2011; Lehmann et al., 2003). These encouraging results from biochar used as an agricultural soil amendment have increased interest in using similar types of carbonized products for stormwater remediation purposes.

Biochar is especially promising for stormwater treatment because of its high potential adsorptive capacity due to increased microporosity and nanoporosity sites (Image 1C and D), which may enable small amounts of biochar to achieve significant pollutant retention (Ulrich et al., 2015). Adsorption of a chemical constituent onto an adsorbent surface can occur through numerous mechanisms such as chemical, electrostatic, or physical attraction. These mechanisms arise from chemical properties, such as relative abundance of iron and aluminum, from increased surface area, changes in redox chemistry, shifts in oxygen content, as well as carbonand oxygen-containing functional groups that influence N and P uptake. Feedstocks that produce low nutrient biochars may increase their nutrient adsorptive capacity and the retention of nutrients within stormwater such as NO₃-N, NH₄-N and orthophosphate (Gul and Whalen, 2016). It is unclear at this time, however, whether biochar amendments will be effective in overall adsorption of soluble nutrients while maintaining the important hydrologic characteristics of a stormwater treatment system.



Figure 1. Idealized biochar structure development as a function of treatment temperature (from Lehmann and Joseph, 2009). Depiction shows changes with increasing temperature: (a) increased proportion of aromatic carbon, highly disordered in amorphous mass; (b) growing sheets of conjugated aromatic carbon, turbostratically arranged; (c) structure becomes graphitic with order in the third dimension.

Currently the Nevada Division of Forestry has been working to develop a forest products industry that confers higher value on wood harvested from forest restoration of regionally overgrown and expanding pinyon-juniper (P-J) landscapes. Pyrolysis of pinyon pine and juniper from forest clearing and thinning practices reduces the volume of wood that otherwise would be burned on-site or chipped and left to decompose. The biochar they produce has been used as a soil amendment and a compost. It could also be useful for stormwater BMPs if nutrient and fine sediment retention characteristics were significantly enhanced by amending BMP soils or stormwater filtration media with P-J biochar. To date, however, no study has been completed on P-J biochar as a potential soil amendment for the reduction of nutrient concentrations from stormwater. In this study we tested the potential efficacy of biochar as a nutrient removal material that could be used to amend soils and compost or other media in stormwater basins or bioretention BMPs. Our objectives were to evaluate the nitrogen and phosphorus adsorption and desorption characteristics of biochar derived from pinyon pine and juniper tree waste. Laboratory tests consisted of batch equilibrium experiments and column experiments with dissolved inorganic phosphorus (as orthophosphate) and dissolved inorganic nitrogen (as nitrate and ammonium). The hypothesis was that:

- P-J biochar amended to washed sand, a common fill material in bioretention BMPs, would improve the removal of dissolved inorganic nutrients from aqueous solutions in the laboratory.
- The null hypothesis was no change in nutrient concentration of aqueous solutions in laboratory tests, conducted as one-sided tests in which the (desired) alternative hypothesis is a decrease in nutrient concentration.

Materials and Methods

Biochar and Sand Media Preparation

Biochar was provided by the Nevada Division of Forestry (NDF), as part of their P-J forestry reduction program. NDF produced the P-J biochar on-site within transportable metal kilns where pyrolysis occurred for 24 hours at temperature ranges estimated between 350–700 °C (Schmidt, 2014). The relative abundance of pinyon pine and juniper in the mixture was dependent on the proportions of those species being cleared. The raw biochar we obtained ranged in size from >63 μ m to <4000 μ m. It was separated for purposes of this study into four test-size categories by mechanical sieving after drying at 105°C to a constant weight. The dried material was placed on the top of a series of U.S.A. Standard Testing Sieves and covered. This sieve stack included from top to bottom a #5 (4mm), a #10 (2 mm), a #35 (500 μ m), a #60 (250 μ m), and a #120 (125 μ m), with a receiving pan at the bottom. The stack

was placed on a vibratory sieve shaker (model SS-10, Gilson Company Inc.) and sieving frequency was set to 8 with a run time of 10 minutes. Size separated material from each sieve batch was collected and stored in labeled Ziploc bags. Prior to use, each size class of biochar was repeatedly washed using 18.2 M Ω deionized water until the effluent was semi-transparent to transparent. This repeated washing rinsed any residual ash and fine suspended sediments from biochar samples (Figure 2).



Figure 2. Pinyon-juniper (P-J) biochar sieved to a size range of 250–500 μ m (a); and Washoe washed sand (WWS), as provided with a size range of 75–4750 μ m (b).

Washoe washed sand (WWS) was obtained locally from R.T. Donovan Company Inc. (Sparks, NV) and came pre-screened within a size range from 75–4750 µm (Lumos & Associates; Reno, NV). Because it is a double-washed, commercially available product, it was not necessary to wash prior to use (Figure 1). It was, however, oven dried in the laboratory at 105°C to a constant weight. Washoe washed sand is provided regionally as a septic sand, but due to its relatively high permeability and low reactivity it has also been used in stormwater filtration to remove fine particulates (Russell Wigart, pers. comm.). In our testing it served as a both a control material and as a base for media mixtures with biochar, which has high porosity and surface area (Figure 3) compared to sand.



Figure 3. Scanning electron microscopy (SEM) images showing the typical surface structure and porosity of PJ biochar particles in the size range class of 250–500 μ m. SEM's courtesy of Dr. Casey Schmidt and Curtis Robbins.

Adsorption Studies

Experiments were conducted using batch techniques and column tests to evaluate the sorption characteristics of soluble nutrients (orthophosphate, nitrate and ammonium) by both WWS and biochar. Batch experiments provided information on the effect of contact time, the effect of dose, and the identification of appropriate isotherm models to represent adsorption. Column tests were used to evaluate the nutrient retention characteristics and potential response to leaching under flowthrough conditions more representative of biochar field application.

Contact Time Tests

Initial tests were conducted on both WWS and P-J biochar (250–500 μ m) to determine an appropriate time interval for use in subsequent batch equilibrium experiments. These tests were run with orthophosphate in duplicate sample tubes (n=2) for each time interval at 0, 6, 12, 24, 36, 48, 60, and 72 hours. Two grams of adsorbent material were placed in 50 mL conical centrifuge tubes (Falcon) with 20 mL of phosphorus solution (200 mg P L⁻¹) added to each sample tube for a typical 1:10 ratio (Bhadha et al., 2012; Cucarella and Renman, 2009). The phosphorus solution was made from potassium phosphate monobasic (KH₂PO₄, Thermo Fisher) with lab-grade double-deionized water (DDW <18.2 MΩ). The tubes were then

placed on an end-over-end rotisserie (Labquake) and mixed continuously for the selected time intervals. Duplicate sample tubes were removed at each time interval, then screened through 0.45 µm nylon membrane filters (Magna, GVS Life Sciences) and analyzed colorimetrically for soluble reactive phosphorus, as described below.

Batch Adsorption Experiments

Laboratory N and P batch adsorption experiments were conducted on both adsorbent materials separately, in duplicate (n=2), using P-J biochar from each of the four sizes classifications obtained from sieving and the WWS as provided. These tests also used the 1:10 ratio of adsorbent to adsorbate solution (Bhadha et al., 2012; Cucarella and Renman, 2009), where two grams of either biochar or WWS were transferred into 50 mL plastic conical centrifuge tubes (Falcon) for each concentration tested, then 20 mL of nutrient solution were added to each centrifuge tube with the pre-weighed adsorbent material inside. Nutrient amounts were chosen to represent a range of stormwater runoff concentrations, using 0.00, 0.20, 0.50, 0.80, 1.0, 2.0, 5.0, and 8.0 mg L⁻¹ for P and equivalent concentrations for N. The solutions were prepared from reagent grade potassium nitrate (KNO₃, ThermoFisher Scientific), ammonium chloride (NH₄Cl, ThermoFisher Scientific) and potassium phosphate monobasic (KH₂PO₄, ThermoFisher Scientific) with lab-grade double-deionized water (DDW, <18.2 MΩ). Fresh solutions were prepared prior to each experiment.

