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Effects of Biochar and Crop Rotation with Pigeon Pea on Soil Phosphorus Availability in Mkushi and Kaoma, Zambia

Ingrid Slettemark Hovden Environment and Natural Resources

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### Abstract

Low phosphorus (P) availability in sub-Sahara African agriculture strongly effects yield and food production negatively. As fertilizer prices increases, the need for human interventions to increase soil plant available P besides fertilization is high. The aim of this thesis was to assess the P availability when implementing a crop rotation with pigeon pea to maize fields, and application biochar the following season made of pigeon pea feedstock. The study took place in two regions in Zambia (Mkushi and Kaoma), and generally these soils are highly weathered and rich in oxides. Pigeon pea is a relatively new crop in Zambia, and its effects on P availability from a crop rotation is not widely studied. A numerous studies on biochar have reported positive effects on P availability, however biochar made from pigeon pea feedstock specifically has not been much studied.

The main results implied that plant available P did not increase with pigeon pea crop rotation in either region (p>0.05). However, extraction of P from the biochar showed that the P content of pigeon pea biochar was quite high. For this reason, the plant available P increased significantly with application of biochar (p<0.05), thus decreasing the amount of fertilizer necessary as biochar contributed with P. Also, due to biochar's ability to retain P, it was concluded that the effects of fertilizer increases when applied together with biochar. Data implied that higher P-AL was connected to higher C:P ratio and higher DPS. DPS was negatively correlated with Q<sub>max</sub> (p<0.05) for Mkushi samples, however some samples did not imply such correlation which may be due to precipitation of Ca- or Al-P.

Furthermore, to use pigeon pea as a crop rotator and as biochar feedstock due to its great potential to increase plant available P, was recommended to the farmers in Mkushi and Kaoma. However, the lack of data for the season with biochar in Kaoma encouraged for further research of pigeon pea biochar in these soils. Furthermore, long term studies on crop rotation with pigeon pea and biochar application to dig further into the crop rotation effects on P availability, was also suggested.

## Sammendrag

Lav fosfor-tilgjengelighet i jordsmonn i Afrika sør for Sahara påvirker avlinger og matproduksjon negativt. Prisen på gjødsel øker, og behovet er høyt for tiltak som vil øke fosfortilgjengeligheten i jorda, foruten gjødsling. Målet med denne oppgaven var å undersøke tilgjengeligheten av fosfor (P) når et vekstskifte med belgplanten «pigeon pea» implementeres med mais, og når det tilsettes biokull laget av pigeon pea-planterester sesongen etter. Studien foregikk i to regioner i Zambia (Mkushi og Kaoma), og generelt er jordsmonnene der sterkt forvitra og rike i oksider. En mengde studier er gjort på biokull og de positive effektene det har på tilgjengeligheten av P. Pigeon pea er en relativt ny vekstplante i Zambia, og effektene veksten av denne planten har på forfortilgjengelighet er ikke mye undersøkt.

Hovedresultatene viste at det var ingen signifikant økning i plantetilgjengelig P etter en sesong med pigeon pea i noen av regionene (p>0.05). Ekstraksjonen av P fra biokullet, viste et høyt innhold av P i biokull laget av pigeon pea, som var noe av grunnen til at plantetilgjengelig P viste en signifikant økning etter biokull var tilsatt i jorda (p<0.05). Med dette minker mengden fosfor nødvendig, også på grunn av evnen biokullet hadde til å holde tilbake P. Det ble også konkludert at effekten av gjødsling økte sammen med tilførsel av biokull. Data viste at høyere P-AL var koblet til høyere C:P forhold og høyere DPS. DPS var negativt korrelert med  $Q_{max}$  (p<0.05) for jordprøver fra Mkushi, men det var derimot noen prøver som ikke viste en slik korrelasjon, som sannsynligvis var på grunn av en utfelling med kalsium eller aluminium.

Videre så ble det anbefalt for bønder i Mkushi og Kaoma å implementere et vekstskifte med pigeon pea og biokull-tilførsel av pigeon pea-planterester på grunn av potensialet til å øke plantetilgjengeligheten av fosfor. Derimot så oppfordres det til videre forskning på pigeon pea biokull i Kaoma på grunn av mangelen på felt-data i denne regionen. Videre vil langvarige studier på et pigeon pea vekstskifte med biokull-tilførsel over flere sesonger kunne øke kunnskapen om hvordan jordas mekanismer i forbindelse med fosfor foregår.

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List of abbreviations Al = aluminiumAL = ammonium lactate  $Al_{ox} = aluminium oxides$ BF = biochar field samples $BL = biochar \ lab \ samples$ C = carbonCa = calsiumCA = conservation agriculture CEC = cation exchange capacity DPS = degree of phosphorus saturation Fe= iron  $Fe_{ox} = iron oxides$ HWEC = hot water extractable carbon HWEP = hot water extractable phosphorus K = Kaoma  $K_L$  = Langmuir affinity constant M = Mkushi N = background samplesOM = organic matterP = phosphorus $PO_4 = phosphate (including HPO_4^-, H_2PO_4^{2-} and PO_4^{3-})$ PP = pigeon pea samples  $Q_{max} = adsorption maximum$ SOM = soil organic matter SSA = Sub-Saharan Africa Tot C = total carbon

Tot N = total nitrogen

## 1. Introduction

Hunger and malnutrition are global challenges, addressed in the second of the 17 United Nations sustainability development goals. Food security is a major concern with a rapidly growing population, especially in sub-Saharan Africa (SSA). SSA food systems are vulnerable to climate change, and with most of the populations' livelihood being highly dependent on agriculture (Serdeczny et al., 2016), there is need for agriculture that is more adaptable to climate change. In addition, the food security challenge in much of Africa is exacerbated by significant and large scale soil degradation which affects soil fertility. Nutrient limitation is a central issue contributing to poor crop yield in SSA as reported by Stewart et al. (2020) For smallholder farmers fertilizers commonly are too expensive (Magnone et al., 2019), especially nowadays as global fertilizer prices have increased substantially the last year (Schmidhuber, 2022). Phosphorus (P) is one of the most essential nutrients for plant growth together with nitrogen (N) and potassium (K), and a P deficiency limits plant growth. Many soils in SSA suffers from low availability of P (Magnone et al., 2019), thus assessing possible solutions for improving the P availability in these soils will be essential to increase yield. This thesis focuses on P availability and possible solutions to enhance available P in agricultural soils of Zambia.

#### 1.1 Agriculture in Zambia

Agriculture plays an important role for livelihoods in Zambia (Chikowo, n.d) where the majority (83%) of the farmers have small scale maize production, both for income and for own consumption (Mulenga et al., 2017). Maize has been the staple food in Zambia, and other crops grown are groundnuts, sorghum, millet and cassava (Britannica, n.d). Pigeon pea is a relatively new crop in Zambia, but Kenya, Malawi, Uganda among other countries in SSA have grown pigeon peas a few decades already (Kaoneka et al., 2016).

In Zambia, smallholder farmers commonly practice conventional methods of land preparation involving animal draught power, while the interest for conservation agriculture (CA) in Zambia started in the early 1980s (Farooq & Siddique, 2015). Conservation agriculture is based on the principles of minimal soil disturbance, permanent residue cover, crop rotations and weed control (Farooq & Siddique, 2015). A meta-study with 933 studies in 16 countries

in SSA (including Zambia), reported that CA had significant positive effects on maize yields compared to conventional agriculture (Corbeels et al., 2020).

#### 1.2 Nutrient availability

There are several biophysical factors affecting plant growth such as water input and soil water retention, light and temperature and nutrient availability (Schlesinger et al., 2020). Plants need sufficient nutrients for growth and apart from fertilizers, the main source in SSA soils is organic matter (OM). However, soils in SSA face alarming negative nutrient balances since the input of nutrients from fertilizer and mineralization of OM is smaller than the output from crop harvest, leaching and erosion (Faerge & Magid, 2004). In Africa, a great number of studies have reported overall negative N, K and P balances (Cobo et al., 2010). However, P is generally less susceptible to losses through leaching because of its lower mobility in soils compared to N and K (Cobo et al., 2010). Thus, issues related to P availability in SSA soils, which is characterized as highly weathered, is often more associated with excessive retention in the soil than leaching (Reed et al., 2012).

