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Phosphorus Transport and Distribution in Kentucky Soils Prepared Using Various Biochar Types

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PHOSPHORUS TRANSPORT AND DISTRIBUTION IN KENTUCKY SOILS PREPARED USING VARIOUS BIOCHAR TYPES

A Thesis
Presented to
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Master of Science

By
Anvesh Reddy

December 2012

PHOSPHORUS TRANSPORT AND DISTRIBUTION IN KENTUCKY
SOILS PREPARED USING VARIOUS BIOCHAR TYPES

Date Recommended 11/5/2012

Stuart Burris, Director of Thesis

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11/30/12

Dean, Graduate Studies and Research Date

I dedicate the thesis to my parents Mr. and Mrs. Kavitha Veera Reddy, my sister Amani Reddy, my friend Akhila Bethi and to Dr. Burris who supported and encouraged me the most during my challenging times here at Western Kentucky University.

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Anvesh Reddy December 2012 38 Pages
Directed by: Stuart Burris, Kevin Williams, Darwin Dahl
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Conserving the environment is an issue that is gaining popularity day by day. Phosphorus transfer from agricultural soils is an important environmental issue that is being closely observed as the transport of phosphorous to water bodies is adversely affecting water quality due to accelerated eutrophication. It is important to establish phosphorous models that accurately account for soil test phosphorous. Standard models like SWAT (Soil and Water Assessment Tool) and EPIC (Environmental Policy Integrated Climate) were designed for serving this purpose. They are now used as the basis for developing new models that can more accurately account for the phosphorus transport, depending on local soil conditions and external factors like climate, addition of biochar or other soil amendments. Our research involved development of new methods from published data that are applied to different soils from Kentucky that are incubated for various time periods, with and without the addition of biochar amendments. Changes in the soil labile phosphorus content after phosphorus addition to and depletion from these incubated soils was measured to discern the effect of biochar on the rates of phosphorus transport. The measured labile phosphorus was further analyzed using statistical analysis software drawing comparisons among treatments without biochar, with low temperature biochar and high temperature biochar for specific soil-biochar combinations. Loamy sand soils with both pine chips and switch grass biochar types have shown slightly increased leeching of phosphorus upon addition of biochar whereas clay loam soils have not shown any significant change upon addition of biochar.

INTRODUCTION

The use of inorganic fertilizers and various manure types for improving the growth of plants has been extensively followed. Excessive use of fertilizers and manures has caused a significant increase in the levels of soil phosphorus. The adverse effects caused by the transfer of excess phosphorus leaching from the agricultural soils to the ground waters are quite evident from the accelerated levels of eutrophication in phosphorus limited surface waters. This significantly impairs the water quality by the growth of algae and aquatic plants; thereby, limiting the use of the water bodies for drinking, industry, and refreshment.[1]

Solving the problem of leeching of excess phosphorus requires computer models that simulate phosphorus transport in the soils to determine the quantitative levels of phosphorus that should be added or maintained in the soils to prevent the leaching of the excess phosphorus that is not taken up by the plants. Knowledge of the pathways of phosphorus transport in the soils is necessary to develop these models. Although there are computer models that simulate phosphorus transport, they are not appropriately updated.[2] It is necessary to update these models and develop new models that accurately predict the changes in soil labile phosphorus depending on the levels of the phosphorus in soils and various agricultural practices.

Our research objective is to generate data from new methods, based on local soil types and soil biochar amendments, which are useful in updating the existing models for a more accurate estimation of soil labile phosphorus and effective use of fertilizers that can promote improvement of crop growth without leading to eutrophication. The methods involve estimation of the amount of phosphorus in different types of Kentucky soils that are readily available for plant uptake or leaching followed by addition of calculated amounts of phosphorus and biochar amendments to the soils and incubation for various time periods. Differences in the amount of phosphorus present in the solution pool, where the phosphorus is readily available for the plant or for leaching, and the active pool, where it is not readily available but bound to the soil, are calculated based on the data that is collected from the soils incubated with or without addition of biochar.

Data obtained will be of great use in developing models through which it can be known beforehand how much phosphorus is to be added to the field, so that it will aid the growth of plants without causing excess deposition of phosphorus in the field, thus preventing its leaching into ground water. Furthermore, the effect of addition of biochar amendments on the amount of soil test phosphorus that is available for leeching through water can also be included in the model.

BACKGROUND

Importance of Phosphorus in Agricultural Practices:

Phosphorus has been classified as macronutrient, as it is required in large amounts by plants.[3] Phosphorus plays a vital role in growth of plants because it constitutes the complex nucleic acid structure of plants, which regulates protein synthesis and is actively involved in cell growth and tissue development. It is also associated with complex energy transformations in the plant. Adding phosphorus to soil low in available phosphorus promotes root growth and winter hardiness, stimulates tiller, and often hastens maturity.[4] Phosphorus is added to the soil as one among the three nutrients supplied through fertilizers to promote growth of plants and crops. Although phosphorus is widely distributed in nature, it is not often found in its elemental form; instead, owing to its highly reactive nature, it combines with oxygen when exposed to air and forms phosphate in soil.[5] Orthophosphate is the simplest phosphate with the chemical formula PO_4^{3-} and is the only form in which the plants uptake phosphorus.[3]

Forms of Phosphorus in soil:

To understand the various forms of phosphorus present in the soil, it is important to understand various pools in which phosphorus exists in soil. Basically, phosphorus can be divided into three pools namely, Labile/Solution P pool, Active P pool, and Stable/Fixed P pool. Only a small amount of phosphorus present in the soil exists in the Labile P pool, and most of it is soluble and in the form of orthophosphate. This is the only pool that has some sort of mobility and constitutes the majority of phosphorus taken up by plants.[3, 6]

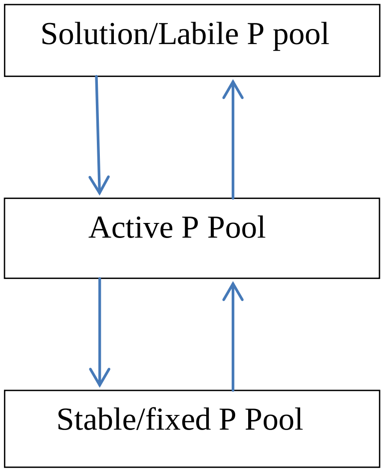


Figure 1: Picture representing the three Pools of phosphorus present in the soil and its cycling between the pools.

The Active P pool will contain inorganic phosphate that is attached or adsorbed to small particles in the soil, phosphate that has reacted with elements like calcium and aluminum to form slightly soluble solids, and organic phosphorus that can be broken down into soluble inorganic phosphorus compounds with the aid of micro-organisms by a process called mineralization. When plants take up phosphate from solution, the concentration of the Solution P pool decreases and it is replenished by the release of phosphorus from the Active P pool. Indirectly the Active P pool is the main source of phosphorus for plants. The Active P pool interacts rapidly with the Solution P pool and slowly with the Stable P pool. The Stable/Fixed P pool contains inorganic phosphate compounds that are insoluble to a greater extent and organic compounds that are resistant to mineralization for a longer period of time. However, some slow conversion between the Fixed P pool and the Active P pool occurs in the soil. A growing crop quickly depletes the phosphorus in the Soluble P pool and the ability of Active P pool to quickly replenish the Solution P pool in a soil is what makes a soil fertile with respect to phosphate.[3]

Role of Fertilizers and Manure in growth of crops and Phosphorus content in soil

When initially added, the phosphate in fertilizers and manure is reasonably soluble and available. When the fertilizer or manure comes in contact with soil, the water or moisture in the soil slowly dissolves the phosphorus in the fertilizers. This dissolved phosphorus in the Solution P pool is slightly mobile and carried away from the applied fertilizer where the phosphorus interacts with minerals already present in the soil either by adsorbing to the surface of soil particles or forming slightly insoluble compounds with calcium, iron, aluminum, etc. Furthermore, over time the adsorbed phosphate and the easily soluble phosphates form insoluble compounds with gradual reactions and cause the phosphate to become fixed and unavailable. Thus, adding to the Active P pool through fertilization will also increase the amount of stable/fixed phosphorus, resulting in the low efficiency of phosphorus fertilizers that is commonly observed. Most of the phosphorus fertilizer applied to the soil is not utilized by the crop in the first season and continuous application of more phosphorus than the plants can utilize increases the fertility of soil; however, much of the added phosphorus becomes fixed and unavailable. Depleting the Active P pool through crop uptake often causes some of the Fixed P pool to slowly convert to the Active P pool. However, an important aspect of the ability of soil to hold phosphate is that it cannot hold increasing amounts of phosphate in the solid phase without also increasing the soil solution phosphate. The increased amounts of phosphate in solution may lead to loss of large amounts of phosphorus through leeching.