The containers were sealed tightly and placed on a tube rotisserie (Figure 4), at 8 rpm and constant temperature for 24 hours with the WWS and for 96 hours with the P-J biochar. These times were selected based on the results from batch equilibrium tests discussed previously (Harmayani and Anwar, 2012). Blank samples were included to provide an estimate of leachable nutrients from the biochar and WWS, while high concentration samples were included to determine maximum potential adsorption capacity. Equilibrated solutions were filtered through 0.45 μ m nylon filters (Magna, GVS Life Sciences) and the nutrients solutes were analyzed colorimetrically via Rapid Flow Analyzer (RFA-300; Alpkem

Corporation Wilsonville, OR). Colorimetric analysis of the filtrate was conducted within 24 hours for soluble reactive phosphorus (SRP or orthophosphate-P) using EPA method 365.1, and within 24 hours for nitrate+nitrite as nitrogen ($[NO_3^-+NO_2^-]-N$) using EPA method 353.2. Filtrate samples for ammonia were preserved with 0.2 mL 18N H₂SO₄ per 50 mL and analyzed colorimetrically within 72 hours for ammonium as nitrogen (NH₄-N) using EPA method 350.1. Method detection limits were 0.002 mg/L for each of the soluble nutrients.

A second series of batch adsorption experiments were conducted for iron (Fe) impregnated P-J biochar obtained from Dr. Erik Bandala (pers. comm.). These tests were done in triplicate (n=3) with both Fe-amended and non-amended P-J biochar in the 250–500 μ m size class at 1:20 adsorbent to solution ratios. Nutrient adsorption tests included orthophosphate as P, nitrate as N, and ammonium as N. All nutrient concentration ranges, equilibrium times and methods used were identical to the methods described above for the 1:10 ratio experiments.



Figure 4. Batch adsorption solutions in end-over-end rotisseries (Labquake). Solutions were mixed in a 1:10 or 1:20 ratios of adsorbent to adsorbate, and equilibrated for 24 to 96 hours.

Column Experiments

Column tests were conducted with different ratios of BC-to-WWS by volume in triplicate (n=3) to investigate the adsorption and desorption behavior of test media for nitrate, orthophosphate and ammonium under flow-through conditions more characteristic of stormwater treatment.

Nine acrylic columns (60 cm length, 3.1 cm inner diameter) were fitted at each end with a #7 rubber stopper that had been bored for a glass tube (10 cm length, 4 mm inner diameter). These columns were each filled with media compositions to a total volume of 403 mL. The triplicate test compositions in these tubes consisted of 250–500 μ m size class BC mixed with WWS in ratios of 0% biochar (WWS control), 15% biochar, and 30% biochar. Material was placed over a bed of 4 mm borosilicate glass beads sandwiched between two Whatman glass fiber filters (GF/C, 1.2 μ m nominal pore size). Column compositions were added in 10 cm increments that were each lightly packed with a force of 1 newton. The final media fill in each column was topped with a GF/C filter and then glass wool occupying the remainder of the column headspace.

Peristaltic pumps (L/S Series, Cole-Parmer) were set at constant flow rates of approximately 1.5 mL/min (~2.0 mm/min column loading) and test solutions were continuously pumped vertically up through each column to create saturated flow (Figure 5). The column testing was conducted in three phases: leaching, adsorption and desorption. Inflow temperature, pH and ionic composition of the test solutions were all held constant during each phase of column testing.

Phase one consisted of material leaching, with 18.2 M Ω distilled-deionized water (DDW) buffered with a conductivity tracer of potassium chlorite (KCl) at approximately 395 μ S (±1 μ S) near neutral pH (7.2) and run continuously until an equilibrium concentration was obtained from each of the columns. The results of

this phase represented the amount of soluble nutrients present on adsorbent media that was initially susceptible to removal.

Phase two consisted of nutrient adsorption from a synthetic stormwater, with a solution of 2.0 mg L⁻¹ each of SRP-P, NO₃-N and NH₄-N added. The KCl conductivity tracer was increased slightly to 430 μ S (±2 μ S) and was near neutral pH (7.2). The nutrient, specific conductivity and pH of this synthetic stormwater are similar to median Lake Tahoe basin stormwater runoff characteristics (Coats et al., 2008; Rios et al., 2014). Adsorption was run continuously until full concentration breakthrough was measured. Time profiles of adsorption show both an initial concentration breakthrough, determined as the time at which increases of nutrient levels first appear within the effluent solution, and the time at which adsorbent media capacity has been reached, where influent concentration equals effluent concentration. At that time, all binding sites were considered occupied and the total adsorbed amounts represented media sorption capacity for each nutrient.

Desorption testing occurred in the third and final phase, where the pumped solution was returned to DDW with a 395 (\pm 1) μ S KCl buffer near neutral pH (7.2) and no nutrients. Desorption determined the percentage of chemical constituent weakly bound to adsorbent media and subsequently released as buffered DDW was flushed through the system.

Samples were taken at 2, 4, 8, 16, 24, 36, 48 hours, and then at every 24-hour interval thereafter; a pattern used for each phase of these experiments. Sample volumes collected were weighed and recorded, assuming grams of mass were equivalent to milliliters of volume, followed by conductivity measurements (Oakton Ion 700) and nutrient analyses. Final filtration, sample preservation, and analytical methods were the same as applied with the batch adsorption experiments.



Figure 5. Column layout for experiment. From right to left, column material mixtures in triplicates include 0% biochar, then 15% biochar, and then 30% biochar by volume in Washoe washed sand. Flows were directed from bottom up and sample effluent was siphoned off the top into pre-tared gallon jugs.

Data Analysis

Estimates of mass removal for orthophosphate-P (as SRP), nitrate-N and ammonium-N solutes were calculated with Equation 1 from results of the batch equilibrium tests.

$$q_e = \frac{\left(C_i - C_{eq}\right) \cdot V}{m} \tag{1}$$

where:

 q_e = solute adsorbed per unit weight of test media at equilibrium (mg kg⁻¹)

 C_i = initial nutrient concentration in solution (mg L⁻¹)

 C_{eq} = equilibrium concentration of solute in contact with the media (mg L⁻¹)

V = volume of adsorbate solution (L)

m = mass of adsorbent test media (g)

Percent nutrient removals were calculated from with Equation 2 from the batch test data.

$$\% Removal = \frac{(C_i - C_{eq})}{C_i} \cdot 100$$
(2)

Isotherm Models

Adsorption isotherms as used here are graphical representations showing the distribution of ions in liquid phase (adsorbent) versus solid phase (adsorbate). This relationship is quantitatively described by an isotherm equation that statistically models the batch adsorption data (see Appendix A for more detail).

The equilibrium data were plotted with adsorption per unit media mass (q_e, mg kg⁻¹) as the dependent variable and with equilibrium concentration in solution (C_{eq}, mg L⁻¹) as the independent variable. Three equations are typically applied to describe the type of solid-liquid adsorption characteristics addressed by this study. These are the linear, the Freundlich, and the Langmuir isotherm equations. All three isotherm equations were tested to determine which model best represents the experimental P-J biochar and WWS batch equilibrium data.

Of these three models the linear isotherm equation is the simplest representation, where the amount of adsorption onto media is directly proportional to the concentration of the solute (Equation 3).

$$q_e = K_d \cdot C_{eq} \tag{3}$$

where:

 q_e = solute adsorbed per unit weight of test media at equilibrium (mg kg⁻¹)

 K_d = distribution coefficient (mg/kg), or adsorption proportionality constant C_{eq} = equilibrium concentration of solute in contact with the media (mg L⁻¹)

Both the Langmuir and Freundlich models follow non-linear curves. Due to the nonlinearity of these models, each model is linearized for graphing and analysis. The Langmuir model (Equation 4) assumes monolayer adsorption and is represented after a 1/x transformation, while the empirically-based Freundlich model (Equation 5) is represented after a logarithmic transformation. The data are then applied to these linearized equations and Pearson correlation coefficients (r²) are derived to inform selection of the isotherm model that best represents the data (Ncibi, 2008).

$$q_e = q_{e(\max)} \cdot \frac{K_l \cdot C_{eq}}{1 + K_l \cdot C_{eq}}$$
⁽⁴⁾

$$q_e = K_f \cdot C_{eq}^{1/n} \tag{5}$$

where:

 C_{eq} = equilibrium concentration of solute in contact with the media (mg L⁻¹)

 q_e = amount adsorbed per unit weight of media (mg kg⁻¹)

- *K*_l = Langmuir adsorption constant related to the binding energy (dimensionless)
- $q_{e(max)}$ = maximum monolayer adsorption capacity (mg kg⁻¹)
- *K_f* = Freundlich isotherm constant, indicative of approximate adsorption capacity (dimensionless)
- n = Freundlich coefficient, where inverse value represents the intensity of adsorption; smaller n (n<1) favors adsorption.</p>

Statistical Analysis

In an effort to identify statistically significant results between treatment types within all batch equilibrium experiments and column tests, both one-way and twoway analysis of variance (ANOVA) tests were performed with Tukey's post hoc analysis to determine differences between groups. Pollutant removal quantity was calculated based on relative concentrations of orthophosphate-P, nitrate-N and ammonium-N during the breakthrough phase of column experiments. Analysis was

(5)

conducted with the Microsoft Excel data analysis package using an alpha of 0.05. Results were considered significant with P<0.05 and are reported with degrees of freedom and the F-statistic.