#### 1.3 Phosphorus

Phosphorus (P) is an essential element for plant growth, which means that the plant does not function optimally without it. P is a key component in ATP (adenosine triphosphate) which provides energy for cellular functions, and it is involved in several functions in plants including photosynthesis and water transport (Blevins, 1999). The forms of P found in soils include dissolved P (1), P sorbed to Fe and Al oxides (Fe<sub>ox</sub> and Al<sub>ox</sub>) and clay minerals surfaces (2), occluded P (captured in crystalline Fe<sub>ox</sub> and Al<sub>ox</sub>) (3), phosphate minerals (4) and P in organic substances and soil organisms (5) (Blume et al., 2016). The inorganic phosphorus species in soil solution considered as plant available are phosphates; H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (at pH 2.1 to 7.2) and HPO<sub>4</sub><sup>2-</sup> (at pH 7.2 to 12.0) (Blume et al., 2016). The optimal pH range for nutrient availability in agricultural mineral soil is between 6 and 7 (Peterson, 1982). For P availability, a pH around 7 is optimal, and here P is found mostly as H<sub>2</sub>PO<sub>4</sub> but also HPO<sub>4</sub> (Barrow, 2017). The global origin of P is mainly weathering of minerals containing P, mostly apatite (Schlesinger et al., 2020). Thus, in old and highly weathered soils, mineralization of SOM often is the most important P supply despite that SOM content may be low in these soils

(Weil & Brady, 2017). When nutrient demand is high, plant roots can release organic acids (oxalate) to enhance the release of P (Fox & Comerford, 1992).

The conversion of organic P to inorganic forms, mineralization, is dependent on temperature, pH, moisture, microbial activity and the nature of the organic matter (Pierzynski et al., 2005). C:N ratio determines the rate of OM mineralization as higher C:N ratio slows down mineralization (Schlesinger and Bernhardt 2020). The C:P ratio of organic matter (C content divided by P content) is used as an indicator for net mineralization or net immobilization of P, where immobilization indicates that inorganic P is incorporated into the microbial biomass. Mineralization of P occurs at C:P ratio of <200:1, and immobilization occurs at a C:P ratio of >300:1 (Pierzynski et al., 2005). In other words, when the organic matter contains more C compared to P, microorganisms use P, thus leaving less of the inorganic form available for plant uptake. Assessing the C:P ratio gives an indication of the turnover rate of organic P to inorganic P, which will then again impact the P availability in the soil as OM is the most important source of P in these highly weathered soils (Weil & Brady, 2017).

The soil properties specifically important for P availability is P adsorption capacity which depends on factors like OM content, Feox and Alox, particle size distribution and pH (Pierzynski et al., 2005). As the organic matter content is low, the Feox and Alox are to minor extent complexed with organic matter, so as phosphate (PO<sub>4</sub>) may be competing with OM for the Fe<sub>ox</sub> and Al<sub>ox</sub> sorption sites, PO<sub>4</sub> is more likely to adsorb to these. The stronger P is adsorbed, the less plant available it is, and the longer time P has been bound, the more P becomes integrated to the oxide structure (Weil & Brady, 2017). As the soil becomes more saturated with P, the strongest binding sites fills up first before the increasingly weaker sites. The ratio of sorbed P to the sorption capacity is defined as the degree of P saturation (DPS) and often expressed as P/(Feox + Alox).de Campos et al. (2018) studied a variety of soil types and stated that lower DPS were observed with stronger adsorption, and higher DPS with lower adsorption. So as the stronger binding sites fills up (the more saturated a soil is with P), the weaker adsorption of P will be because the weaker sorption sites are left. P adsorbed to clay is a reversable process and therefore more accessible for plants than the Fe- and Albound P (Weil & Brady, 2017). As P adsorption is highly associated with clay content (Pierzynski et al., 2005), the particle size distribution of the soil is important when assessing the availability of P.

pH also affects the adsorption of PO<sub>4</sub> to Fe<sub>ox</sub> and Al<sub>ox</sub> (*Figure 1*), because the net surface charge of oxides turns positive at a certain pH. The lower the pH the more H<sup>+</sup> is attached to the hydroxyl groups of the oxides which means that more PO<sub>4</sub> will adsorb to these positively charged surfaces. Similarly, at increasing pH, the oxide surfaces will deprotonate, rendering them increasingly negative and PO<sub>4</sub> is "released" from the oxides due to charge repulsion. At pH higher than approx. 6, PO<sub>4</sub> will precipitate with calcium (Ca) (Figure 1).



Figure 1: Phosphorus (P) availability as impacted by pH. X-axis represent the pH, and y-axis present how well P fixate in the soil. Fixation is a terminology often use to describe both the adsorption and precipitation of P to Fe, Al and Ca (Singh & Schulze, 2015). Figure is from: Penn, C. J. and J. J. Camberato (2019). "A Critical Review on Soil Chemical Processes that Control How Soil pH Affects Phosphorus Availability to Plants." <u>Agriculture</u> **9**(6): 120.

As previously mentioned, low levels of plant available P has been reported in SSA soils. To increase the content of available P fertilizer is used. However this can be too expensive for smallholder farmers in SSA.Yerokun (2008) determined different P fractions in twenty soils with different properties in Zambia and concluded that the low P availability in Zambia was due to high amounts of oxides in the highly weathered soils. The effects of fertilizer on P availability can diminish if the adsorption is strong because the plants will have trouble accessing it later (Nziguheba et al., 2016). A low effect due to strong adsorption of P is relevant in the oxide rich soils. Also, in the sandy soils with low P adsorption, the fertilizing effects can be low due to leaching (Martinsen et al., 2014). Therefore, assessing the effect on

plant available P of specific soil properties and human interventions are essential in soils of small holders in SSA. Other human interventions besides fertilization have been researched for P availability improvement, such as the use of biochar and pigeon pea in crop rotation. These will be introduced in the following sections.

#### 1.4 Pigeon pea

Pigeon pea (*Cajanus cajan*) is a nitrogen (N) fixing legume crop used in the tropics and the sub-tropics (Saxena et al., 2002; Saxena, 2008). It can handle drought well (Udensi et al., 2021) and contributes to soil moisture retention (Odeny, 2007). Also, biomass production is high and the plants have high tolerance to stress (Odeny, 2007). Pigeon pea will improve diets as they are nutrient rich; they contain minerals and vitamins in addition to proteins (Odeny, 2007), thus including pigeon pea in crop rotation will improve diets as maize has been and still is the primary crop in Zambia. Harvesting and exporting pigeon peas can be an important cash income for smallholder farmers. Furthermore, pigeon pea has shown to have effects on P availability.

In a study from 1990 in, Ae et al. (1990) claimed that pigeon pea can mobilize and utilize P strongly bound in the soil better than other crops. Pot experiments were done with application of added Fe, Al and Ca-bound P (FePO<sub>4</sub>, AlPO<sub>4</sub> and CaHPO<sub>4</sub>) and the researchers concluded that pigeon pea did absorb all these forms of P. It was highlighted that pigeon pea can mobilize and utilize Fe-bound P better than other crops. This involves a mechanisms where the plant roots exudate piscidic acid which chelates Fe, thus dissolve Fe-oxides and mobilizing P (Ae et al., 1990). Later a study by Otani and Ae (1996) also concluded that pigeon pea can take up Fe- and Al-bound P. In Tanzania and Malawi, Adu-Gyamfi et al. (2007) studied the effects of a pigeon pea-maize intercropping system on N and P availability, but the results did not imply that the PP mobilized P from oxides, based on data for P accumulation in plant components. So, this study could not support the results of Ae et al. (1990). It has also been suggested that pigeon pea can mineralize organic P based on measurements of acid phosphatase activities (Ascencio, 1996; Garland et al., 2016).