Role of Soil phosphorus in altering the quality of water

Even though it is an essential element, phosphorus can be a strong pollutant. In spite of its low solubility, phosphorus has unfavorable effects on the quality of water due to the fact that the presence of it, even in low concentrations, can promote hazardous changes in water. This is the reason for the growing concern about the loss of phosphorus from soils to nearby water bodies. A careful examination of some properties of soil phosphorus will provide awareness regarding the main causes for the potential loss of phosphorus to water bodies. As most of the phosphorus in soil is present either loosely or strongly adsorbed to soil particles, when the soil particles are carried to nearby water bodies by rainfall, erosion, or irrigation methods, the water acts as sink and the phosphorus is slowly released from the soil particles to water. Soils have the capacity to hold larger amounts of phosphorus than what the plants require, but most of it is either in the Fixed P pool or the Active P pool, as the capacity is related to the amount of particles present in the soil. Therefore, overloading the soil (which is already rich in phosphorus that is not readily available to the plants because of either its state or several other external factors like soil pH, water content, climatic conditions, etc.) with excess phosphorus leads to two possibilities – leeching of increasing amounts of phosphorus in the Solution P pool or loss of soil particles or sediment enriched with phosphorus to water bodies by rainfall or erosion.

Relating extractable soil Phosphorus to Phosphorus loss in run-off

As discussed earlier, elevated levels of soil phosphorus can result from long term application of fertilizers at rates exceeding that required for uptake by plants. This has been proven in the case of Delaware soils where 65% of tested soils were found to contain excessive levels of phosphorus.[7]

Soil test phosphorus (STP) is the term used to signify the amount of phosphorus present in the soil as tested by a specific or suitable extractant. Dissolved reactive phosphorus (DRP) signifies the amount of phosphorus present in the runoff from a soil that is capable of dissolving in water and is reactive.[8] Biologically available phosphorus (BAP) is the amount of phosphorus from DRP that can be utilized by algal plants for their growth.[9] Compared to the application of manure in an inappropriate way, elevated levels of STP are a major and unmanageable source of DRP in runoff. In a recently concluded work on fescue pasture watersheds with a measured level of 150 mg/hectare of STP, mean annual phosphorus concentrations of 1.25 – 2.60 mg/liter were found in the runoff where elevated STP levels were responsible for 65 to 90% of annual phosphorus losses.[10] As the concentrations of STP and runoff DRP are related, elevated levels of STP may result in runoff adequately high in DRP to hasten eutrophication in phosphorus limited aquatic systems.[8] This relation must be considered in developing soil tests aiding in the measurement of STP and for developing phosphorus management approaches that endure high crop production and limit eutrophication.

Prominently used Extractants in Soil tests and their applications

The capacity to measure phosphorus concentration in soils is significant from both agricultural and environmental viewpoints. Initially the objective of designing the soil tests was to estimate the phosphorus fertility grade of soils for crop production, without much emphasis on their latent release of phosphorus to surface water.[11] However, now soil tests are being developed not only to identify the response of soils to addition of fertilizers but also to evaluate the soils for excessive phosphorus that can actually contribute to runoff or eutrophication.

Solid samples like soils should be brought into solution, as the soil tests used for phosphorus measurements necessitate that the phosphorus be present in a liquid matrix. This is done either by digesting the soil using acids or by extraction with a liquid such as water, weak acids, or weak salt solutions. The sample solutions from digestion or extraction should be filtered to remove solid particles before they are analyzed. For example the samples that are analyzed by extraction using water should be passed through a filter of specific pore size; the phosphorus analyzed from the filtered sample is considered to have been dissolved in the water. Some of the colloidal particles may pass through small pore filter papers, and the phosphorus adsorbed to these colloidal particles may or may not interfere with the results when analyzing the sample, depending on the method of analysis.[12]

Mehlich-III, Bray-Kurtz, and Olsen are among a few widely used extractants for testing soils and are commonly used in soil laboratories for the analysis of STP. The main aim of using these extractants is to evaluate the fertility status of soils for crop production, so they do not serve in the prediction of runoff phosphorus in soils.[13, 14, 15] Distilled water as a extractant is most appropriate for predicting runoff DRP in spite of its poor capability for dissolving phosphorus compared to other extractants.[8] Iron oxide strips (FeO) serve as the best extractant in closely estimating BAP, the amount of phosphorus in the runoff that can be available for the growth of algae.[9] Acidified ammonium oxalate is used in estimating the percent of phosphorus saturation in soils.[16]

The major source for pollution of streams and rivers in the USA is excessive use of phosphorus in agricultural production. Since 2007, about 200 million dollars has been spent by the US Environmental Protection Agency to alleviate the non-point source of pollution in several states.[17] Tools that are being developed to estimate phosphorus loss as a result of conservation practices involve monitoring simple export coefficients to complex process-based models.[18]

Recent advancements towards controlling eutrophication have brought into focus the potential of biochar to reduce the leeching of nutrients from agricultural soils.[19] Biochar is a by-product of the pyrolysis of biomass. Previously available data reveals that there is a strong affinity for biochar to adsorb phosphorus[20] (and some other nutrients), which suggests that this property of biochar may be used to control the leeching of phosphorus from agricultural fields and aid in improving the fertility of soil as well as decrease the possibility of eutrophication.

Biochar and its application in agricultural fields

Energy demands are increasing at a rapid pace along with increasing population. Researchers are in search of alternative sources that meet global energy demands, as the already existing non-renewable sources of energy like fossil fuels will not be able to satisfy the growing demands for energy.[21] Pyrolysis of biomass is one technology that is currently gaining popularity as an alternative energy source.[22] Pyrolysis involves heat aided chemical conversion of biomass to generate combustible gases, volatile oils, tar, and a carbon-rich, solid by-product charcoal, which can be used as soil amendment. Biochar is the term that is currently in use for pyrolysis derived charcoal when labeled for use as a soil amendment.[23]

One of the distinct characteristic of biochar is, though it contains carbon in stable aromatic forms similar to the forms of carbon in regular char, even in most favorable conditions like that existing in soil, carbon in biochar cannot be released into the atmosphere as carbon dioxide, unlike char.[24] Therefore, the process of pyrolysis is in use not only to generate biofuels, but also to withdraw carbon dioxide from the atmosphere by storing it in soils in the form of biochar. Due to its resistance against mineralization, it can also act as a sink for new carbon to be fixed by plants. Because of the ability of biochar to reduce greenhouse gases, the practice of applying biochar to soils is now slowly on the rise. When researchers started exploring the properties of biochar (before it was widely used to reduce greenhouse gases), it was found that the use of biochar as a soil amendment was prominent since the early 19th century. This practice has been recently reawakened with increased concerns for alternative energy sources and environmental pollution. Several reports of using charcoal in soil management in the past[25] and present, suggests that the practice has been followed worldwide for a long time.[26]