Results

Batch Leaching

Contact time tests showed that 200 mg L⁻¹ orthophosphate (oPO₄-P) solutions equilibrated with WWS at 12 hours and with P-J biochar at 72 hours (Figure 6), with less than a 5% change in solute concentrations after these intervals within 24 hours. Therefore, subsequent batch equilibrium experiments used a 96 hour equilibrium time for the P-J biochar and a 24 hour equilibrium time for the WWS.



Figure 6. Percentage change in orthophosphate (oPO₄-P) solute concentration over contact time with pinyon-juniper (P-J) biochar and Washoe washed sand (WWS). Tests used 200 mg L^{-1} phosphorus and demonstrated minimal change in solute concentration after 12 hours for WWS and after 60 hours for the P-J biochar.

Nutrient leaching in the 0 mg L⁻¹ batch samples was observed from each of the biochar size classes and from the Washoe washed sand (Table 1). Nitrogen leaching was relatively minor (<0.1 mg L⁻¹) and there was not much difference between the two media types for leaching of nitrate-N and ammonium-N, but the phosphorus leaching was much greater from biochar in all size classes than was measured from WWS. On average, the P-J biochar released an order of magnitude more phosphorus (0.61 mg L⁻¹) than did the WWS (0.06 mg L⁻¹). Interestingly, Fe-amended biochar did not release much phosphorus during leach testing (0.005 mg L-1) with 1:20 mediato-solute ratios, but showed much more ammonium-N leaching (1.37 mg L⁻¹) than non-amended biochar. The 250-500 μ m non-amended biochar tested at the 1:20 ratio released about twice as much phosphorus (1.37 mg L⁻¹) compared to tests at the 1:10 ratio.

Table 1. Soluble orthophosphate (oPO_4 -P), nitrate (NO_3 -N), and ammonium (NH_4 -N) equilibrium leachate concentrations (with laboratory DDW) from P-J biochar (BC), Washoe washed sand (WWS) and Fe-amended biochar (BC-Fe).

S	ample	Leached Concentrations from Media						
Media*	Size Class	Orthophosphate-P	Nitrate-N	Ammonium-N				
	(µm)	(mg L·1)	(mg L-1)	(mg L-1)				
BC	125-250	0.61	0.04	0.08				
BC	250-500	0.76	0.03	0.03				
BC	500-2000	0.48	0.08	0.03				
BC	2000-4000	0.60	0.09	0.02				
BC	mean	0.61	0.06	0.04				
WWS	75-4750	0.06	0.03	0.03				
**BC	250-500	1.37	0.02	0.13				
**FeBC	250-500	0.005	0.02	1.37				

* Based on biochar equilibrium time of 96 hours and WWS equilibrium time of 24 hours ** With 1:20 media-to-solution ratio; all other tests at 1:10

Batch Adsorption

Batch adsorption experiments with different size classes of P-J biochar and WWS showed higher percentages of phosphorus and nitrate removals from the smaller size biochars, but an opposite effect with ammonium. Given the high leachate concentrations observed for phosphorus, data were normalized by subtracting these values from the batch adsorption results. Nitrate and ammonium leachate concentrations were low, however, so these data were not adjusted before graphing.

The results for phosphorus showed that smaller particle sizes of biochar yielded significantly higher percentages of phosphorus removal than the larger particle classes (Figure 2); Tukey's post-hoc F(4, 35) = 209, p << 0.05. When comparing differences between both small particle size groups (125–250 and 250–500 μ m), there was no significant difference, and similarly there was no difference between both large size classes (500-2000 and 2000–4000 μ m). Percentage of (normalized) phosphorus removal was 82–85% for the two smallest biochar classes (125-250 and 250–500 μ m) with optimal removal at initial concentrations less than 5.0 and greater than 0.8 mg-P L⁻¹. Percentage removal by the larger particles sizes ranged from 57–62%, with optimal removal at initial concentrations at greater than 1.0 mg-P L⁻¹. For WWS the maximum phosphorus removal was only 35% (at 0.2 mg-P L⁻¹) and this decreased as the solute concentration increased.



Figure 7. Percent removal of phosphorus by P-J biochar in several size classes and by the Washoe washed sand (WWS). Data have been normalized to initial leachate concentrations (see text). Data show highest removal efficiency from the smaller size classes of biochar.

Nitrate-N adsorption patterns were similar to that of phosphorus, with highest removal percentages observed from the smallest size classes and less removal by the larger sizes of biochar. Removal effectiveness decreased with increasing solute concentrations, however (Figure 7). Biochar size classes from 125–250 and 250–500 μ m yielded maximum percent removals of 98–99% for solute-N concentrations up to 1.0 mg L⁻¹, but percentage adsorption dropped rapidly at higher concentrations. Biochar sizes from 500–2000 and 2000–4000 μ m removed 70–75% across this same concentration range. Percentage removal for all size classes except the smallest (125-250 μ m) declined below 30% at 8.0 mg N L⁻¹. For WWS the percentage removal was less than 10% across all tested solute concentrations. All biochar sizes produced significantly higher percent removals than that of WWS; Tukey's post-hoc F(4, 35) = 418, P < 0.05.



Figure 7. Percent removal of nitrate-N by P-J biochar in several size classes and by Washoe washed sand (WWS). Data show highest removal efficiency from the smaller size classes of biochar.

Ammonium-N percentage removal was relatively high (>85%) across all biochar size classes when initial solute N concentrations were greater than 0.2 mg N L⁻¹. In these cases, however, even the WWS control media showed relatively effective adsorption (>60%), so the additional amount adsorbed by biochar is much less. Also of interest is that smallest size class of biochar (125–250 μ m) did not perform as well as any of the larger size classes across the range of test concentrations. In any case, with the exception of the smallest biochar at the lowest concentration, all other biochar size categories significantly outperformed WWS in percent removal efficiency; Tukey's post-hoc F(4, 35) = 23.7, P < 0.05.



Figure 8. Percent removal of ammonium-N by P-J biochar in several size classes and by Washoe washed sand (WWS). Data show highest removal efficiency from the larger size classes of biochar.

Adsorption Characteristics of Isotherm Models

As usual when constructing equilibrium adsorption plots, the quantity adsorbed was normalized by the mass of adsorbent to allow comparison across different types of materials. Steeper slopes of normalized adsorption versus equilibrium concentrations (i.e., q_e / C_e) indicate superior performance because there is relatively more solute adsorbed per unit mass of media, yielding lower equilibrium concentrations in solution.

For soluble phosphorus the highest adsorptive capacity was observed within smaller particle size ranges of the P-J biochar (Figure 9). Biochar ranging from 125–250 μ m presented the steepest slope for adsorption, followed by the smallest size class of 125–250 μ m, then the 500–2000 and 2000–4000 μ m classes with successively lower slopes, and finally WWS with the lowest adsorption slope.



Figure 9. Batch adsorption data for orthophosphate-P over the tested size class series of P-J biochar and the Washoe washed sand (WWS). Results indicate higher removal efficiency per unit adsorbate mass with the smaller size classes of biochar. Washoe washed sand showed lowest adsorptive capacity overall.