If pigeon pea could utilize Fe- and Al-bound P, it would be beneficial if the plant available P in the soil increases next year, potentially enhancing maize yield. Ae et al. (1990) suggested that pigeon pea would increase the total phosphorus availability in a soil with low phosphorus

levels (Ae et al., 1990). In a study by Myaka et al. (2006) in Tanzania and Malawi the soil P pool as well as total maize yield increased significantly in a system with pigeon pea and maize intercropping compared to sole maize. However, results from an intercropping system does not necessarily transfer to a crop rotation system. Whether P uptake is higher in pigeon pea than in other crops, and if pigeon pea uses other mechanisms for P uptake involving mobilization of Fe- and Al-bound P or organic P, will be further discussed. A knowledge gap exists around whether pigeon pea enhances soil plant available P or not, and this is what will be tested in this thesis.

#### 1.5 Biochar

Biochar is a charcoal product made from pyrolysis of organic matter or waste such as plant residues, food waste, animal manure or sewage sludge, with limited or no access to oxygen (Joseph et al., 2021). The effects of biochar application in soil for soil amendment has been widely studied. Biochar increases soil pH (with highest effects in acid soils) due to its negative surface charge and improve water-holding capacity due to it porosity (Joseph et al., 2021). Further properties, stability and soil amending effects of biochar vary widely and is determined by feedstock, and of the pyrolysis time and temperature (Joseph et al., 2021). A meta-study by Jeffery et al. (2011) with 23 studies (including a range of biochar feedstock, and type of fertilizer, soil and crops used), reported soil pH increase and improved water-holding as major mechanisms to improve nutrient availability enhanced by biochar. A later meta-study by Jeffery et al. (2017) included 111 studies and their main find was that higher nutrient content in the biochar had greater positive effects on yield than biochar with low nutrient content. In the tropics, both a liming and fertilizer effect caused by the biochar was what the authors explained the yield increase with (Jeffery et al., 2017).

With regard to biochar and P availability, a meta-analysis by Gao et al. (2019) with 124 studies reported significant increase in soil P availability, and they concluded that the biochar's C:N ratio and the type of biochar (biochar feedstock) strongly influenced the P. Further, Zhang et al. (2016) highlights that biochar can retain fertilizer P and thereby improve the availability of P in soil, however this is greatly dependent on biochar type. In acid soils (pH<6.5), biochar was reported in a meta-study by Glaser and Lehr (2019) to increase P availability significantly, as opposed to in neutral soils (pH 6.5-7.5), due to biochar's alkaline effects.

Studies done on biochar claim that the biochar feedstock used can affect the soil properties and the possible benefits. Biochar made from pigeon pea has not been much studied, especially not its effect on availability of soil P. Based on what meta-analysis have concluded with, the content of P in the biochar will affect the P availability directly in the soil, and widely reported effects are a rise in pH and thus a weaker P adsorption to Al<sub>ox</sub> and Fe<sub>ox</sub>. Also, biochar can potentially reduce aluminium toxicity (Al<sup>3+</sup>) due to pH increase. P content of pigeon pea biochar compared to other biochar types will be mirrored by the uptake and content of P in the pigeon pea plant, which some studies have claimed is higher than for other crops. There is lack of knowledge on biochar made from pigeon pea feedstock related to soil P availability specifically, and this thesis will contribute to this specific knowledge gap.

#### 1.6 ClimChar

This study was part of the research project "Testing biochar-pigeon pea agroforestry businesses in Zambia" (ClimChar Zambia) funded by the Nordic Climate Facility, coordinated by Menon Economics. The aim of this project is to implement maize – pigeon pea rotation, where pigeon pea biomass can be used as feedstock for biochar production and applied as soil amendment. In addition, pigeon pea consumption may improve diets. The project will study the effects of using pigeon pea and if it can be a new important part of the agricultural practice in Zambia.

#### 1.7 Research question and hypotheses

The aim of this thesis was to assess the effects of crop rotation with pigeon pea and addition of biochar from pigeon pea feedstock on P availability in two different soils: a sandy loam and a sand, under conservation agriculture in Zambia. The following research question was addressed: What are the effects of crop rotation with pigeon pea and biochar application in the field and in the lab on P sorption, availability of P and other selected soil properties? To address this, the following hypothesis were tested:

H1: Crop rotation with pigeon pea will increase plant available P in soils in both regions

H2: Adding biochar will increase the plant available P in soils in both regions

## 2. Materials and methods

## 2.1 Study site

The experiment was carried out with soil samples taken in Zambia in southern Africa at two field sites: Mkushi in the central part of Zambia at S13 44.839, E29 05.972 and Kaoma in the western part of Zambia at S14 50.245, E25 02.150 (Obia et al., 2017) (Figure 2).



*Figure 2: Map over Africa (left) and Zambia (right). Mkushi in the central region and Kaoma in the western region were marked. The maps were compiled at 22<sup>th</sup> of March 2022 from the software Google Earth Pro 7.3.4.8573.* 



*Figure 3: Maps of the selected farms where soil samples were taken. Kaoma, western region (left) and Mkushi, central region (right). The coordinates for the points (yellow) are in Appendix A. The maps were compiled at 22<sup>th</sup> of March 2022 from the software Google Earth, date 23.03.2022 Pro 7.3.4.8573.* 

The soils in Mkushi were weathered grey loams, classified by the World Reference Base for Soil Resources (WRB) as an acrisol (Obia et al., 2017). In Kaoma, the soils were aeolian sands, and classified by WRB as an arenosol (Obia et al., 2017). Annual mean temperature in Kaoma is 20.2 °C (Weatherspark, n.d.-a) and 20.1 °C in Mkushi (Weatherspark, n.d.-b). The rain season in Zambia is from around November to May, thus the remaining months are dry. In Kaoma and Mkushi it has been reported 930 mm and 1220 mm annual precipitation respectively (Martinsen et al., 2014). Also, Figure 4 shows the rainfall during the last three seasons for Mkushi and Kaoma measured by farmers contributing to the ClimChar project.



Figure 4: Mean precipitation for the seasons 2018-2019, 2019-2020 and 2020-2021 in Mkushi (Central region; n=22 farms) and Kaoma (Western Region; n=15 farms). Monthly averages from October to April as well as total cumulative amounts for each season is presented. Data is based on manual measurements by farmers participating/attending the ClimChar project (Martinsen, 2022).

#### 2.2 Materials

#### 2.2.1 Experimental setup and soil sampling

Five farms in Mkushi (central region) and five farms in Kaoma (the western region) in Zambia were selected for the experimental site in September 2019. All farms were selected based on homogeneous soil conditions and slope for the experimental trials. At each farm, an area of 500-2500 m<sup>2</sup> was marked (Figure 5). Land preparation included preparation of permanent planting basins (i.e. CA with minimal with min tillage). In the first season (2019-2020) pigeon pea was planted on the entire experimental area at each of the farms and no fertilizer was applied. The pigeon pea was harvested in June 2020. After harvest and drying of the biomass, the pigeon pea was used as feedstock to produce biochar as described by Munera-Echeverri et al. (2020). In November 2020, the experimental area at each of the farms was divided into one portion where biochar was applied at a rate of 4 t/ha (Munera-Echeverri et al., 2020) and one portion with no biochar addition (Figure 5). Maize was planted on the entire experimental area in the second season (2020-2021). Fertilizer "Compound D" (N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, 10:20:10) was applied at a rate of 200 kg ha<sup>-1</sup> yr<sup>-1</sup> before planting and urea (46:0:0) applied as top dressing at a rate of 100 kg ha<sup>-1</sup> yr<sup>-1</sup> about four to five weeks as well as eight weeks after planting (i.e. a total of 200 kg ha-1 yr-1) (Martinsen et al. 2019). Maize was harvested in May 2021.