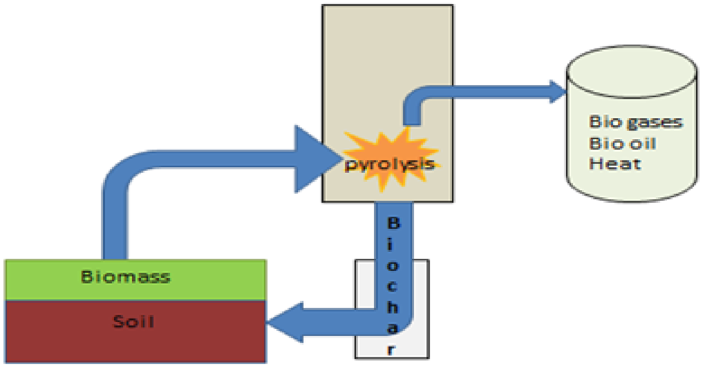


Figure 2: Schematic representation of pyrolysis process producing bioenergy and biochar.[2]

A study of the soils of the central Amazon basin, because of its high fertility compared to surrounding land that is infertile, revealed that these special soils called terra preta consists of high amounts of charcoal, which is thought to be the reason for the high fertility of this soil.[27] Deposits of charcoal dated back several hundred years. Though the reason for the high amounts of charcoal in the soil is thought to be of combustion of wood through forest fires, most of the researchers also believe that it may be part of a management strategy followed to improve the fertility of the soil. When the terra preta soils were tested, they were high in organic contents, nutrients like phosphorus, potassium, and calcium, and the water retention was 18% higher when compared to adjacent soils where charcoal is low or absent.[28] Researchers started observing various properties of biochar that may contribute to the fertility of terra preta. Studies on biochar have revealed that it has a cationic exchange capacity which is higher than the soil, minerals, and organic matter, due to its greater surface area and greater negative surface charge.[29] It is because of these properties that, when added to soil, biochar increases the pH of soil, improves the water holding capacity, and retains nutrients in the soil.[26,30] Biochar also appears to have the capacity to strongly adsorb phosphate with a mechanism that is not yet clear.[20,31]

The distinctive properties of biochar to transform the physical structure of soil and chemically stabilize nutrients offers the opportunity to improve crop yields while reducing the environmental pollution caused by the leeching of nutrients. The properties of biochar greatly depend on the production conditions, temperature used for pyrolysis, type of biomass used, soil type, and climatic conditions. Pyrolysis is done at low and high temperatures and for short and long time periods. Fast pyrolysis and high temperature pyrolysis are desired for generation of large amounts of bio-oil and combustion gases, respectively. Slow pyrolysis at moderate temperatures results in high yields of biochar.[32] Properties of biochar such as cationic exchange capacity, surface area, and pH vary greatly with production temperature. Both cationic exchange capacity and surface area are higher for biochar produced at higher temperatures (but the carbon recovery is very poor) and lower for biochar produced at a temperature range of 350-400°C. The optimum values can be derived by producing biochar using a temperature of 450-500°C.[24] There are no standardized procedures that are followed in the production of biochar; therefore, biochar may have varied effects on soil, depending on the temperature at which it is produced.[33] The application of biochar in controlling the loss of phosphorus from soils has been extensively studied in recent times because of the valuable role it can play in controlling increased eutrophication levels. Studies on several tropical, sub-tropical, and temperate soils revealed that biochar has significantly improved the nutrient or mineral levels in soils by preventing their leeching.[28, 29, 34] Although several possibilities have been reported showing that biochar may help in reducing eutrophication, there are also few evidences suggesting that biochar either has no effect or that it causes increased leaching of applied fertilizers under some conditions. [35, 36]

To determine the extent to which biochar is useful in improving the fertility of soil and in preventing the contamination of the environment through nutrient leaching, a thorough study needs to be done by taking biochars produced from various feedstocks, produced at various temperatures, and amending them with different types of soils at various rates under various conditions. To address the above issue to some extent, we have focused our study on understanding the effect of two different types of biochar on the rates of transport of phosphorus in two different soils from Kentucky that are treated with and without different phosphorus concentrations and incubated for various time periods.

MATERIALS AND METHODS

Soil and Biochar characterization

Two types of soils that originated from different parts of Kentucky were used for this study. Loamy Sand soil (L.S) was taken from the Pembroke area, which is an officially maintained land area near the USDA lab in Bowling Green. Clay Loam soil (C.L) was taken from the Smithdale area near Murray State University. The reason for choosing these soils was that they represented the general soil compositions of Kentucky. The composition of L.S soil is 65% sand, 22.5% slit and 12.5% clay while in C.L soil it is 32.5% sand, 40 % slit and 27.5% clay, as determined by the hydrometer method. The pH of the C.L and L.S soils were measured as 4.98 and 4.94, respectively. The soils have been previously tested for mineral content using ICP. Each soil was air-dried and passed through 2-mm sieve before use.

The two biochar types used for testing were produced from different feedstocks, namely pine chips and switch grass. In each biochar type, both low-temperature pyrolyzed (350ºC) and high-temperature pyrolyzed (700ºC) forms have been used for the study. The biochars were already tested for pH, elemental composition, dissolved organic carbon (DOC), percent carbon, and percent nitrogen prior to use. Soil and biochar pH was measured using an Orion combination probe manufactured by Thermo Electron Corporation. DOC was measured using an Elementar Americas / Model Vario TOC cube. Percent carbon and nitrogen were measured using an Elementar Americas / Model Vario Mx CN analyzer.

Element	C.L SOIL	L.S SOIL	PC 700	PC 350	SG 700	SG 350
Arsenic	< LOD	< LOD	1.36	< LOD	< LOD	3.07
Aluminum	72.2	51.9	603	478	52.9	66.4
Calcium	86.9	8.02	6750	5210	5870	4590
Cadmium	< LOD	< LOD	5.31	5.53	5.30	5.10
Copper	0.0690	0.0220	10.4	5.93	13.0	10.9
Iron	5.69	7.66	586	255	1670	252
Potassium	12.6	3.97	4040	3010	6290	4450
Magnesium	29.1	3.40	1680	1260	3790	2820
Manganese	3.34	2.18	185	136	139	95.1
Sodium	1.90	0.847	622	483	1250	929
Phosphorus	0.0440	3.14	601	445	2150	1490
Lead	0.0260	0.0390	< LOD	< LOD	< LOD	< LOD
Sulphur	2.77	0.847	262	231	508	625
Silicon	< LOD	< LOD	448	422	718	1530
Zinc	0.0320	0.0300	57.1	48.9	57.1	41.9

Table 1: Elemental composition in the soils and biochar used for this study as measured by ICP (mg/kg).

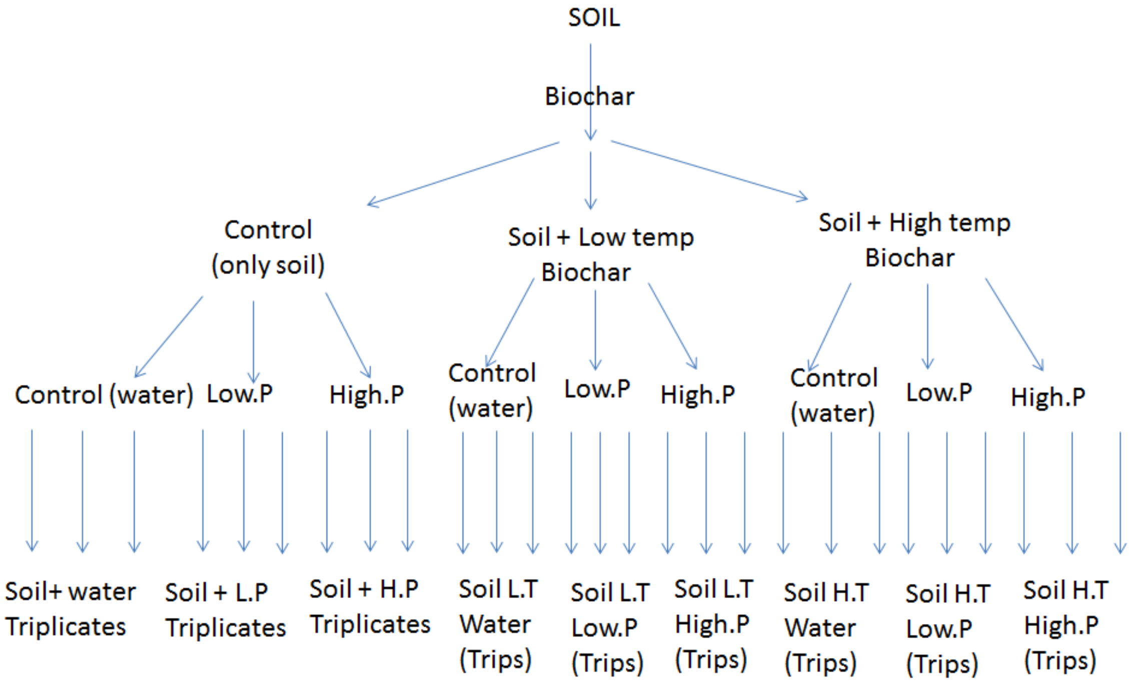
BIOCHAR TYPE	pH	DOC (mg/L)	%C	%N
PC 700	7.90	3.60	63.2	0.23
PC 350	6.20	20.5	73.9	0.18
SG 700	6.63	6.42	59.6	0.23
SG 350	9.51	66.3	74.1	0.35