The data from each size class of P-J biochar and from WWS were tested against all three isotherm models, with appropriate model selection based on highest value of the Pearson correlation coefficient (r^2). Results shown in Table 2 indicate that larger sized biochar classes (500-2000 and 2000-4000 µm) were best represented linearly with r² values of 0.98 and 0.91 (Figure 10A). Both smaller biochar particle sizes (125–250 and 250–500 μ m) were best represented by the Freundlich model, with corresponding r² values of 0.94 and 0.97, respectively (Figure 10B). The WWS isotherm data was best represented by the Langmuir model with an r^2 of 0.98 (Figure 10C), but had a much lower adsorptive capacity than that of P-I biochar, as previously described (Figure 9). Linear isotherm constants derived from the biochar batch adsorption experiments were somewhat better than observed from soils collected at stormwater treatment basins at Lake Tahoe (Heyvaert et al., 2006), which would suggest that biochar exhibits better nutrient removal characteristics. The iron-amended biochar showed much greater affinity for phosphorus (K_d) than any of the other media, including dolomite, while Washoe washed sand fell within a range represented by the fine and coarse Truckee sand (Table 2).

	Linear Co	onstants	Langn	nuir Consta	Freundlich Constants					
Media or Soil Type	K _d r ²		q e(max)	q _{e(max)} K _l		n	K _f	r ²		
	(L/kg)	()	(mg/kg)	(L/kg)	()	()	(mg/L)	()		
BC (125-250 μm)	21.8	0.912	26.3	-1.1	0.910	0.88	28.1	0.943		
BC (250-500 μm)	33.9	0.938	40.7	-1.6	0.974	0.93	39.4	0.978		
BC (500-2000 μm)	9.8	0.984	4.7	-2.3	0.958	1.24	8.3	0.965		
BC (2000-4000 μm)	7.9	0.909	8.4	0.5	0.841	0.95	7.7	0.895		
Bulk BC (all sizes)	15.1	0.991	14.8	-1.7	0.969	1.00	17.3	0.973		
WWS	2.1	0.898	5.8	1.9	0.988	0.66	3.4	0.975		
*BC (250-500 μm)	23.9	0.888	-8.8	2.6	0.013	3.57	0.20	0.891		
*FeBC (250-500 μm)	5975	0.945	2500	-2.0	0.198	1.31	20338	0.691		
20-mesh Dolomite	256.3	0.956	7976	3.60E-02	0.882					
Coon Basin	12.9	0.703	3659	1.76E-03	0.882					
Round Hill	3.8	0.379	1149	6.62E-03	0.945					
Eloise Basin	19.9	0.937			0.687					
Fine Truckee Sand	3.6	0.996								
Coarse Truckee Sand	0.8	0.577								

Table 2. Soluble orthophosphate-P isotherm results for tested adsorbent media. Results for dolomite, Round Hill, Coon and Eloise basins and Truckee sands from Heyvaert et al., 2006.

* Batch adsorption tests conducted at 1:20 adsorbent to solution ratio; all others at 1:10.



Figure 10. Orthophosphate-P isotherm models. (A) Linear isotherms for biochar classes 500–2000 and 2000–4000 μ m, along with the mean of all biochar sizes. (B) Freundlich isotherms for biochar classes 125–250 and 250–500 μ m. (C) Langmuir isotherm for Washoe washed sand (WWS).

The nitrate-N batch equilibrium data was more scattered than observed with phosphorus, indicating variable adsorptive capacity and no specific pattern with biochar sizes (Figure 11). Results shown in Table 3 indicate that data could be represented by both Freundlich (Figure 12A) and Langmuir (Figure 11B) isotherm models. Mean adsorption across all biochar size ranges (125–4000 μ m) follows the Langmuir model (r² = 0.94) with an estimated maximum adsorption of nearly 50 mg NO₃-N kg⁻¹ (q_{e(max)} in Equation 3). Adsorption by WWS was best represented by the Freundlich model, with r² = 0.99, although its adsorptive capacity was much lower than that of the P-J biochar.



Figure 11. Batch adsorption data for nitrate-N over the test size class series of P-J biochar and the Washoe washed sand (WWS). Results indicate variable removal efficiency per unit adsorbate mass. Washoe washed sand showed lowest adsorptive capacity overall.

	Linear Co	onstants	Langm	uir Const	ants	Freundlich Constants			
Media or Soil Type	K _d r ²		q e(max)	Kı	r ²	n	K _f	r ²	
	(L/kg)	()	(mg/kg)	(L/kg)	()	()	(mg/L)	()	
BC (125–250 μm)	9.7	0.366	313	0.26	0.614	0.35	38.0	0.774	
BC (250–500 μm)	3.6	-1.03	400	0.12	0.513	0.20	24.3	0.595	
BC (500-2000 μm)	3.4	0.159	22.9	3.9	0.906	0.45	13.3	0.802	
BC (2000-4000 μm)	4.6	-0.309	23.8	7.9	0.906	0.58	17.3	0.716	
Bulk BC (all sizes)	5.1	0.038	48.5	2.9	0.938	0.45	21.1	0.822	
WWS	1.0	0.980	0.40	-6.4	0.980	1.30	0.52	0.994	
*BC (250–500 μm)	0.8	-0.527				-0.26	2.85	0.221	
*FeBC (250-500 μm)	83.5	0.972	75.2	-0.67	0.942	0.97	95.68	0.973	

Table 3. Soluble nitrate-N isotherm results for tested adsorbent media.

* Batch adsorption tests conducted at 1:20 adsorbent to solution ratio; all others at 1:10.



Figure 12. Nitrate-N isotherms models. (A) Freundlich isotherms of nitrate-N for biochar classes 125–250 and 250–500 μ m, along with Washoe washed sand (WWS). (B) Langmuir isotherms for biochar classes 599–2000 and 2000–4000 μ m.

Ammonium adsorption data were highly variable (Figure 13) with fitted isotherm models suggesting a linear relationship on all biochar size ranges, including averaged biochar sizes and WWS (Table 4). WWS provided the best model fit ($r^2 = 0.99$) followed by biochar of 125–250, 250–500 µm size classes, then averaged biochar, 500–2000 and 2000–4000 µm, with corresponding r^2 values of 0.86, 0.81, 0.80, 0.70, and 0.69 respectively. The steepest slope was indicated at a biochar size range of 250–500 (Table 4), which represents the highest adsorptive capacity for ammonium (Figure 12A). Ammonium showed the steepest slope for adsorptive capacity of all the analytes, indicating strong media binding of NH₄-N from aqueous solution.



Figure 13. Batch adsorption data for ammonium-N over the tested size class series of P-J biochar and the Washoe washed sand (WWS). Data indicate relatively high adsorptive capacity from biochar across all size classes, resulting in low equilibrium concentrations.

	Linear Co	onstants	Langm	uir Const	Freundlich Constants			
Media or Soil Type	K _d	r ²	q _{e(max)}	Kl	r ²	n	K _f	r ²
	(L/kg)	()	(mg/kg)	(L/kg)	()	()	(mg/L)	()
BC (125-250 μm)	74.5	0.862	-175.4	-0.01	0.001	1.07	60.3	0.395
BC (250–500 μm)	195.7	0.811	107.5	-1.39	0.159	1.18	288.3	0.624
BC (500–2000 μm)	139.7	0.695	111.1	-0.37	0.264	1.01	185.7	0.643
BC (2000-4000 μm)	100.8	0.690	51.8	-3.33	0.110	1.15	144.0	0.527
Bulk BC (all sizes)	116.3	0.800	94.3	0.14	0.062	1.12	141.5	0.570
WWS	22.7	0.998	17.1	-2.09	0.989	1.07	42.7	0.994
*BC (250–500 μm)	59	0.652	58.5	-0.05	0.003	1.07	57.2	0.436
*FeBC (250-500 μm)								

Table 4. Soluble ammonium-N isotherm results for tested adsorbent media.

* Batch adsorption tests conducted at 1:20 adsorbent to solution ratio; all others at 1:10.

Batch equilibrium test of the Fe-amended (FeBC) showed much stronger affinity for phosphorus than did the equivalent $250-500 \mu m$ non-amended biochar (see K_d values in Table 2). There was a similar, but much weaker increase in affinity for nitrate-N adsorption with FeBC (Table 3). However, batch adsorption of ammonium-N by FeBC resulted in a negative slope (-4.5, not shown), which is indicative of high leaching concentrations where no adsorption occurred. Therefore, the FeBC ammonium-N adsorption could not be fitted to any adsorption isotherm model. The results from FeBC equilibrium adsorption experiments (Appendix B) were consistent with the leaching tests (Table 1), suggesting that FeBC substantially increased anion adsorption but diminished the cation adsorption.