All soil samples were taken using an auger (diameter 2 cm) at a depth 0-20 cm. The first and second set of soil for background characterisation (abbreviated "N") and after one season with pigeon pea (abbreviated "PP"), respectively, were sampled at four locations on each farm in September 2019 and June 2020, respectively. At each of the four locations, four soil samples were randomly taken and pooled (i.e. a total of 4 soil samples per farm for each of the two sampling events). Following the season with biochar (abbreviated "BF) the third set of soil was sampled in June 2021. Triplicate samples, each consisting of four samples randomly taken at selected positions within the experimental area with biochar (Fig.X) were taken at each of the five farms in Mkushi, but not in Kaoma due to experimental failure.



Figure 5: Procedure of soil sampling and bulking of the samples from season 1 with pigeon pea and season 2 with biochar. This procedure applies for each farm. At each farm, four randomly selected sample plots was bulked into one soil sample at four different spots. These was again bulked into one sample (M.2, M.3 etc.). (Martinsen, 2022)

#### 2.2.2 Soil samples

Table 1: Overview of the soil samples shows an overview of the soil samples with treatments and regions. From Mkushi there was a total of 20 samples: five soil samples for background characterization (abbreviated "N"), five samples after one season of pigeon pea crop (season 1, abbreviated "PP")), and then five samples following maize with 4/ha biochar field application (season 2, abbreviated "BF"). Biochar application rate of 4/ha corresponded to ~2% biochar (on a weight basis). To assess the potential of fresh biochar, 2% biochar (on a

weight basis) was added to the five soil samples from the background sampling in the lab (abbreviated "BL"). For Kaoma it was 15 soil samples: five soil samples for background characterization (N), five samples after one season of pigeon pea (PP) (season 1) and five soil samples from background sampling with 2% biochar added in the lab (BL). In total there was 35 soil samples. In addition, some analyses were done on a triplicate of a biochar sample containing pure pigeon pea biochar.

Name/season	Background,	Pigeon pea, PP /	Biochar field, BL/	Biochar lab, BL /
and	N /	Season 1 w. pigeon	Season 2 w. maize +	Background, N w.
treatment	w. maize	pea	biochar	maize and 2%
// Region				biochar added on lab
Mkushi, M	5 samples:	5 samples:	5 samples:	5 samples:
	M.2.N	M.2.PP	M.2.BF,	M.2.BL
	M.3.N	M.3.PP	M.3.BF	M.3.BL
	M.6.N	M.6.PP	M.6.BF	M.6.BL
	M.8.N	M.8.PP	M.8.BF	M.8.BL
	M.9.N	M.9.PP	M.9.BF	M.9.BL
Kaoma, K	5 samples:	5 samples:	No samples	5 samples:
	K.2.N	K.2.PP		K.2.BL
	K.3.N	K.3.PP		K.3.BL
	K.6.N	K.6.PP		K.6.BL
	K.7.N	K.7.PP		K.7.BL
	K.9.N	K.9.PP		K.9.BL

Table 1: Overview of the soil samples

#### 2.3. Methods

To assess the plant availability and properties of P, several lab analyses were done. Firstly, plant available P was determined with the P-AL method on all 35 soil samples. Sorption experiments were done to assess the sorption of P to all soil 35 samples. Hot water extraction of both C and P (HWEC and HWEP) was done on 20 samples (N and PP) to assess the labile fraction of organic P and C. The remaining lab analyses were done to assess auxiliary soil properties which may contribute to further discussion of the results: pH, Total C and N and oxalate extraction of P, Fe and Al was done on all 35 samples. To assess some of the properties of the biochar, several analyses were done with a pure biochar sample: P-AL, oxalate extraction, total C and N in addition to an P extraction with KCl and H<sub>2</sub>O on triplicate samples. Data for size distribution and soil classification was received from Mirriam Phiri in Zambia who did the analysis at University of Zambia (UNZA).

#### 2.2.3 pH

pH is an important parameter influencing the behaviour of P in soils as well as several other processes. pH was measured in a soil-water suspension with 10 ml soil and 25mL distilled water in plastic beakers with lids, which were shaken a few times (by hand). The beakers were left overnight to let the soil-water achieve equilibrium. The morning after they were shaken a few times again (by hand). The pH meter, PHM210, was calibrated with pH 7 and pH 4 buffer solutions. Then a solution with a known pH of 6,87 was measured as a control for accurate measurements. pH in the soil samples was measured making sure the electrode did not touch the soil sediment. Between each measurement, the electrode was rinsed thoroughly with water.

#### 2.2.4 Total C and N

Total carbon and nitrogen (Tot C and Tot N, respectively) were analyzed as described by Nelson and Sommer (1982) and Bremmer and Mulvaney (1982) respectively. For sample preparation, soil was crushed with a mortar, and dried at 55 degrees beforehand to remove the last water remains. Approximately 200 mg of each sample was weighed in on a foil of tin. The samples were analyzed on Leco CHN628.

#### 2.2.5 Phosphate sorption isotherms

This experiment was carried out to assess the sorption of P. The principle of the experiment is to add a solution with a certain phosphate (PO4) concentration to the soil, let the soil and water achieve equilibrium and then measure the PO4 concentration. PO4 concentration after the equilibrium is achieved will indicate a net adsorption or desorption. The method description from Murphy and Riley (1962) was used.

In preparation for the experiment 10 bottles with different P concentrations were made from 1M KH<sub>2</sub>PO<sub>4</sub>: 0 mg/L, 0.5mg/L, 1mg/L, 2 mg/L, 4 mg/L, 8 mg/L, 16 mg/L, 32 mg/L, 64 mg/L and 128 mg/L. To make a 0.5mg/L P solution it was extracted 1mL from a 1000mM KH2PO4 solution (then for 1mg/L it was extracted 2mL and for 2mg/L extracted 4mL etc.) 1 M CaCl<sub>2</sub> was also added each of the P solutions by adding 5mL of a 2.5mM CaCl<sub>2</sub> solution. CaCl<sub>2</sub> is used as a background electrolyte in order to have the same ionic strength in all bottles, as ionic strength may affect adsorption and adsorption capacity.

Two grams of soil was weighted in and each added to a 50mL centrifuge tube. By adding each one of the P concentrations (ranging from 0 mg/L to128 mg/L) the tubes were gently shaken for 24 hours on an end-over-end shaker at room temperature (20°C) for 125 oscillations per minute. The samples were then centrifuged for 10 minutes at 20 °C with 2867 G in a Beckman Avanti JXN-26 with rotor JA-14.50, and filtered through a 0.45 µm cellulose nitrate membrane filter. The filtrate was diluted to concentrations within the calibration range the spectrophotometer was able to analyse at a wavelength of 660nm, after adding 0,4mL ascorbic acid and 0,4mL Mo blue, both made with the NS 4725 (Norwegian Standard no. 4725) procedure. The absorbance of PO4 was measured colorimetically on Gilford Instruments Laboratories Inc. Oberlin Ohio 44074. A calibration curve was created from four PO4 concentrations (0mg/L, 0.2mg/L, 0.5 mg/L and 1mg/L). The calibration curve was used to convert data for absorbance to PO4 concentration since there is a linear relationship between those.

Amount of adsorbed P (q) in the sorption experiment was calculated based on the difference between added PO4 concentration and the concentration of PO4 after equilibrium ( $C_{eq}$ ). A linear regression showed that for all soil samples from Mkushi a Langmuir model fitted to describe the adsorption. A linear curve was constructed by plotting  $C_{eq}$  and  $C_{eq}/q$ . From the linear curve ( $C_{eq}/q=a*Ceq+b$ ), the slope (a) and intercept (b) was used to calculate  $Q_{max}$  and KL as  $Q_{max}=1/a$  and KL= $(1/a)*Q_{max}$ .  $Q_{max}$ , (mg/g) represent the theoretical maximum potential the soil can adsorb and is an estimated value, and K<sub>L</sub> (L/mg) describes the affinity between the sorbent and the sorbate (soil and water respectively). Based on these parameters, a curve fitting was done with adsorption (q) estimated as:  $q = (Q_{max}*K_L*C_{eq})/(1+K_L*C_{eq})$ .  $C_{eq}$ and q was then plotted in a graph. Soil samples from Kaoma did not fit into a linear Langmuir model, so a curve fitting with an estimated q was not done for Kaoma samples. Therefore, adsorption, q, was estimated as the concentration of PO4 added subtracted from the concentration of PO4 after adsorption ( $C_{eq}$ ).