Table 2: pH, DOC, Carbon and Nitrogen composition of the biochars used for this study

For each soil and biochar type combination, nominally 19 grams of Biochar was added to nominally 931 grams of soil in a cylindrical glass jar to obtain 2% w/w concentration. A control was prepared with just the soil (without addition of any biochar). All the glass jars were placed on a roller mixer and allowed to roll for 72 hours before they were used for the study so as to obtain a homogenized mixture of soil and biochar. Soil-biochar mixtures were incubated after addition of inorganic phosphorus (in the form of KH_2PO_4) at three rates, 0 ppm, 167 ppm (low-P) and 333 ppm (high-P) over a period of six months.[37]

Incubation Studies

From each Soil-biochar mixture, approximately 100 grams was accurately weighed out and transferred to a labeled plastic container. To each plastic container containing 100 grams of soil-biochar mixture, 20 milliliters of any one of deionized water, Low P solution, or High P solution was added so as to obtain triplicates of each combination of soil, biochar, and phosphorus concentration. Then the containers were closed and incubated for six months.



L.P = low phosphorus, H.P = High phosphorus, L.T = low temp Biochar, H.T = High temp Biochar

Figure 3: Schematic representation of the number of incubated microcosms for each Soil-Biochar combination.

At the end of 0, 1, 3, 7, 14, and 28 days, and 2, 4, and 6 months, soil samples were collected from each microcosm and subsequently analyzed for phosphorus. Occasionally, water was added to microcosms so as to maintain the moisture content as calculated by differences in the weight of incubated soils.

Extraction Experiments:

The purpose of using extractants is to bring the soil phosphorus present in various forms into solution so that it can be measured.[12] Three different extractants were used to perform extraction studies on the soil samples collected at the end of each sampling period. Extraction using water is performed to estimate the amount of phosphorus present in the solution pool and that is easily leachable. Mehlich-III extractant is a combination of 0.250 N NH_4NO_3 + 0.015 N NH_4F + 0.200 N CH_3COOH + 0.013 N HNO_3 + 0.001 M EDTA. Mehlich-III extraction is used to estimate phosphorus that is both loosely bound to the soil and in complexes with other cations apart from soluble phosphorus, which gives a rough estimate of total phosphorus available to the plant and not necessarily leachable. Extraction with acid digestion was used to estimate the total phosphorus present in the soil sample. About 6 grams of soil was collected at the end of each sampling period and used for the different extractions.

Two different sampling sizes, 0.5 grams and 2 grams were used to perform water extractions. For this, 0.5 grams and 2 grams of each soil sample collected were accurately weighed into separate centrifuge tubes and 40 milliliters of deionized water was added into each tube. The centrifuge tubes were then placed on a shaker for an hour and then centrifuged at 4000 rpm for 15-20 minutes, depending on sample size. The centrifuge tubes were then removed and the contents were filtered through a syringe fitted with a 0.45 µm filter.[38] The pH of the filtrate was measured and followed by colorimetric analysis.

For Mehlich-III extractions, 2 grams of soil were weighed out from each soil sample collected. These were placed into centrifuge tubes and 20 milliliters of Mehlich-III extractant was added to each of the centrifuge tubes.[13] Centrifuge tubes were then placed on a shaker for an hour and then transferred to a centrifuge. The samples were centrifuged for 10 minutes at 4000 rpm and subsequently filtered through a syringe with a 0.45 µm filter. The pH of the filtrate was measured and it was then used for colorimetric analysis.

Microwave Assisted soil Extraction

The remaining soil (after being sampled for water and Mehlich-III extractions) was allowed to dry. Once dry enough, 0.25 grams of it was accurately weighed and transferred to a reaction vessel to be treated with 3 milliliters of concentrated hydrochloric acid and 9 milliliters of concentrated nitric acid in a hood. The soil was allowed to react with acids for half an hour and then placed in a Microwave Assisted Reaction Station (MARS) to further digest the soil samples at high temperature (175°C) and pressure (>50 psi). Almost all the Phosphorus present in the soil comes into the solution through this treatment.[39] Reaction vessels are then removed from the MARS and the samples allowed to cool down in the hood. The samples were then filtered to remove particulate matter and the filtrate was diluted before being analyzed using ICP.

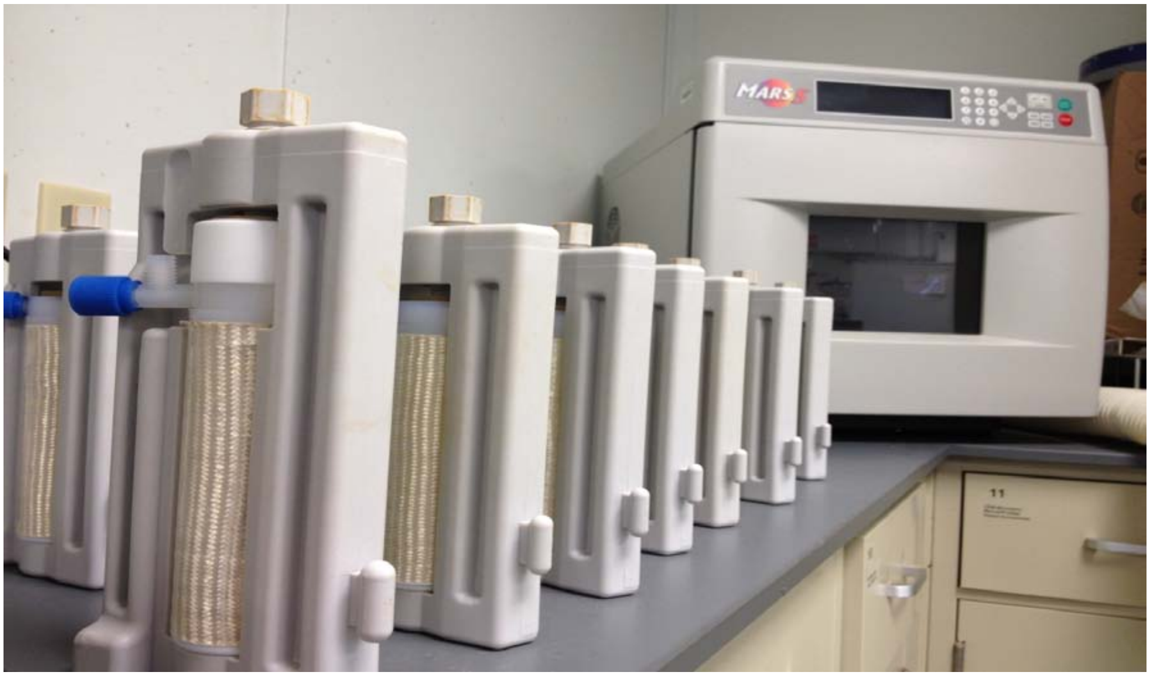


Figure 4: Reaction vessels and Microwave Assisted Reaction System Instrument.