Figure 14. Ammonium-N isotherm models. (A) Linear isotherms for 125–250 and 250– 500 μ m biochar classes. (B) Freundlich isotherms for biochar classes 500–2000 and 2000–4000 μ m. (C) Langmuir isotherms of Washoe washed sand (WWS) and the average of all biochar sizes.

Column Experiments

Based on results from the batch adsorption experiments it was decided that the $250-500 \mu m$ biochar would be used with WWS as mixed media in subsequent column tests. Column tests results are presented in terms of exchange pore volumes rather than by elapsed time for each of the three phases: leaching (Figure 15), adsorption (Figure 16) and desorption (Figure 17). The initial leaching phase lasted for 20 days, until minimal nutrient concentrations were observed in effluent from all columns. Columns were then immediately switched to the adsorption phase that lasted about 20 days, after which the desorption phase commenced and lasted for an extended period of more than 15 days. Each pore volume was approximately equivalent to 8 hours of media contact time.

Leachate concentrations converged after approximately 122, 18 and 18 pore volumes, respectively for orthophosphate-P, nitrate-N and ammonium-N (Figure 15). The biochar columns produced much more phosphorus during the leaching phase than did WWS, despite repeated laboratory washing of sieved material before its use. Interestingly, even the WWS yielded an average 0.06 mg L⁻¹ phosphorus at the end of the leaching phase (Table 5), which was about the same as the 30% biochar columns at that time (0.05 mg L⁻¹). Higher concentrations of nitrogen were leached from columns with greater amounts of biochar, but they all ultimately decreased to levels of detection for ammonium and nitrate N (0.002 mg L⁻¹).

Corr		Leachate Concentration (mg L ⁻¹) ^a							
San	Phosphate-P		Nitrate-N		Ammonium-N				
Туре	Column ID	Initial	Final	Initial	Final	Initial	Final		
WWS Control	1, 2, & 3	0.08	0.06	0.7	0.002	0.1	0.002		
15% BC	4, 5, & 6	1.4	0.04	1.3	0.002	0.9	0.002		
30% BC	7, 8, & 9	2.3	0.05	1.4	0.002	1.3	0.003		

Table 5. Column initial and final leachate concentrations for orthophosphate, nitrate and ammonium.

^aLeachate values are the mean concentration of triplicate columns.



Figure 15. Mean leachate concentrations of (A) orthophosphate-P, (B) nitrate-N, and (C) ammonium-N for 100% WWS as control, 15% BC:WWS and 30% BC:WWS. Error bars are coefficient of variance between triplicate columns.

Adsorption began after the leaching phase ended, when sample intake lines were placed into a mixed 2 mg L⁻¹ solution of each nutrient (oPO₄-P, NO₃-N, and NH₄-N). Adsorption profiles are represented by break-through curves, as the ratio of effluent to influent concentrations (Figure 15). Phosphorus breakthrough convergence occurred after 30 pore volumes, while nitrate-N convergence occurred after only 8 pore volumes. Ammonium-N effluent convergence relative to inflow concentrations never did occur completely, even after 60 pore volumes (approx. 480 hours), although column effluent concentrations were nearly equivalent to inflow concentrations by the end of the adsorption phase.

Over the complete time span of adsorption treatment, the total mass of nutrients retained by media in each column was greatest for 30% biochar and least for the WWS (Table 6). The 30% biochar retained about twice as much phosphorus as the 15% biochar, and this difference was significant; Tukey's post hoc F(2, 6) = 18.62, P << 0.05. However, the net adsorption for both phosphorus and nitrogen was small on a percentage basis, and the best adsorption was observed for ammonium-N. Significant differences in adsorption between all three media types was observed for ammonium-N; Tukey's post hoc F(2, 6) = 896, P<0.05. There were no significant differences between media types for nitrate-N adsorption.

Madia	Column Nutrient Adsorption*												
Meula		Phosphate-P			Nitrate-N		Ammonium-N						
	Added	Adsorbed	Net	Added	Adsorbed	Net	Added	Adsorbed	Net				
	(mg)	(mg)	(%)	(mg)	(mg)	(%)	(mg)	(mg)	(%)				
WWS	73	-0.6	-0.9	74	1.0	1.3	76	8.7	11				
15% BC	74	1.0	1.3	74	1.1	1.4	76	10.8	14				
30% BC	75	2.1	2.8	76	1.0	1.4	77	16.5	21				

Table 6. Total mass of nutrient added by inflow to each column and adsorbed by media, with corresponding percentage removals for each nutrient tested.

* Values shown are based on mean concentrations observed for triplicate columns.



Figure 16. Mean adsorption by columns of (A) orthophosphate-P, (B) nitrate-N, and (C) ammonium-N for 100% WWS as control, 15% BC:WWS and 30% BC:WWS. Data on y-axis are normalized to initial concentration, where effluent concentration is divided by influent concentration. Error bars are coefficient of variance between triplicate columns.

The desorption phase with buffered DDW lasted approximately 60 pore volumes, although only the first 40 pore volumes are shown in Figure 17. Phosphorus desorption slowed after approximately 10 pore volumes of DDW treatment, and asymptotically approached final concentrations of 0.08, 0.06 and 0.07 mg-P L⁻¹ for WWS, 15% BC, and 30% BC, respectively. Nitrate desorption occurred rapidly, with concentrations dropping from 2 mg NO₃-N L⁻¹ to near detection limit (0.002 mg NO₃-N L⁻¹) within about 18 pore volumes. Desorption of ammonium-N lasted longer, as seen in effluent concentrations, but also dropped to near detection limit at about over 35 pore volumes. Losses of ammonium occurred more rapidly in both the 15% and 30% biochar treatments compared to the WWS columns.

These desorption phase results are consistent with findings from the other phases of this study, showing that some percentage of the adsorbed nutrients can be released under conditions of continuous flushing with buffered DDW. On a net basis, accounting for both the adsorption and desorption phases of this experiment, there was a loss of phosphorus by WWS and modest percentage retention by the biochar mixtures. Nitrate results were similar for all media treatments, with minimal retention. Ammonium retention showed the best results, overall, with 30% biochar retaining the most after flushing (21%) and WWS retaining the least (Table 7).

Madia		Net Nutrient Adsorption by Columns*												
меша		Phosphate-P			Nitrate-N		Ammonium-N							
	Added	Retained	Net	Added	Retained	Net	Added	Retained	Net					
	(mg)	(mg)	(%)	(mg)	(mg)	(%)	(mg)	(mg)	(%)					
WWS	73	-0.7	-1.0	74	0.9	1.3	76	8.6	11					
15% BC	74	0.9	1.2	74	1.1	1.4	76	10.7	14					
30% BC	75	2.0	2.7	76	1.0	1.3	77	16.4	21					

Table 7. Nutrient retention by media, accounting for both adsorption and desorption phases of the column experiments.

* Values shown are based on mean concentrations observed for triplicate columns.



Figure 17. Mean desorption by columns of (A) orthophosphate-P, (B) nitrate-N, and (C) ammonium-N for 100% WWS as control, 15% BC:WWS and 30% BC:WWS. Error bars are coefficient of variance between triplicate columns.

Discussion

There is increasing interest worldwide in the identification and application of alternative non-proprietary filtration media to treat stormwater runoff. Biochar is an especially promising alternative for this purpose because of its high surface area and porosity, which contribute to greater potential adsorptive capacity and pollutant retention. In this manner it essentially functions as simple cheaper form of activated charcoal. The purpose of this study was to evaluate whether pinyonjuniper biochar, produced as a by-product of forestry management by the Nevada Division of Forestry, could potentially serve as a media amendment for nutrient capture and retention in stormwater BMPs.

Batch adsorption experiments showed that P-J biochar did remove phosphorus and nitrogen from nutrient spiked solutions in the laboratory. On average, across all biochar size classes tested, this adsorption was particularly effective for ammonium-N removal (97% of 2 mg L⁻¹), but was less effective for orthophosphate (60% of 2 mg L⁻¹) and nitrate-N (58% of 2 mg L⁻¹) removals. When corrected for corresponding nutrient adsorption by the control media (WWS), however, these nutrient removal rates were not as impressive (27%, 43% and 45%, respectively). Column adsorption tests with synthetic stormwater yielded similar results, with substantially more ammonium removed on a net basis than either nitrate or phosphate; although, as seen with the batch adsorption, WWS also removed ammonium so "excess" adsorption by the 30% biochar mixture was about half of the total observed. Net nutrient retention by media in column experiments was much lower on a percentage basis following both the adsorption and desorption phases than observed simply from the batch equilibrium tests.