#### 2.2.6 Plant Available P (P-AL)

A number of different methods have been developed to determine plant-available P. A common method is using ammonium lactate as an extractant (P-AL), as described by Egner et al. (1960). The method is developed to imitate the amount of P plants can access in the field and is therefore helpful to evaluate how much available P there is for plants to utilize. Phosphate sorbed to cations on the soil surface is exchanged with lactate ions from the AL-solution, and thereby is phosphate ions released (HPO<sub>4</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>2-</sup>) from oxide surfaces. This process mimics the ion exchange root exudates do in the field.

The ammonium lactate (AL) solution consists of hydrolyzed lactic acid, acetic acid and ammonia. 40mL of the solution was added to two grams of soil in 100mL glass flasks and immediately shaken for 90 minutes on an end-to-end shaker at room temperature (20°C) with 100 oscillations per minute. It was also analysed one sample with pure biochar. The samples were then filtrated into 100mL glass beakers through 125 mm folding filter papers type Schleicher & Schuell placed in plastic funnels. A control sample with just the AL-solution but no soil was included. Phosphate concentration was measured on ICP-OES.

#### 2.2.7 Hot water extractable C and P

Hot water extractable carbon (HWEC) is a method developed to determine the amount of labile C, which is the fraction easily degradable organic matter. The extraction is used to determine how soil C is affected by changes in soil management. Other labile nutrients can also be extracted by HWEC (Ghani et al., 1996). Phosphate (PO4) was also determined (hot water extractable P (HWEP)), and the lab procedure for HWEC and HWEP follows the method description of Ghani et al. (2003) and Dong et al. (2021).

Two grams of soil and 20mL of distilled water was added to 50mL centrifuge tubes. These were put in a hot water bath with 80°C for 17 hours. The tubes were then centrifuged for 10 minutes with 3803G and filtered through 0,45 µm cellulose nitrate membrane filters. A control sample with no soil was also included. The filtrate were put in a fridge to keep them cool until they were analysed for both dissolved PO4 and C. The concentration of C in the filtrate was measured by a TOC analyser (TOC V CPN), and P was analyzed using ICP-OES.

#### 2.2.8 Oxalate extractable Fe, Al and P

This analysis extracts the amorphous inorganic forms of Fe and Al oxides from the soil (Krogstad et al., 2018). P bound to these is also extracted, so thereby one get data of the amount of P bound to Al- and Fe- oxides in the soil. The method description of Van Reeuwijk (1995) was followed. To 1g soil, 50mL of oxalate solution (pH 3) was added to a 100mL shaking bottle. One sample containing pure biochar and three blank samples was also included. The bottles were shaken with a horizontal end-over-end shaker for 4 hours in the dark, decanted and analysed for Fe, Al and P using ICP-OES. The data for oxalate extractable P, Fe and Al was used to determine the degree of P saturation (DPS) defined as DPS = P/(Fe+Al).

#### 2.2.9 Biochar extraction

Phosphate (PO<sub>4</sub>) in biochar was extracted with  $H_2O$  and with KCl. Three replicates of 0.5g biochar and 20 ml distilled  $H_2O$  (conc 25mg/L) was shaken for 30 minutes before filtration through 0.45 µm cellulose nitrate membrane filter and analyzed for P with ICP-OES. The same procedure was also done with KCl.

#### 2.3 Statistical analyses

All statistical work was done in Microsoft Excel version 16.59. A two-sided t-test between treatments (N, PP, BF and BL) (n=5) and regions (Kaoma and Mkushi) was carried out to access p-values to examine possible significance at level p<0.05. Regression analyses was used to assess correlations between different parameters (P-AL, DPS, CP-ratio,  $Q_{max}$ ) in scatter plots and accessing p-values to assess possible linear relationship. Linear regression was also used to determine  $Q_{max}$  and  $K_L$ . Also, p<0.05, p<0.01 and p<0.001 was used as levels of significance where smaller p-value indicates higher significance.

## 3. Results

#### 3.1 Soil properties

The soil properties in the two regions are presented in Table 2. The soil in Mkushi was classified as a sandy loam, and in Kaoma as a sand. The pH in Kaoma was significantly higher than in Mkushi (p<0.05) for both N, PP and BL samples. In Mkushi, pH in samples after biochar was applied in the field (BF) were lower than BL. Tot C and tot N data showed higher tot C for BL samples than N and PP in both regions. For BF samples in Mkushi, tot C was lower than for BL samples. The C:N ratio was calculated as tot C divided with tot N. CN-ratio was significantly higher for PP compared to N (p<0.05). However it is worth mentioning that the C:N data is highly sensitive due to low N values in some samples, so small changes in the instruments' accuracy affect the CN data notably (Table 3).

Table 2: Soil classification and mean grain size distribution for Mkushi and Kaoma

Region	Soil ID	Texture	Sand	Silt	Clay
		USDA	%	%	%
Mkushi, M	M.N	Sandy loam	74.4	21.2	4.4
Kaoma, K	K.N	Sand	92.8	4.8	2.4

Table 3: Different soil properties for each soil sample with mean values with SE (n=5) for Mkushi (M) and Kaoma (K), Zambia. N=background samples from maize fields, PP= soil samples after one season with pigeon pea (a crop rotation), BF= samples after one season with maize and application of biochar in the field made from pigeon pea feedstock, BL= background samples (same as N) with 2% biochar added in the lab. Based on individual two-sided t-tests, the significance at p<0.05 level was tested. Lower case letters indicate differences within region between treatments. Upper case letters indicate differences between treatments.

Region	Soil ID	рН		Tot C %		Tot N %		<b>CN-ratio</b>	
		mean	SE	mean	SE	mean	SE	mean	SE
Mkushi, M	M.N	5.2 aA	$\pm 0.1$	0.48 aA	$\pm 0.02$	0.06 aA	$\pm 0.02$	8.75 aA	$\pm 0.55$
	M.PP	5.5 aA	$\pm 0.1$	0.63 aA	$\pm 0.28$	0.04 bA	$\pm 0.02$	17.88 bA	±1.39
		< <b>- 1</b>				<b>.</b> .	<b>.</b>		<b>a</b> 40
	M.BL	6.5 b	$\pm 0.0$	1.97 bA	$\pm 0.88$	0.05 aA	$\pm 0.02$	41.30 cA	±3.49
	MDE	55	10.2	0.75 . 1	10.22	0.04 ha		10 60 Jb	1 77
	WI.DF	3.3 aA	±0.2	0.75 CA	±0.33	0.04 00	±0.02	19.08 00	±1.//
		( 0, D	1	0.61		0 0 <b>-</b> 1		11.00 D	
Kaoma, K	K.N	6.0 aB	$\pm 0.1$	0.61 aA	±0.27	0.05 aA	$\pm 0.02$	11.90 aB	$\pm 0.34$
		(21)	10.1	0.50	10.00	0.021.4	0.01	22 241 D	1004
	K.PP	6.2 bB	$\pm 0.1$	0.59 aA	$\pm 0.26$	0.02 bA	$\pm 0.01$	32.24 bB	$\pm 6.04$
	KBI	7.3 cB	+0.1	188 hA	+0.84	0.04 bc	+0.02	56.20 cb $\Lambda$	+8.38
	K.DL	/.JCD	$\pm 0.1$	1.00 UA	+0.04	0.04 00	+0.02	50.20 CDA	$\pm 0.30$

#### 3.2 Phosphate sorption isotherms

#### 3.2.1 Mkushi

The sorption curves of P for the soils in Mkushi is in Figure 6. All sorption data from Mkushi were described well by the Langmuir isotherm. A linearized version of Langmuir was used, where  $R^2$  from the linear plot ranged from 0.99 to 0.85 (Table 4 and Appendix B & C) to calculate the maximum sorption capacity,  $Q_{max}$ , and the Langmuir affinity constant,  $K_L$ . A higher  $Q_{max}$  means that the sorbent have higher potential to adsorb. A high  $K_L$  value indicate that the affinity between the sorbent and the sorbate is higher.