Colorimetric Determination of Phosphorus

The wet chemical colorimetric analysis only works for orthophosphates; therefore, other forms of phosphates were brought into the solution using various extraction procedures. The samples from water extractions and Mehlich-III extractions are diluted to have the phosphorus concentrations in samples within the detection limit of the colorimeter (<0.8 ppm). The method that was used for colorimetrically analyzing the phosphorus present in the extraction samples was the ascorbic-acid method. In this method ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an intensely colored antimony phosphomolybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The absorbance is proportional to the phosphorus concentration. The complex is not stable and analysis must be performed within 30 minutes of adding the ammonium molybdate and antimony potassium tartrate.[40]

Figure 5: Colorimeter used for analysis of phosphorus by the 72 well plate method. Model: EL 80S.

RESULTS

The amounts of phosphorus in different soil samples extracted using water and Mehlich-III extractants over a 120 day incubation period were analyzed. Decay curves for the amount of extractable phosphorus were plotted for different soil treatments over the 120 day incubation periods. From these curves, the data was analyzed for a relationship among the different soil treatments. The decay curves from the 2 gram water extractions were irregular because the large sample size could not be handled by the centrifugation method followed during extraction. The decay curves from Mehlich-III extractions did not show any appreciable changes; rather, they were straight lines, which supports the fact that the Mehlich-III extraction gives the total amount of phosphorus in the soil active pool, which generally stays constant.[13] The curves for the 0.5 gram water extractions exhibited an exponential decay with good correlation, and that data was used to evaluate the effect of biochar on various soil treatments.

Among the 0.5 gram extractions, the soil treatments that were without biochar or added phosphorus (blank soil treatments) yielded constant curves over the period of time. These were not significant for the comparison models. Comparisons were made within the low phosphorus and high phosphorus treatments for each soil-biochar combination. Phosphorus sorption coefficient (PSC) values were used in comparison models that give the amount of added phosphorus that remains labile, which is PSC = P [Soil BC with added LP/HP] – P [Soil BC without added Phosphorus] / LP/HP .[37] PSC values from water extractions were then plotted against the incubation periods to observe the change in values with time and difference in slope of curves with various biochar treatments. In order to more easily observe the relationship between the various treatments, the data was transformed into a linear format by taking the natural logarithm of the PSC and of the day of the measurement.

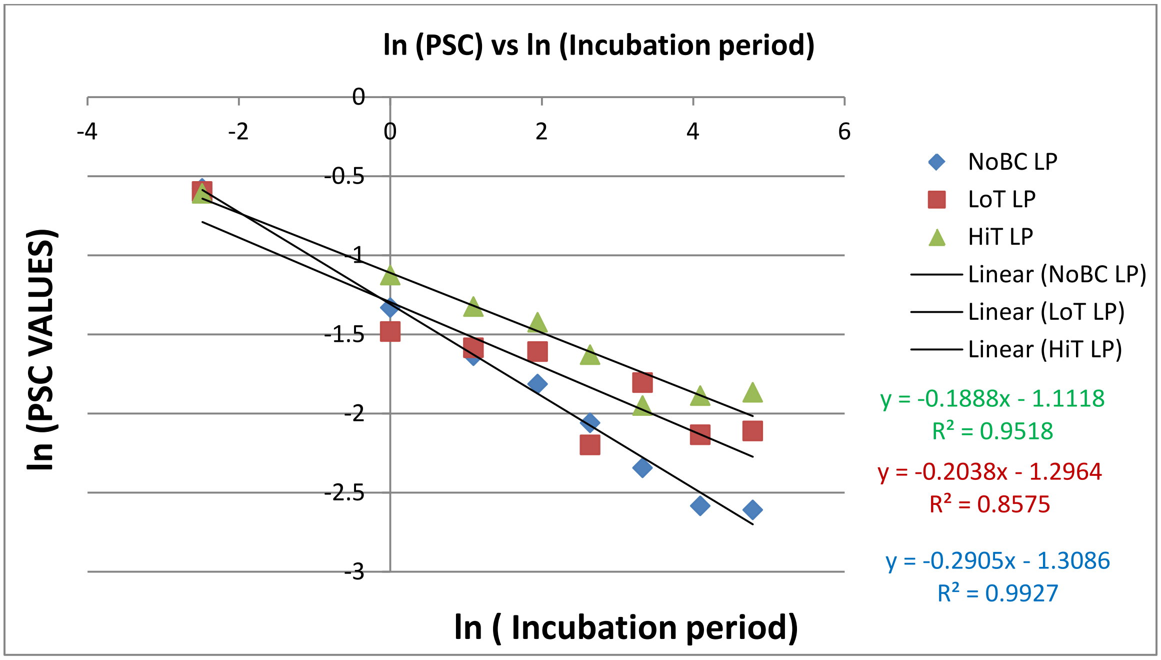


Figure 6: Biochar comparative logarithmic decay curves with PSC values plotted against incubation period (days) for sandy loam soil with low phosphorus (LP) concentration added.

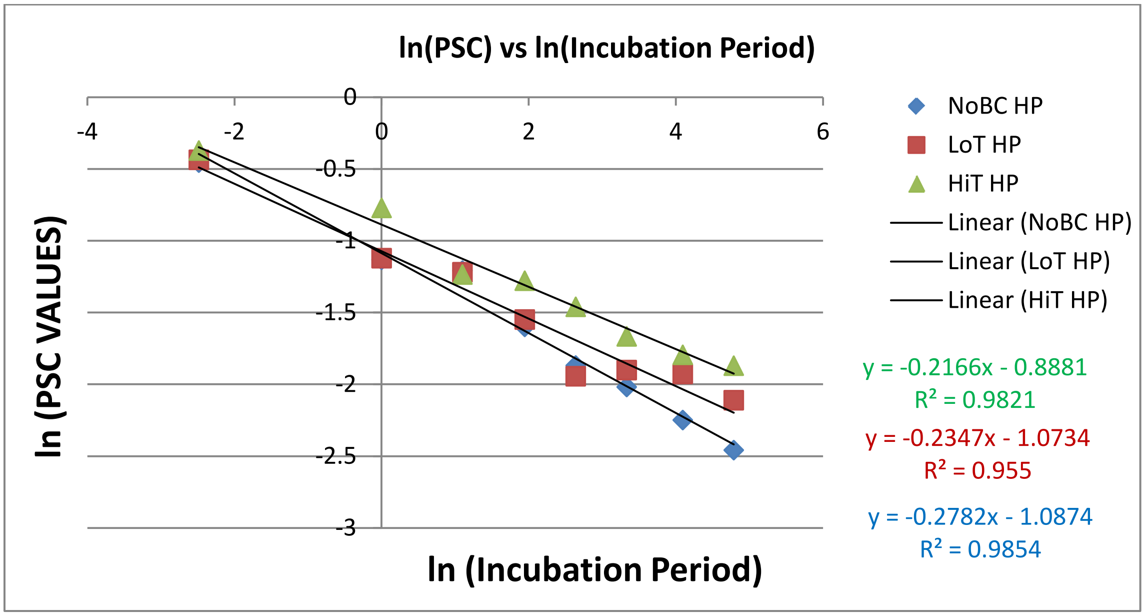


Figure 7: Biochar comparative logarithmic decay curves with PSC values plotted against incubation period (days) for sandy loam soil with high phosphorus (HP) concentration added.

To understand the differences among the curves, they were further analyzed using Statistical Analysis Software (SAS). The main evaluative tool utilized was ANALYSIS OF COVARIANCE (ANCOVA) in the generalized linear model. For those whose slopes were significantly different from each other, pairwise comparisons were made at Day 7, Day 60 and Day 120 to observe the differences with progressing time of incubation.