Adsorption isotherm models help describe and predict the retention characteristics of adsorptive materials. Differences in isotherm model types and plot slopes reflect diverse binding mechanisms that regulate surface adsorption. Mechanisms controlling surface adsorption of ammonium from solution include cation exchange and ionic surface adsorption, but also chemisorption in the presence of various functional groups such as carboxyl (Hollister et al., 2013). Fast reaction adsorption processes are generally characterized as reversible physisorption onto media surface sites (McGechan and Lewis, 2002), and it is likely that surface Van der Walls charge characteristics of both the WWS and the biochar induced some of the ammonium adsorption. Ammonium sorption on all biochar particle size classes and on the WWS tested was best described (highest r^2) with the linear isotherm model, which is generally interpreted as representing an infinite number of available binding sites (Ryan, 2014). (Note that batch equilibrium data that fit a Langmuir or Freundlich isotherm models often manifest as near linear at low concentrations.) At some point the ammonium adsorption would likely have become saturated, but media capacity was greater than the supply of ammonium in our batch adsorption experiments, even at 8 mg L⁻¹. Higher slopes derived from linear isotherm models are sometimes interpreted as indicating faster reaction times (Schweich and Sardin, 1981). The ammonium isotherm slopes were much higher for all P-J biochar size classes than for WWS, although the quality of the model fits dropped for larger P-J biochar sizes (>500 μ m, r² <0.70).

Biochar also showed a higher capacity for phosphate anion adsorption than did WWS. Net adsorption of phosphorus in the column studies doubled between the 15% and 30% biochar mixtures, and was net negative (effluent loading occurred) with WWS. Batch adsorption data for phosphorus in the two smallest biochar size classes were best represented by the Freundlich isotherm model, while the linear isotherm model best described data from the larger biochar classes. The Freundlich isotherm is an empirical equation for describing multilayer, heterogeneous adsorption sites. These differences in model fits with phosphorus may be due in part to reaction time, with faster reactions in the smaller size biochar classes, as well as due to differences in adsorption binding mechanisms. The most commonly used isotherm models for representing phosphorus adsorption are Langmuir and Freundlich (Cucarella and Renman, 2009). However, the modeled fits can depend on the type of mechanism regulating adsorption. For instance, precipitation reactions tend to occur at higher initial phosphorus concentrations, while surface adsorption dominates P removal at low concentrations (Cucarella and Renman, 2009). Previous studies have shown that the Langmuir isotherm model can accurately describe phosphorus adsorption to sand if no precipitation reactions occur (Del Bubba et al., 2003). This may explain the difference in phosphorus adsorption observed in WWS compared to biochar. Washoe washed sand was the only phosphorus adsorption data that best fit the Langmuir model, while biochar adsorption data could be reasonable fit by either the Freundlich or the linear isotherm models.

Differences in phosphorus adsorption onto biochar may also result from the highly porous surface structure, where much longer equilibrium times were required for adsorption onto biochar versus WWS, due to increased surface area from micro- and nanoporosity. Increased surface area slows the intra-particle diffusion movement of phosphorus (Cucarella and Renman, 2009). The differences in intra-particle diffusion may explain observed differences not only between WWS and biochar, but the modeled differences between all size ranges of biochar. As biochar increased in size, phosphorus had a further distance to diffuse into the particle itself. This can be seen in the distribution coefficients derived from linear isotherm models of biochar size classes, which decreased with increasing biochar size.

Nitrate adsorption data for the coarser biochar particles (>500 μ m) conformed best to Langmuir isotherms, as did the WWS. Finer biochar size classes (<500 μ m), however, did not fit any of the isotherm models very well for nitrate adsorption (r² <0.78). A wide range of production temperatures (300–700°C) in P-J biochar could have had a variable effect on nitrate adsorption characteristics. For instance, biochars derived from bagasse (sugar cane residue) showed a steady increase of adsorption at production temperatures from 700 to 800°C, with nitrate adsorption data described by the Freundlich isotherm model giving corresponding r² of 0.98 and 0.99 (Kameyama et al., 2012). Although adsorption increased with production temperatures (>700°C), both surface area and micropore volume decreased, suggesting that surface adsorption itself may not be the only factor controlling nitrate adsorption. Low or variable temperatures during biochar production can affect development of nitrate binding functional groups, with acid functional groups formed at lower temperatures and base functional groups formed at higher temperatures (Kameyama et al., 2012). The differences observed in P-J biochar isotherm adsorption models may reflect a net negative charged surface, limiting both nitrate and orthophosphate binding. Although there was a net removal of nitrate in the column experiments with biochar, there was no significant difference between biochar and WWS in the amounts adsorbed.

One of the more important findings from this study was that soluble phosphorus was released from previously washed biochar in all size classes. Average leachate concentrations were an order of magnitude higher in batch tests of biochar (0.61 mg L⁻¹) compared to the WWS (0.06 mg L⁻¹). Corresponding leachate concentrations for both nitrate and ammonium were low in all media ($\leq 0.09 \text{ mg L}^{-1}$). One possible explanation for the high orthophosphate leachate concentrations may be from weathering type effects, where washing and drying during sample preparations mobilized particulate biochar. Organic phosphorus can mineralize as mobilized particulates come into contact with water (Sharpley and Moyer, 2000) and measurable concentrations of dissolved phosphorus are seen. Indeed, increased mobilization of biochar from both dry-wet and freeze-thaw treatments has been previously reported (Igbal et al., 2015; Mohanty and Boehm, 2015), although those studies did not report on effluent concentrations. Measurable losses of orthophosphate reported as leachate are consistent with findings reported by other biochar studies (Gray et al., 2016; Yao et al., 2012). Similarly, (Iqbal et al., 2015) observed a 16.7% loss of orthophosphate in biochar produced from Douglas fir, relative to the total amount of phosphorus, compared to 0% nitrate losses from leaching.

In contrast, we found that leachate concentrations of orthophosphate from Feamended biochar were very low (0.005 mg L⁻¹). Phosphorus leaching in soils is

commonly dependent on cation exchange and the relative abundance of Fe and Al oxides present (Iqbal et al., 2015), which may have contributed to the low phosphate concentrations observed in WWS leachate. Soils with higher abundance of metals can increase anion retention based on opposing charges. The Fe-amended biochar used in our batch equilibrium experiments increased soluble phosphorus adsorption at all concentrations (Appendix B). The partition coefficient for FeBC (5795 L/mg) was higher even than for a 20-mesh dolomite (256 L/mg) previously tested (Heyvaert et al., 2006). Phosphorus sorption has been shown to increase after iron impregnation of biochars produced at a low pyrolysis temperature (500 °C) from corn, garden wood, and wood chip feedstocks (Michalekova-Richveisova et al., 2017). That study used 24 hour equilibrium times with a 1:30 adsorbent to adsorbate ratio and additions of 10-200 mg-PO4³⁻ L⁻¹, which were an order of magnitude greater than the concentrations used in our study. Their results at high concentrations, however, are consistent with our results at the lower phosphorus concentrations characteristic of stormwater. Another study compared removal efficiencies of phosphate by raw biochar feedstock with iron-impregnated biochar, and found that adsorption increased by 20% from the non-amended feedstocks (Ramola et al., 2014). Neither Michalekova-Richveisova et al. (2017) nor Ramola et al. (2014) tested batch sorption of soluble nitrogen. Interestingly, it was reported that surface area decreased from iron impregnation of biochars (Michalekova-Richveisova et al., 2017), which again suggests that surface area may play a less important role in surface adsorption than the quality and type of binding sites present for specific nutrient uptake. In our experiments, the Fe-amended biochars did substantially increase ammonium concentrations in leachate, however.

The initial leaching phase in column testing of media clearly showed that as biochar composition increased, the leachate concentrations also increased. It appears that some nutrient leaching is a consequence of biochar production. During pyrolysis, many nutrients are volatilized or gassed off. Indeed, reductions in total nitrogen and additions in total phosphorus were measured with increasing incineration temperatures in cornstalk (Huang et al., 2011). The nutrients not lost to volatilization remain within the biochar. Therefore, as the percentage of biochar increases in bioretention media the relative abundance of nutrients available for leaching also increases, as seen in with our column effluent concentrations. Out of the three analytes tested, phosphorus required the longest time for column effluent concentrations to fall and it leached the highest concentrations, similar to batch adsorption leachate results. Indeed, final effluent concentrations of phosphorus from the leaching phase of column experiments remained an order of magnitude higher than nitrate or ammonium concentrations from all media types.