Figure 6: The PO<sub>4</sub> adsorption potential of soils in Mkushi is presented where N=background samples, PP= samples after one season of pigeon pea, BL= background samples with biochar added in the lab and BF=samples after application of biochar in the field. The different curves represent each farm (M.2, M.3 etc.) in addition to one curve with mean values for the farms (n=5). The x-axis is the amount of PO<sub>4</sub> in solution at equilibrium, Ceq (mg/L). The y-axis is the amount of PO<sub>4</sub> adsorbed to the soil is q (mg/kg), estimated from the Langmuir equation where  $q = Q_{max}*K_L*C_{eq}/1+K_L*C_{eq}$ . For BF samples the 128mg/L concentration was not included to the already low and flat adsorption curve, thus the maximum value for this x-axis was just 70 mg/L.

Table 4: Mean estimated values and SE (n = 5) for adsorption maximum ( $Q_{max}$ ), Langmuir affinity constant ( $K_L$ ) and  $R^2$  from the linear regression of Langmuir, in Mkushi (M) for N=background samples, PP=samples after one season of crop rotation with pigeon pea, BF=biochar applied in the field and BL=biochar added at the lab. Based on individual two-sided t-tests the level of significance at p<0.05 was tested. Lower case letters indicate differences within region and between treatments

Soil ID	Qmax		KL		R <sup>2</sup>	
	mg/kg		L/mg			
	mean	SE	mean	SE	mean	SE
M.N	198 a	±0.033	0.044	±0.014	0.967	±0.012
M.PP	108 b	$\pm 0.018$	0.014	$\pm 0.005$	0.968	$\pm 0.006$
M.BL	299 с	$\pm 0.015$	0.090	$\pm 0.009$	0.910	±0.016
M.BF	94 bd	$\pm 0.018$	0.011	$\pm 0.005$	0.963	±0.015

Overall, the different soil samples within the treatments followed more or less the same trend (Figure 6). For the background samples (N) mean adsorption maximum ( $Q_{max}$ ) and Langmuir affinity constant ( $K_L$ ) was 198 mg/kg and 0.044L/mg respectively (Table 4). After one year of crop rotation with pigeon pea (PP),  $Q_{max}$  was significantly lower than in the N samples (at p<0.05), and mean  $Q_{max}$  and  $K_L$  for PP samples was 108mg/kg and 0.014 L/mg respectively. The next season when biochar was applied in the field (BF),  $Q_{max}$  and  $K_L$  decreased even more: 94mg/kg and 0.011 L/mg, respectively, and the decrease in  $Q_{max}$  from N samples to BF was significantly lower (p<0.05). The background samples where biochar was added in the lab (BL) had det highest  $Q_{max}$  and  $K_L$ : 299 mg/kg and 0.090 L/mg, respectively, with a significant increase from N to BL (p<0.05). Also, BL samples had significantly higher  $Q_{max}$  than BF (p<0.05).

#### 3.2.2 Kaoma

For Kaoma, the sorption curves is presented in Figure 7. The results from these soil samples did not the Langmuir sorption isotherm due to low  $R^2$  values from the linearization (Appendix C). Therefore, the adsorption potential cannot be referred to with  $Q_{max}$  and  $K_L$  values, but information from the curves (Figure 7). Background samples showed both net adsorption and net desorption. From N samples to PP samples, there was observed an increase in adsorption. From N samples to BL samples, the adsorption also increased some, however less than for PP samples.



Figure 7: The PO<sub>4</sub> adsorption potential of soils in Kaoma is presented where N=background samples, PP= samples after one season of pigeon pea and BL= background samples with biochar added in the lab. There are no curve for each farm as there was no curve fitting with the Langmuir isotherm. Thus, the different curves are mean values for the farms (n=5). The x-axis is the amount of PO<sub>4</sub> in solution at equilibrium, Ceq (mg/L). The y-axis is the amount of PO<sub>4</sub> adsorbed to the soil is q (mg/kg).

#### 3.3 Plant Available P (P-AL)

The data for plant available phosphorus (P-AL) is presented in (Figure 8). For both Mkushi and Kaoma, one year with pigeon pea did not significantly increase the P-AL (p>0.05). However, in both regions, P-AL increased significantly (p<0.001) upon biochar addition in the lab (BL). For Mkushi, the P-AL increased significantly both from N to BF (p<0.01), and from PP to BF (p<0.01). Between the regions, P-AL was significantly higher for Kaoma than for Mkushi (N, PP and BL samples) (p<0.001). Between the farms, the P-AL values vary as shown left in Figure 8.



Figure 8:Plant available phosphorus (P) data from P-AL analysis. Bar diagram with mean values (n=5) for the farms in both regions Kaoma and Mkushi. N=no treatment, background sample. PP= after one year of pigeon pea. B= after one year of pigeon pea and one year of biochar. BL= background samples (N) added 2% biochar at the lab. Error bars show standard error (SE). Based on individual two-sided t-tests, the significance at p<0.05 level was tested. Lower case letters indicate differences within region between treatments. Upper case letters indicate differences between regions for the same treatment

#### 3.4 Hot Water Extractable C and P (HWEC and HWEP)

The HWEC data for neither Mkushi nor Kaoma changed between treatments, presented in Table 5. There was no difference between regions. The HWEP data however, showed significantly higher values in Kaoma than Mkushi for both N and PP (p<0.01). There was no change between treatments within the regions (Table 5).

Table 5: Data from hot water extraction of C and P (HWEC and HWEP), as well as C:P ratio calculated from the HWE data, is presented as mean values where n=5 with standard error,  $\pm$ SE. Based on individual two-sided t-tests, the significance at p<0.05 level was tested. Lower case letters indicate differences within region between treatments. Upper case letters indicate differences between regions for the same treatment.

Region	Treatment	HWEC		HWEP	
		mg/kg		mg/kg	
		mean	SE	mean	SE
Mkushi	M.N	268 aA	±120	1.83 aA	$\pm 0.82$
	M.PP	302 aA	±135	2.81 aA	±1.26
Kaoma	K.N	296 aA	±132	9.2 aB	±4.11
	K.PP	288 aA	±129	9.1 aB	±4.07

The C:P in Figure 9 represent the amount of labile C relative to the labile P, and is based on data from hot water extraction of C and P (Table 5 & Appendix A) Between regions Kaoma and Mkushi a significant difference (p<0.05) was observed. Between treatments however, there was a non-significant (p>0.05) decrease for both Mkushi and Kaoma from N to PP. A C:P over 300:1 indicate immobilization, and mineralization happens at a ratio lower than 200:1. The results imply that mineralization occurred in all fields, and that Kaoma had higher mineralization rate than Mkushi based on a significantly higher C:P ratio.



Figure 9: The ratio of C divided by P is based on data from the hot water extraction (HWEC and HWEP) Bar diagram with mean values (n=5) with standard error (SE) for each region Kaoma and Mkushi for N and PP. N=no treatment/background sample. PP= after one year of pigeon pea. Based on individual two-sided t-tests, the significance at p<0.05 level was tested. Lower case letters indicate differences within region between treatments. Upper case letters indicate differences between regions for the same treatment.