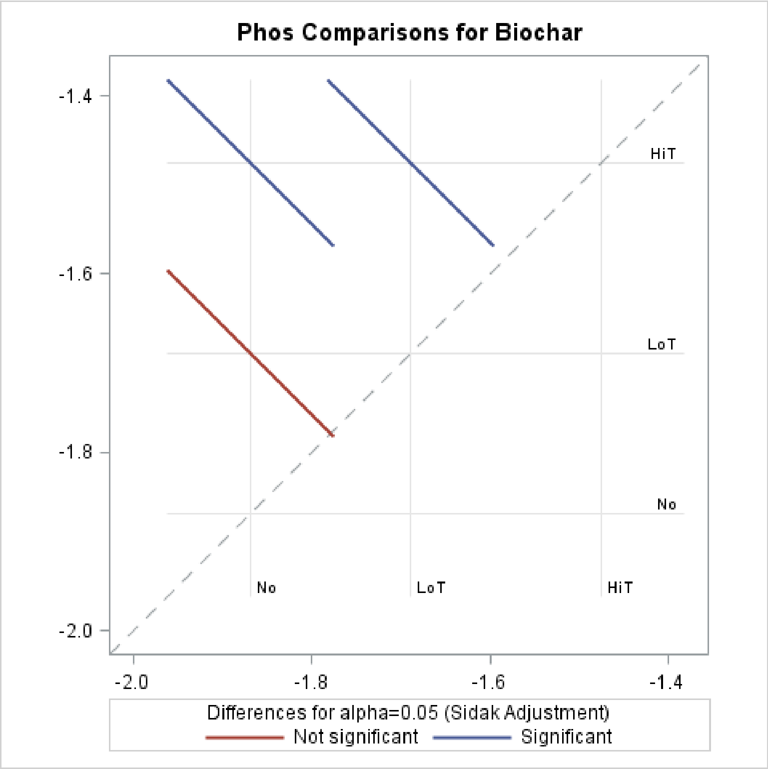


Figure 8: Pairwise comparisons of PSC values at Day-7 for various pine chips biochar treatments of sandy loam soil with low phosphorus (LP) concentration added.

Comparisons similar to Figure 8 were made at Day-60 and Day-120 and the significance of the differences was established based upon t-test values. SAS provides P-values for various comparisons to determine if the compared values are significantly different. If the P-value for a comparison is <0.05 then the compared values are said to be significantly different. The accuracy of the analysis through SAS was verified by performing ANCOVA using XL Stat and SPSS software packages.

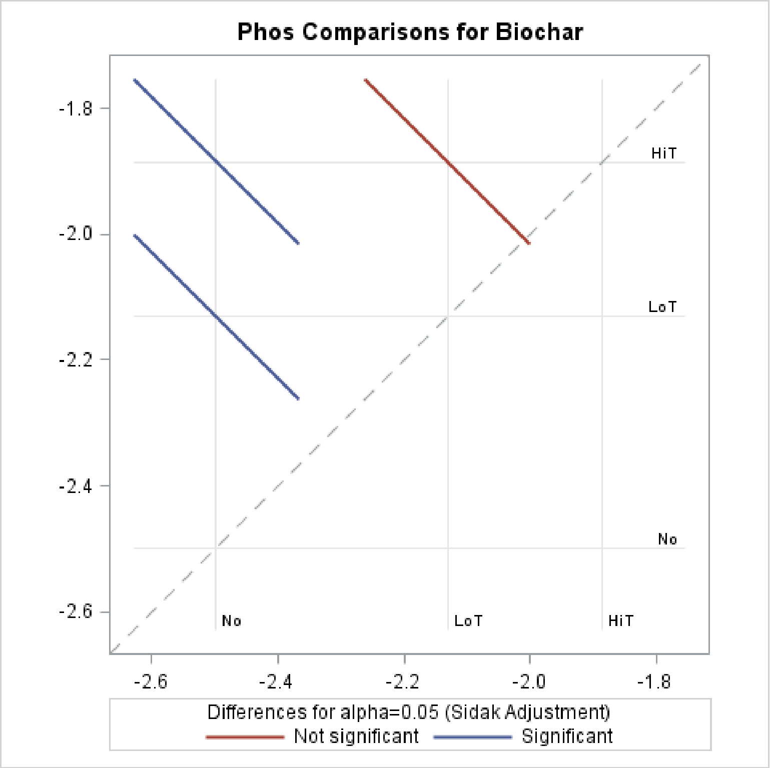


Figure 9: Pairwise comparisons of PSC values at Day-60 for various pine chips biochar treatments of sandy loam soil with low phosphorus concentration (LP) added.

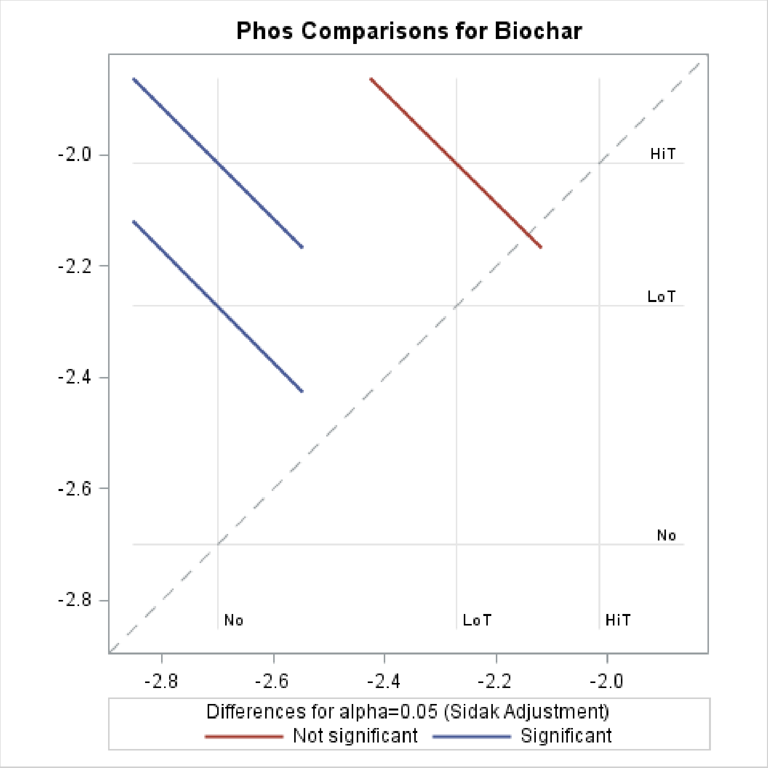


Figure 10: Pairwise comparisons of PSC values at Day-120 for various pine chips biochar treatments of sandy loam soil with low phosphorus (LP) added.

Loamy Sand soil with Pine chips biochar and LP	Day-7	Day-60	Day-120
No BC Vs LoT BC	0.0639	0.0050	0.0053
No BC Vs HiT BC	<0.0001	<0.0001	<0.0001
LoT BC Vs HiT BC	0.0231	0.0700	0.1177

Table 3: P-values from pairwise comparison of PSC values at Day 7, Day 60 and Day 120 of various treatments of sandy loam soil with pine chips biochar and added low phosphorus (LP). Red color indicates the value is not significant.

Loamy Sand soil with Pine chips biochar and HP	Day-7	Day-60	Day-120
No BC Vs LoT BC	0.1866	0.0397	0.0419
No BC Vs HiT BC	<0.0001	<0.0001	<0.0001
LoT BC Vs HiT BC	0.0010	0.0049	0.0112

Table 4: P-values from pairwise comparison of PSC values at Day 7, Day 60 and Day 120 of various treatments of sandy loam soil with pine chips biochar and added high phosphorus (HP). Red color indicates the value is not significant.

Loamy Sand soil with Switch grass biochar and LP	Day-7	Day-60	Day-120
No BC Vs LoT BC	0.0050	0.0006	0.0008
No BC Vs HiT BC	<0.0001	<0.0001	<0.0001
LoT BC Vs HiT BC	0.0003	0.0032	0.0088

Table 5: P-values from pairwise comparison of PSC values at Day 7, Day 60 and Day 120 of various treatments of sandy loam soil with switch grass biochar and added low phosphorus (LP).

Loamy Sand soil with Switch grass biochar and HP	Day-7	Day-60	Day-120
No BC Vs LoT BC	0.0020	<0.0001	<0.0001
No BC Vs HiT BC	<0.0001	<0.0001	<0.0001
LoT BC Vs HiT BC	<0.0001	0.0012	0.0067

Table 6: P-values from pairwise comparison of PSC values at Day 7, Day 60 and Day 120 of various treatments of sandy loam soil with switch grass biochar and added high phosphorus (HP).