Adsorption treatment of phosphorus was relatively ineffective in all column treatment types, as indicated by the relatively rapid breakthrough of phosphorus during adsorption phase testing. Column and leaching results indicate that P-J biochar may act as a source of soluble phosphorus, which is consistent with other findings (Gray et al., 2016). Adsorption treatment of nitrate was also minimal. Indeed, the lack of nitrate removal has been reported from column studies with biochar produced from poultry litter and hardwood pellets (Tian et al., 2016) and from feedstocks of sugarcane bagasse, peanut hull, Brazilian pepperwood, and bamboo (Yao et al., 2012). While these feedstocks are considerably different than the pinyon-juniper used in our biochar experiments, a more similar feedstock of oak indicated no nitrate adsorption (Hollister et al., 2013), which was conjectured to be due to insufficient anion exchange capacity for adsorption of nitrate.

Column tests did show that that ammonium was retained at higher rates than the other nutrients. These results were in line with our findings from batch adsorption experiments. Transport of ammonium through the columns was slower than phosphorus or nitrate. This retardation of ammonium occurred within all treatment types, although the degree of retardation was dependent in part on the relative percent additions of biochar. While WWS control column triplicates also retarded soluble ammonium, it was to a lesser degree than the biochar amended columns. Increased retention of a positively charged ion over the negatively charged nitrate

and phosphorus ions indicates that biochar may be negatively charged. The negatively charged surface of P-J biochar has previously been suggested (Hollister et al., 2013; Mukherjee et al., 2011; Yao et al., 2012). However, (Takaya et al., 2016) advocates instead that surface functional groups enhance ammonium uptake, where ammonium uptake is governed by the presence of O- containing functional groups. Furthermore, it has been concluded that biochar surface reactivity is dependent on simple carbon oxygen reactions (Vallejos-Burgos et al., 2016). Nevertheless, enhanced ammonium retention is most likely a combination of factors that include surface area and charge, porosity, CEC, and the presence of O-containing functional groups. These binding mechanisms may also explain the slowed release rates observed during the column desorption phase.

Column desorption rates were prolonged and were observed for both orthophosphate and ammonium, indicating stronger adsorptive binding strength compared to nitrate. Owing to the unreactive nature of nitrate with both biochar and WWS, this rapid decrease in nitrate is attributed to low bonding energy and more exchangeable ions (Chintala et al., 2013). Prolonged phosphorus desorption rates were likely due to the higher leachable concentrations seen in every other phase. These results are consistent with observations made on phosphorus desorption after adsorption charging of native Lake Tahoe soils from differing locations (Heyvaert et al., 2006). Although P-J biochar leached some phosphorus during column experiments, it was less than observed from the native Tahoe soils (Table 8). Furthermore, the adsorption to desorption ratio (A/D) of phosphorus retained by biochar media during column experiments was much greater than for Tahoe soils or the WWS. This suggests that mixing biochar with native soils could enhance the total nutrient adsorptive capacity of these soils, especially for ammonium and phosphorus.

	Extractable P*	Leached P	Percentage Leached	P Adsorption	P Desorption	Ratio A/D
Media	(mg kg ⁻¹)	(mg kg-1)	(%)	(mg kg ⁻¹)	(mg kg-1)	()
WWS	0	0.1		-1.0	0.08	-12
15% BC	72.3	1.7	2.4	1.61	0.11	14
30% BC	72.3	3.5	4.8	4.0	0.16	25
Coon Basin	22.9	10.9	48	9.2	10.6	0.9
Round Hill	36.6	5.4	15	10.2	4.6	2.2
Eloise Basin	18.3	6.3	34	32.2	14.5	2.2

Table 8. Comparison of extractable to leached phosphorus from media leach tests, and adsorbed to desorbed phosphorus from both phases of the column experiments. Data from Coon Basin, Round Hill and Eloise Basin were taken from Heyvaert et al. (2006).

* Based on chemical analysis of test media and soils.

In terms of reactivity, ammonium presented the highest retention of all analytes tested. The strong binding capacity of ammonium onto both biochar and WWS treatment materials was witnessed throughout the column experiments and is supported by results from the batch equilibrium tests. Estimates of nutrient retention on a mass (kg) and volumetric (m³) basis are shown in Table 9 for media application to Tahoe stormwater BMPs, which is likely how it would be specified when amending BMP soils or if used in bioretention systems.

Table 9. Nutrient net retention on a media mass basis derived from column adsorptiondesorption test results.

	Phosphate-P		Nitrate-N		Ammonium-N	
Media	(mg kg ⁻¹)	(g m ⁻³)	(mg kg ⁻¹)	(g m ⁻³)	(mg kg ⁻¹)	(g m ⁻³)
WWS	-1.1	-1.8	1.5	2.4	13.8	21.3
15% BC	1.5	2.0	1.8	2.6	17.9	26.4
30% BC	3.8	4.8	1.9	2.5	31.2	40.7

In summary, each media tested showed net nutrient retention, except that WWS exported some phosphorus overall. It is likely that environmental application of these media would result in higher overall retention compared to native soils typical of the Tahoe stormwater BMPs. In addition, normal wet-dry cycles, similar to runoff events, tend to recharge active adsorption sites over time, and captured nutrients would be potentially available for uptake by plants if they were a desired presence on the landscape of these treatment sites.

Conclusions

Using batch adsorption experiments, isotherm models and laboratory column filtration, we examined the potential efficacy of pinyon-juniper biochar as a soil amendment for adsorption and retention of dissolved inorganic nutrients common to urban stormwater flows. The main findings from this study include the following.

- Batch adsorption experiments showed that P-J biochar did remove phosphorus and nitrogen from nutrient-spiked solutions in the laboratory.
- Biochar adsorption of dissolved inorganic nutrients was most effective with the smaller size classes (125–500 μ m) compared to larger size classes of biochar (500–4000 μ m)
- On average, with 2 mg L⁻¹ nutrient concentrations across all biochar size classes tested, this adsorption was particularly effective for ammonium-N removal (97% removal), but was less effective for orthophosphate-P (60%) and nitrate-N (58%) removals.
- Washoe washed sand also demonstrated some nutrient adsorption in the batch experiments, although less than observed with the P-J biochar.
- When adjusted for adsorption by the Washoe washed sand, used as a control media in batch experiments, biochar removal rates from 2 mg L⁻¹ nutrient solutions were 27% for ammonium-N, 43% for orthophosphate-P, and 45% for nitrate-N.
- Column adsorption tests with synthetic stormwater yielded similar patterns, with more ammonium removed on a net basis than either nitrate or

phosphate. Although, as seen with the batch adsorption tests, WWS also removed some ammonium-N.

- Pinyon-juniper biochar increased the initial leachate concentrations of phosphorus in column experiments. Observed as well in the batch leaching tests, this indicates that P-J biochar may act as a low-level background source of soluble phosphorus.
- Adsorption of orthophosphate onto biochar is negligible at concentrations below 2 mg/L because of these increased leachate concentrations.
- P-J biochar did not increase concentrations of nitrate or ammonium in the batch leaching or column tests.
- Mixing biochar with native soils may marginally enhance the total nutrient adsorptive capacity of these soils, especially for ammonium and phosphorus.
- On a mass basis, over the full period of adsorption-desorption column testing, the 30% mixture of biochar with Washoe washed sand retained 4.8 g of orthophosphate-P per cubic meter and 41 g of ammonium-N per cubic meter (43 g m⁻³ of dissolved inorganic nitrogen).
- Iron-amended biochar can substantially increase the adsorptive capacity of P-J biochars for orthophosphate, but may also contribute to higher ammonium concentrations in leachate.

These results indicate that the use of P-J biochar as an adsorptive media amendment has some potential to reduce stormwater nutrient concentrations. Careful attention would be required, however, to determine whether P-J biochar is the appropriate corrective action needed, especially concerning typical concentrations of nutrients in the runoff and desired effluent concentrations. Nutrient leaching can occur for phosphorus and may be an undesirable effect if runoff concentrations are relatively low to begin with. In contrast, Fe-amended biochar appears to be very effective at phosphorus adsorption, but is likely to leach some ammonium-N. One additional observation is that many studies on adsorptive media simply conduct batch adsorption tests on the media of interest. We found that column adsorption and desorption experiments contributed to a better interpretation of these results, also yielding mass estimates of net adsorption. Finally, improved vegetation health could be an additional benefit from the use of biochar in bioretention systems by increasing the soil moisture-holding capacity and sustaining a base supply of adsorbed nutrients for growth.