#### 3.5 Oxalate Extractable Fe, Al and P

From the oxalate extraction, the degree of phosphorus saturation (DPS) was calculated as the ratio of oxalate extractable P and the sum of oxalate extractable Fe and Al: P/(Fe+Al) (Figure 10). Overall, the DPS was higher for Kaoma than Mkushi. Between N and PP the DPS showed no difference in neither Mkushi nor Kaoma (p>0.05). Between BL and N in Kaoma there was no significant increase but it was in Mkushi. For the soils in Mkushi with biochar applied in the field (BF), the DPS did increase significantly (at p<0.05) from N, PP and BL samples.



Figure 10: The degree of phosphorus saturation (DPS) is shown between the treatments where n=5 and error bars shows the standard error (SE). DPS was calculated from the oxalate extractable P, Fe and Al where P/(Fe+Al. N= background soil samples with no treatment, PP= after one season of pigeon pea. BF= one season of pigeon pea and one season of biochar applied. BL= background soil added 2% biochar at the lab. Based on individual two-sided t-tests the treatments and regions were compared at a 0.05 level of significance. Lower case letters indicate differences within region between treatments. Upper case letters indicate differences between regions for the same treatment.

#### 3.6 P Extracted from biochar

P extracted from pigeon pea biochar with different extraction methods is presented in Figure 11. Results indicate that P-AL and oxalate extract similar amounts of P (500 and 470 mg/kg, respectively). Both extractants mobilize significantly more P than KCl and H<sub>2</sub>O (193.3 and 250 mg/kg respectively) (p<0.05).



Figure 11: Extraction of P from biochar with different extraction methods. Error bars represent the standard error (SE) for n=3 for KCl and H2O. For P-AL and oxalate, n=1

#### 3.7 Linear correlations

Figure 12 shows the correlation between P-AL and DPS, thus how the plant available P was associated with the DPS. There was a linear relationship in both regions where Mkushi had a stronger relationship between P-AL and DPS than Kaoma did (where p<0.001 and p<0.05 in Mkushi and Kaoma respectively). Then, a higher increase in DPS was required in Kaoma for a certain increase in P-AL than in Mkushi.



Figure 12: DPS= degree of P saturation, P/(Fe+Al) and plant available P (P-AL) plotted for both regions, Mkushi and Kaoma with data from all treatments from both regions and all soil samples.

Figure 13 shows that Kaoma obtained a stronger relationship between the C:P ratio and P-AL than Mkushi did, as Kaoma had a significant correlation (p<0.01) and Mkushi did not. Thus, a lower C:P ratio was correlated with higher P-AL. Figure 14 show that  $Q_{max}$  was associated with DPS at p<0.05 level of significance.



Figure 13: C:P ratio and P-AL plotted for both regions. Soil samples used are N=background samples and PP= pigeon pea. A level of significance p<0.05 was used to determine if there was a significant linear relationship.



Figure 14: DPS and  $Q_{max}$  plotted for Mkushi due to no data for  $Q_{max}$  from Kaoma. A p<0.05 was used as level of significance to determine if there was a significant linear relationship.

## 4. Discussion

#### 4.1 Background and pigeon pea samples in Mkushi and Kaoma

4.1.1 P-AL

Plant available P measured as P-AL had no significant increase from background samples (N) to pigeon pea samples (PP) (Figure 8). Therefore, the first hypothesis (H1) stating that crop rotation with pigeon pea will increase plant available P, must be rejected. The amount of plant available P in Mkushi and Kaoma (Figure 8) was lower than what Krogstad et al. (2008) considered optimal (Table 6) where the classification of P-AL ranges from "low" to "very high". In Mkushi and Kaoma, the P-AL for N and PP plots was about 6-8 mg/kg and 12 mg/kg respectively (Figure 8). Both groups of samples fitted into the class "low" (Krogstad et al., 2008). This means that plant available P in both soils were quite low, as assumed.

 Table 6: Classification of P-AL levels labelled from "low" to "very high" based on what is optimal for plant
 growth. Table is constructed from: Krogstad, T., et al. (2008). New P recommendations for grass and cereals in

 Norwegian agriculture. Uppsala, Sweden. 4.

Name of class	P-AL
	mg/kg
Low	10-50
Medium/Optimal	50-70
Moderate high	70-100
High	100-140
Very high	≥140

#### 4.1.2 Labile C and P

The HWEC data did not differ significantly between regions. Data from N plots in Mkushi  $(268 \pm 120 \text{ mg/kg})$  were directly comparable to data from Munera-Echeverri et al. (2020) as this study also examined conservation agriculture plots in Mkushi. Mean HWEC for samples with no added biochar was approx. 500 mg/kg for samples taken at the end of the growing season, and approx. 300mg/kg in the middle of the growing season (Munera-Echeverri et al., 2020). The HWEP data showed significantly higher values in Kaoma than Mkushi (p<0.01), and there was no change between N and PP in either region (Table 5). Kaoma's higher HWEP levels would mean that the organic matter in Kaoma contains more labile P than Mkushi. The data for Mkushi fell in the range of data published by Tutua et al. (2013) in an acidic loamy sand.

C:P ratio was calculated from the HWEC and HWEP data (Table 5 & Figure 9). Data for C:P ratio often ranges between 100 and 1000 (Blume et al., 2016) however C:P ratio is more often calculated from tot C and tot P than from the labile C and P fractions. Kaoma had significantly lower C:P than in Mkushi (Figure 9), thus the SOM in Kaoma contains a larger fraction of labile P than in Mkushi. The C:P ratio showed a linear negative relationship with P-AL in Kaoma (R<sup>2</sup>=0.78 at p<0.01) (Figure 13). In Mkushi there was no linear relationship between C:P and P-AL (p>0.05) (Figure 13). A strong negative correlation suggests that the lower C:P ratio (thus a higher P fraction), the more P-AL. Therefore, there is a connection between P-content in the SOM to the plant available P as higher P-AL in Kaoma correlates with lower C:P. However, DPS will also control the plant available P as higher DPS is associated with a weaker adsorption potential and more P available. So both C:P ratio and DPS is connected to P-AL but neither of them alone determine plant availability of P.

#### 4.1.3 P saturation and sorption

The DPS ( $P_{ox}/(Fe_{ox}+Al_{ox})$ ) data showed levels of 0.05 in Mkushi (both N and PP) and 0.13 in Kaoma (both N and PP) (Figure 10), which fell in the range of what de Campos et al. (2018) published for different highly weathered tropical soils. DPS was overall higher in Kaoma than in Mkushi (p<0.05) for both N and PP plots, and did not change between treatments. de Campos et al. (2018) claimed that DPS is negatively correlated with adsorption, as shown in Figure 14.

The adsorption of P in Mkushi for background samples (N) had  $Q_{max}$  values at 198 ±33 mg/kg (Table 4). The data fell into the range reported by Martinsen et al. (2017) who carried out sorption experiments for P in soils in Mkushi where mean  $Q_{max}$  was approx. 220 mg/kg. After one season of implementing pigeon pea, the adsorption decreased significantly to  $Q_{max}=108$  ±18 mg/kg in Mkushi (p<0.05). P-AL in Mkushi N samples and PP samples were 5.8 and 8.3 mg/kg respectively, which illustrates that the potential amount adsorbed was substantially higher than to the amount plant available. The high adsorption for N plots can be connected to oxide content and low DPS.

P sorption in the sandy soils in Kaoma did not fit a Langmuir linearization (Appendix C), thereby there are no data for  $Q_{max}$  for the Kaoma samples. P-AL in Kaoma was approx. 12 mg/kg for both N and PP, and it seems as Kaoma N samples had low net adsorption.

However, PP plots showed potential of adsorbing much higher P levels than was plant available. Earlier research has not been done on P adsorption in soil samples after crop rotation with pigeon pea specifically, so these data cannot be compared to earlier experiments. Figure 7 shows that adsorption of P in Kaoma increased greatly from (N) to (PP). Some explaining parameters to the difference between regions are DPS, SOM content and pH.