The slopes of the decay curves for all treatments groupings (same soil, biochar, P addition) involving clay loam soil were similar to each other when analyzed using SAS, that is, the P-values were greater than 0.05 for all the comparisons performed so there was no requirement for performing pairwise tests as the slopes were almost equal but the curves were further tested for difference in intercepts using the equal slopes model by SAS.

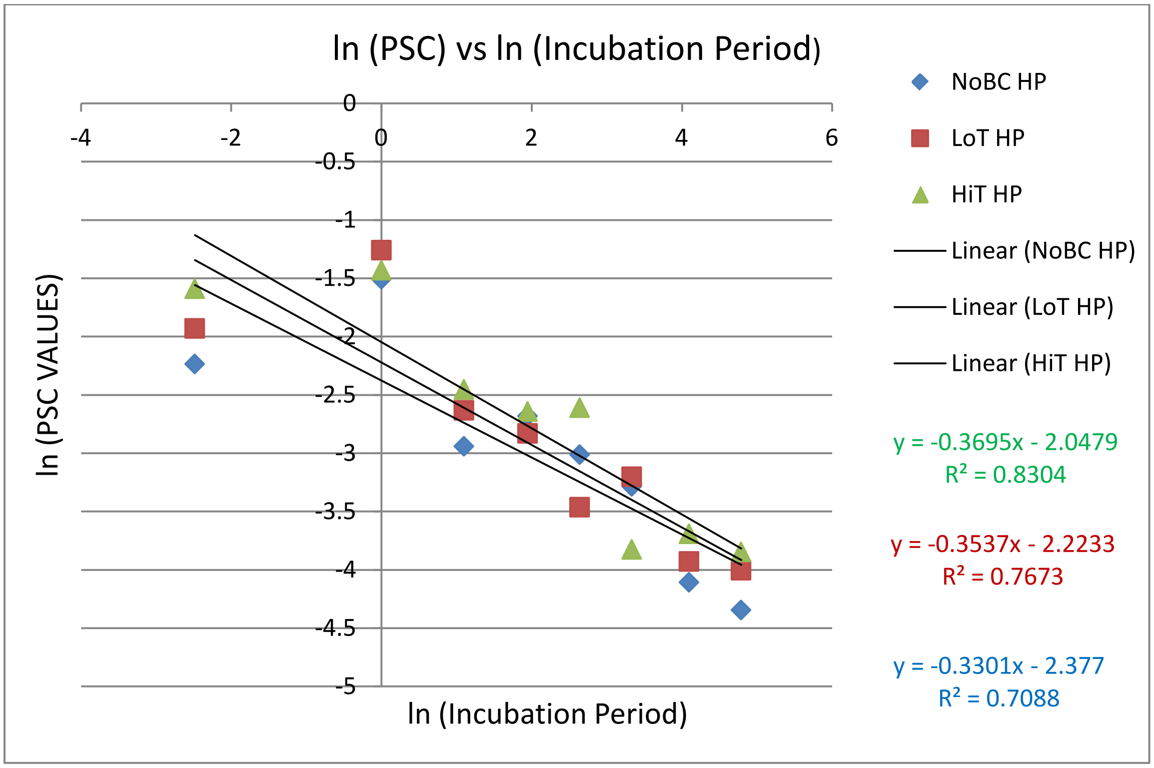


Figure 11: Biochar comparative logarithmic decay curves with PSC values (mg/kg) plotted against incubation period (days) for clay loam soil with high phosphorus (HP) concentration added.

The decay pattern of phosphorus in the active pool was studied by using the phosphorus concentrations that are a result of the difference between Mehlich-III and water extractions. The decay pattern of phosphorus in the stable pool was studied by using the phosphorus concentrations that are a result of the difference between total digestion and Mehlich-III extractions.

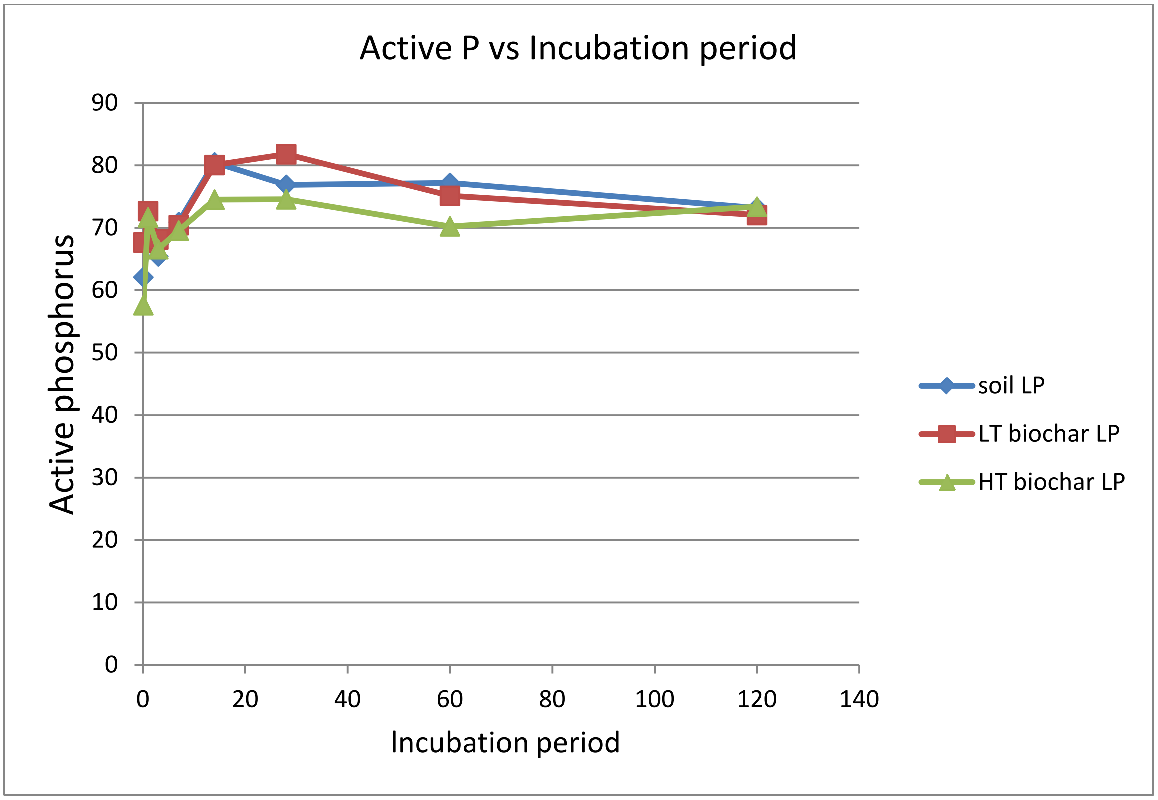


Figure 12: Curves of Active P Vs Incubation period for various biochar treatments of sandy loam soil with pine chips biochar and low phosphorus (LP) concentration added.