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Appendix A. Using isotherms in adsorption experiments.

Adsorption isotherm curves are based on theoretical models that describe the adsorption of a soluble constituent in solution to the sorbent surface at a constant temperature. Many factors control adsorption such as pH, temperatures, kinetics, residence time, and ion competition. However, adsorption models do not differentiate between the adsorption controlling factors. Some models can represent particular adsorption mechanisms. The three most widely used isotherm models are the Freundlich, Langmuir and linear models (Cucarella and Renman, 2009). The best-fit model is usually selected from among these three. Best-fit models are determined by linearizing the Langmuir and Freundlich models respectively. Linearization places the model into a linear equation where a given intercept and slope are determined. Statistically calculated correlation coefficients and p-values help determine if the data adequately fit the most statistically correct modeled representation. Residual analysis on linearized data has been shown to be unreliable in isotherm model development and show significant deviation from model assumptions. Therefore, no residual analysis was completed on application of the linear models to our and reliance on the Pearson correlation coefficient (r²) was used to verify linear relationships (Ncibi, 2008).

For our purposes the amount of solute (e.g., phosphorus) adsorption per gram of adsorbent at equilibrium (mg/kg) is calculated through the following equation:

$$q_e = \frac{\nu(C_i - C_f)}{M_i} \tag{1}$$

where: q_e is adsorption in (mg/kg), v is the volume of solution in (L), C_i is the initial concentration of solution (mg/L), C_f is the final concentration after adsorption (mg/L), and M_i is the mass of adsorbent material (kg).

The simplest isotherm is the linear version. The linear version makes several assumptions, (1) the adsorbent has an unlimited number of binding sites, and (2) the rate of adsorption as concentration increases does not decrease as binding sites

become occupied. These assumptions can be described as physisorption or constant portioning that results in a linear correlation between adsorption and increasing concentration (Ryan, 2014). The linear isotherm is described by the following equation:

$$q_e = K_d C_{eq} \tag{2}$$

where: C_{eq} is the equilibrium concentration of adsorbent solution in contact with the soil (mg/L), K_d is an equilibrium constant that describes the tendency of the solute to adsorb onto a given sorbent, and q_e is the amount of solute adsorbed per unit weight of soil (mg/kg).

The linearized Langmuir isotherm describes the adsorption of neutral particles with the assumption that there is only coverage in a monolayer structure (Vesting et al., 2015). Monolayer adsorption is considered a chemisorption process controlled by the available binding sites on a particle surface (Ryan, 2014). Langmuir isotherm allows for the calculation of the maximum quantity of solute that can be adsorbed to the adsorbent surface, described by the following equation:

$$\frac{C_{eq}}{q_e} = \frac{1}{K_l q_{e(\max)}} + \frac{C_{eq}}{q_{e(\max)}}$$
(3)

where: C_{eq} is the equilibrium concentration of solution in contact with the soil (mg/L); q_e is the amount of solute adsorbed per unit weight of soil (mg/kg); K_l is the Langmuir adsorption constant related to the binding energy (dimensionless); and maximum monolayer adsorption capacity (mg/kg) is $q_{e(max)}$.

The linearized Freundlich isotherm model signifies a heterogeneous surface coverage and does not account for a finite number of adsorption sites. Instead the Freundlich model reflects the potential for adsorbates to increasingly become weakly adsorbed over time in the outer binding sites and is described through the following equation (Ryan, 2014):

$$\log q_e = n \cdot \log C_{eq} + \log K_f \tag{4}$$

where: C_{eq} is the equilibrium concentration of solution in contact with the soil (mg/L), *n* describes the adsorption intensity and is the slope of the linear model, q_e is the amount of solute adsorbed per unit weight of soil (mg/kg), K_f is the Freundlich isotherm constant, indicative of approximate adsorption capacity. The Freundlich isotherm constant is represented as the intercept of the linear model.

Isotherm models aid in describing the adsorptive capacity of solute to sorbent surfaces. The most appropriate isotherm model, whether linear, Langmuir or Freundlich, provides data that can support the description of contaminant migration through a soil column. Assuming no production or decay, in a homogenous saturated soil, with one dimensional contaminant transport we can model the retardation as migration occurs through a mass balance approach as described:

$$\frac{\partial C_{eq}}{\partial t} = D_L \frac{\partial^2 C_{eq}}{\partial x^2} - \nu_x \frac{\partial C_{eq}}{\partial x} - \frac{\rho_b}{\theta} \frac{\partial (K_d C_{eq})}{\partial t}$$
(5)

where: D_L is the longitudinal dispersion coefficient, v_x is water velocity through soils; θ is the gravimetric water content; C_{eq} is the equilibrium contaminant concentration in the water; q_e is the contaminant concentration in the solid phase, and ρ_b is the dry bulk density of the soil.

Equation 5 is manipulated to yield contaminant velocity (vc) as follows:

$$v_c = \frac{v_x}{1 + \frac{\rho_b K_d}{\theta}} \tag{6}$$

This simplifies to a final equation for the retardation coefficient (R_d), which can be defined by the ratio of the water velocity to the contaminant velocity. R_d , under ideal conditions where contaminant transport is considered one dimensional, in a homogeneously saturated soil (Zhang et al., 2008), can then be defined as follows:

$$R_d = 1 + \frac{\rho_b K_d}{\theta} \tag{7}$$

where: K_d is the adsorption partitioning coefficient, obtained by taking the derivative of the ratio of contaminant adsorbed per unit weight of soil (mg/kg), and concentration of solution in contact with the soil (mg/L). In some cases, $K_l q_{e(max)}$ at low concentrations is less than one, where $K_d = K_l q_{e(max)}$ (Drever, 1997). However, in the event that $K_l q_{e(max)}$ is larger than one within the Langmuir model K_d is evaluated through the following (Fetter, 1999) :

$$K_d = \left(\frac{k_l q_{e(\max)}}{(1 + K_l C_{eq})^2}\right)$$
(8)

In the event that the Freundlich model best represents the data set in question, K_d must be evaluated through equation 9.

$$K_d = \left(\frac{\rho_b k_f n C_{eq}^{n-1}}{\theta}\right) \tag{9}$$

All three models (linear, Langmuir and Freundlich) provide a given K_d coefficient. This coefficient can then be used in the advective-dispersion equation in an effort to model contaminate transport of a particular chemical constituent. By applying the distribution coefficient in the retardation calculation, we can solve for the advectivedispersion equation (Equation 5) based on specific boundary conditions and obtain a breakthrough curve. The breakthrough curve is used in an effort to predict the advancement of a chemical constituent through a ground water system. Predicted advancement is dependent on the retardation ratio (Fetter, 2001). If the chemical constituent is reactive and adsorption occurs, the retardation coefficient is at higher values, indicative of high contaminant retention relative to the water velocity through the sorbent medium. Under ideal conditions with no other chemical constituent competing for available binding sites, the constituent in question will advance only as adsorption sites increasingly become saturated, filling total adsorption capacity.

Appendix B. Iron-amended P-J biochar batch results.

Iron-amended biochar was developed from the $250-500 \mu m$ size class of P-J biochar and then used in batch equilibrium tests (Figure B1).



Figure B1. Percent nutrient removal by iron-amended P-J biochar (FeBC) in batch equilibrium tests with a sorbent to solution ratio of 1:20. Ammonium show net release (leaching) of ammonium from the FeBC.

Iron-amended biochar was then compared in batch equilibrium tests to the corresponding non-amended P-J biochar and to Washoe washed sand (WWS), used as a control media. These tests were run at a 1:20 adsorbent to solution ratio. Results shown in Figure B2 for phosphorus demonstrate the improved performance by Fe-amended biochar (FeBC) over non-amended biochar (BC), and show that both biochar materials yield superior performance compared to the WWS for phosphorus adsorption from solution.



Figure B2. Percent removal of phosphorus by P-J biochar (BC) compared to ironamended P-J biochar (FeBC) and by Washoe washed sand (WWS). Both types of biochar media are the 250–500 μ m size class. Data show consistently high removal efficiency from the FeBC.