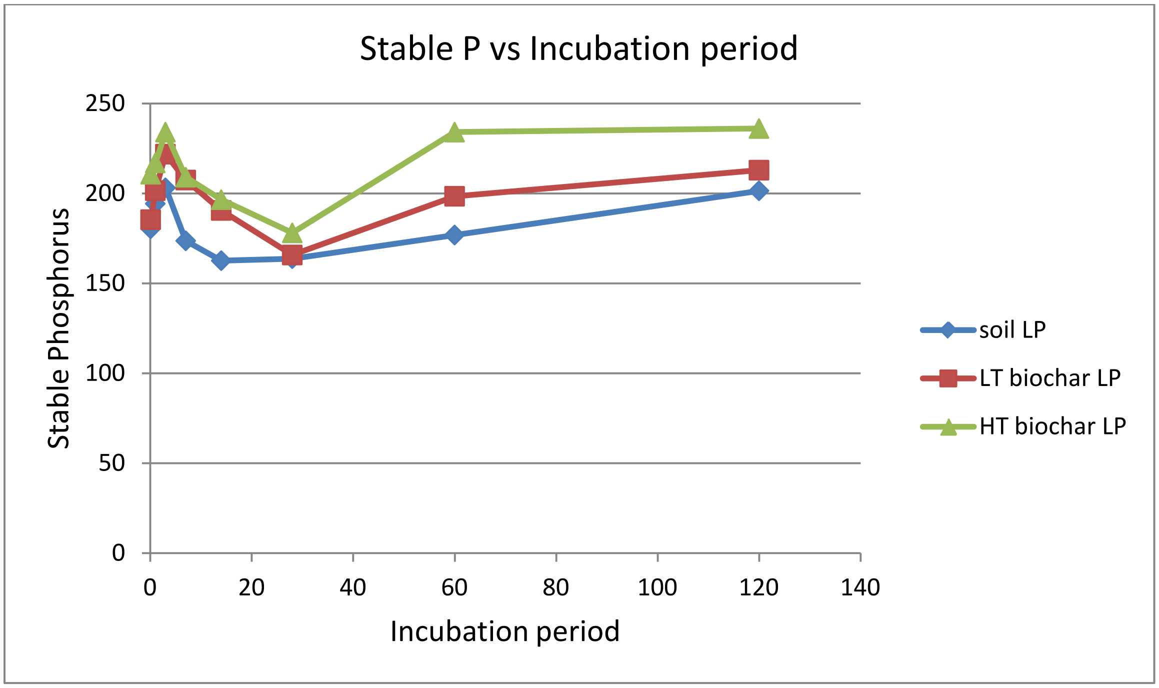


Figure 13: Curves of Stable P Vs Incubation period for various biochar treatments of sandy loam soil with pine chips biochar and low phosphorus (LP) concentration added.

DISCUSSION

Statistical analyses of phosphorus concentrations from water extraction experiments for various treatments of sandy loam soil have indicated that there are significant differences in the slopes among different treatments within a type of biochar; however, in case of clay loam soil treatments, there were no significant differences in the slopes of different biochar treatments within a biochar type. P-values mentioned in Tables 3 and 4 indicate that for the sandy loam soil pine chips biochar combination treatments there are significant differences in the slopes between treatments without biochar, with low temperature biochar, and with high temperature biochar, irrespective of whether it is a low phosphorus treatment or high phosphorus treatment. In the case of treatments of sandy loam soil with pine chips, the pairwise comparison indicates that there is no significant difference in the PSC values of treatment with no biochar and that with low temperature biochar at day-7, but as the incubation time progresses, there is a difference among the PSC values at day-60 and day-120. There is a slight difference between the low phosphorus and high phosphorus treatments of sandy loam and pine chips biochar combination. For the low phosphorus treatment with low temperature biochar compared to high temperature biochar, the PSC values are not different at prolonged incubations. However, in the case of high phosphorus treatment with low temperature biochar and high temperature biochar, the PSC values are significantly different from each other at prolonged periods of incubation. All the combinations of sandy loam and switch grass biochar combinations, irrespective of whether they are low phosphorus treatments or high phosphorus treatments, show that the slopes are significantly different for treatments without biochar, with low temperature biochar, and with high temperature biochar. Further, the P-values from the pairwise comparison as provided in Tables 5 and 6 indicate that the differences in the PSC values between the treatment without biochar, with low temperature biochar, and with high temperature biochar are more pronounced with increased incubation time although the differences are small.

Treatment	Sandy loam Pine chips with LP	Sandy loam Pine chips with HP	Sandy loam Switch grass with LP	Sandy loam Switch grass with HP
No Biochar	-0.2905	-0.2782	-0.2905	-0.2782
LT Biochar	-0.2038	-0.2347	-0.1912	-0.1883
HT Biochar	-0.1888	-0.2166	-0.1731	-0.2069

Table 7: Slopes of decay curves for various Loamy sand soil-biochar treatments.

Quantitatively the slopes of the logarithmic decay curves indicate that in each combination of sandy loam soil and biochar type the treatment with no biochar holds more of the labile phosphorus back in the soil. The excess loss of phosphorus in sandy loam treatments with biochar thus indicates that the addition of biochar, irrespective of whether it is a low temperature biochar or high temperature biochar, leads to excess runoff phosphorus in the water extractions even though the difference is very small comparatively. The loss of phosphorus is more pronounced in the case of high temperature biochar treatment in all cases of sandy loam except for high phosphorus treatment of loamy sand and switch grass biochar combination. Even though the treatments with biochar are expected to have low PSC values compared to soil only treatments, as biochar is viewed more as a medium to prevent leeching, our observations with loamy sand soil have shown that treatments with biochar reportedly had higher PSC values than soil only treatments in congruence with a few studies that have shown similar results.[35, 36]

All the treatments involving clay loam soil have shown that the slopes are not different for the treatments with or without biochar. A careful look at Figure 11 showing decay curves for the clay loam pine chips biochar combination with added high phosphorus indicates that the curves stabilize with progressing incubation period and almost have equal slopes. Similar behavior is observed for other combinations of clay soil treatments. Further, the equal slopes model for the clay soil treatments indicates that even the intercepts do not have any significant differences between the treatments with or without biochar.

Soil – Biochar treatment	ANCOVA P-value for slope comparison (No BC vs LoT BC vs HiT BC)
Clay loam soil with Pine chips Low phosphorus	0.6692
Clay loam soil with Pine chips High phosphorus	0.9383
Clay loam soil with switch grass Low phosphorus	0.7190
Clay loam soil with switch grass High phosphorus	0.3789

Table 8: P-values for logarithmic decay curves slopes compared using SAS for various treatments of clay loam soil.

The fact is further supported by the P-values that are well over 0.05 for all slopes compared using SAS, for no biochar, low temperature biochar and high temperature biochar treatments for each soil biochar combination of clay soil, irrespective of whether it is low phosphorus or high phosphorus treatment. No striking changes have been observed in active or stable P pools as indicated in Figures 12 and 13 apart from phosphorus movement between active and stable P pools to stabilize the system. The same pattern is observed for all soil biochar combinations for loamy sand soil; whereas, for clay soil the changes in active and stable P pools were much less.

As discussed earlier in the introduction, the effect of biochar on the leeching of nutrients in soil is dependent on the type of biochar and its sources, kind of soil, climatic conditions like temperature and humidity, and the conditions in which the studies are performed. The biochar studies that we have performed are at lab scale and in closed conditions so they might not be in complete agreement with the natural phenomenon occurring outside of the lab. However, they are performed to gain more insight into the interactions of biochar and soil. Among the two types of soils that we used in our study, loamy sand soil was easier to handle compared to clay loam soil that reacts strongly with the biochar and minerals present in the soil. The studies indicated that more complex experimental variables are needed for handling clay soil. The studies also provided enough knowledge for improving several methods used in the experiments such as selecting appropriate sample sizes for extraction studies. The 2-gram water extractions used in the study were complex in handling, as centrifugation could not clearly separate the soil and water. More sophisticated methods are indicated to maintain the moisture content in the incubated soil treatments, as depleting moisture from treatments with time had a large impact on the amount of phosphorus extracted. Adding up of the calculated amount of water to all the treatments merely by using a pipette had a major impact in disturbing the phosphorus levels in various pools in the soil.

The accuracy of the experiments should be tested further at field scale before it can be assured that the biochar behaves the same way in the natural conditions existing in the environment. Models can be developed from the data obtained that can provide information beforehand for effective use of biochar amendments, organic and inorganic fertilizers, and prevention of excess deposition of phosphorus in the field, thus preventing its leeching into ground water. Water run-off models are also an alternate way of estimating the run-off phosphorus by artificially creating a system with water draining through soil-biochar mixtures and analyzing the amount of phosphorus in the collected run-off water.[10, 21, 33, 35] Water run-off models can be of great significance where comparison with the model being used could help in learning the credibility of the model and aid in development of new models.

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