In Kaoma, pH was the only one of the above mentioned parameters that changed significantly from N and PP in Kaoma. None of those changed significantly in Mkushi (Table 3 & Figure 10). A significant increase in pH in Kaoma was observed (p<0.01) from N to PP, which will have increased negative charges on oxides and thus more P would desorb. However, the method for adsorption experiment cannot differentiate between adsorption and precipitation in the results. A precipitation of calcium phosphate (CaPO4) due to a significant pH increase could have occurred, even though there are lack of data for soil Ca content to assess this. pH in Kaoma PP plots were 6.2 and Ca precipitation would occur around pH 6 (Figure 1). Tunesi et al. (1999) executed sorption experiments with PO<sub>4</sub> saturated with Ca which indicated that adsorption dominated up to a certain phosphate concentration (16 mg/L), and at higher concentrations precipitation dominated. The sorption experiment of Tunesi et al. (1999) with solutions rich in Ca did not fit into the Langmuir isotherm, and these curves were rather linear. This may explain adsorption in Kaoma N samples and why the sorption did not fit into a Langmuir isotherm. If pigeon pea mobilize Ca-P (as some research have claimed (Ae et al., 1990; Otani & Ae, 1996)), it may be that more Ca ions were available for precipitation in PP plots than N plots, which could explain the adsorption curves (Figure 7). No change in DPS in Kaoma between N and PP strengthens the assumptions that a precipitation of Ca occurred and not just surface adsorption to oxides. The soil pH in Mkushi would then be too low (5.5) for Ca precipitation, or have significantly lower Ca content than Kaoma due to no change of neither pH, DPS nor SOM between N and PP. A precipitation with Al may have occurred in Mkushi N samples at pH 5.2, but probably not in PP plots due to the slight increase in pH up to 5.5.

#### 4.2 Biochar lab samples from Mkushi and Kaoma

#### 4.2.1 P-AL and P extraction

For samples where biochar was added in the laboratory (BL), P-AL was 15 and 23 mg/kg for Mkushi and Kaoma respectively, and they fell in the "low" class according to Krogstad et al. (2008) (Figure 8 & Table 6). In both Mkushi and Kaoma P-AL was significantly higher (p<0.001) for BL samples than background samples (N). This difference can be explained by the P content in the biochar and the significant increase in pH. Since the P-AL experiment extracted 500mg P/kg biochar, and 2% of biochar was added in the lab, the P-AL in BL samples should be approximately 10mg/kg higher than N samples, which was the case for both regions.

Oxalate extraction, which is a stronger extraction than P-AL (at least for most soils) extracted a bit less from the biochar than P-AL did (470 mg/kg and 500mg/kg respectively). This signifies that substantial amounts of P is easily accessible and not associated with oxides. H<sub>2</sub>O and KCl extracted respectively 250 and 193 mg/kg P. Angst and Sohi (2013) had a similar method; extraction of nutrients by shaking or soaking biochar with distilled H<sub>2</sub>O. The biochar they used was from hardwood, and between 30 and 130 mg/kg P was extracted. Also, comparing the data to corn cob and cacao shell biochar, Hale et al. (2013) received  $204 \pm 135$ mg/kg P with desorption from corn cob (maize) and 748 ±96 mg/kg P from cacao shell biochar of shaking with KCl during a three day period. An extraction during a three day period will probably extract more P than 4 hours will (as was done for pigeon pea biochar), so biochar made from pigeon pea feedstock contain quite a lot of P compared to maize do. Also, earlier research emphasizes that accumulation of P in pigeon pea is higher than in maize, where Otani and Ae (1996) claimed that pigeon pea had "much higher" P uptake than maize, however they do not mention if it the increase was statistically significant. Myaka et al. (2006) reported that pigeon pea intercropped with maize depleted the soil with P more than pure maize did, which also would suggest a higher P uptake, although a higher nutrient uptake would be required as the plant biomass is larger than maize. Extraction data implied that available P in pigeon pea biochar was quite high, thus higher P content in the biochar.

The high uptake and content of P in pigeon pea could raise the question whether the plant has specific mechanisms to access P, as was mentioned in earlier sections and suggested by Garland et al. (2016), Ascencio (1996), Ae et al. (1990) and Otani and Ae (1996). Maybe

more data, f example where P uptake is controlled, like a pot experiment as Otani and Ae (1996) did, could improve understanding of those mechanisms.

#### 4.2.2 P sorption and DPS

From the sorption isotherms for Mkushi  $Q_{max}$  was 299 mg/kg for BL samples (Table 4) which was a significant increase from N to BL. In Kaoma,  $Q_{max}$  has not been calculated, but Figure 7 shows an increase in adsorption from N to BL also. Higher adsorption in BL samples can probably be explained by the biochar which increase soil pH. pH is the only parameter (which determines sorption) that had a significant change. It increased significantly for both regions: from 5.2 to 6.5 in Mkushi and from 6.0 to 7.3 in Kaoma (both p<0.001) (Table 3). This pH increase would enhance precipitation of Ca-PO<sub>4</sub>. Biochar contain Ca, and pigeon pea biochar had higher Ca content than biochar from other crops did (corn cob and rice husk) (Munera-Echeverri et al., 2018). Also, a high biochar P content will enhance precipitation with Ca. Possibly, biochar could also act as a PO<sub>4</sub> sorbent where Al, Fe, Ca or other cations functions as a bridge between biochar and PO<sub>4</sub>, as Mukherjee et al. (2011) emphasized.

Results from BL samples can be confirmed by Alling et al. (2014) that reported both PO<sub>4</sub> adsorption and pH in Kaoma to increase significantly as it was added 5% biochar (made from a brachystegia tree) compared to no biochar. Hale et al. (2013) did P sorption experiments of P to biochar (corn cob and cacao shell), and they found mostly desorption and little adsorption. But after rinsing it thoroughly (removing PO<sub>4</sub>), the adsorption increased, and Hale et al. (2013) discussed that it may be due to more available sorption sites. This match the sorption and the biochar extraction data, and it also coincided with DPS data showing that DPS for pure biochar was significantly higher than for soil samples (Appendix A). As Hale et al. (2013) found, after some of the P from biochar desorbs and DPS is lower, sorption sites are available for adsorption. Therefore, applying biochar in the soil together with fertilizer may be beneficial.

#### 4.2 Biochar applied in the field, Mkushi

Data for tot C (Table 3) showed significantly (p<0.001) higher C in soil samples from biochar added on the lab (BL) than biochar applied in field (BF), even though the added amount was the same (2%). In the field, biochar could have been distributed unevenly in the soil over time, so when soil samples were taken after one season they could have had varying and also lower content of biochar, which is also what the tot C data showed. Therefore, one cannot expect a significant increase in pH (which also was the case). In the P-AL analysis, it was extracted 500mg P per kg biochar, which would mean that approximately 20kg/ha plant available P was applied in the field through biochar (calculations in Appendix D). In Mkushi it was added 17.5kg/ha P fertilizer (Martinsen et al., 2019) which means that almost the same amount P was added in fertilizer as what biochar contributed with given that all that biochar "stayed" in the soil.

#### 4.2.1 P-AL

The biochar and fertilizer application in Mkushi resulted in P-AL values of  $26 \pm 4.74$  mg/kg, significantly higher than both N and PP plots (p<0.01 and p<0.05 respectively) (Figure 8). However P-AL levels was still in the class "low" according to Krogstad et al. (2008) (Table 6). Martinsen et al. (2017) presented data for Bray-P, which is another method for plant available P often used in neutral or acid soils. Data for Mkushi showed Bray-P to be 12.74  $\pm 1.95$  mg/kg in plots added fertilizer (17.5mgP ha<sup>-1</sup> year<sup>-1</sup>) and no biochar (Martinsen et al., 2017). Bray-P data match the P amount BF samples would have had if no biochar was added: 10.29 mg/kg P (Appendix D). However, P-AL has shown to extract more P than Bray-P does (Neyroud & Lischer, 2003). Overall, P-AL data imply that even more plant available is required for optimal plant growth, according to Krogstad et al. (2008).

The second hypothesis (H2) stating that biochar application will increase plant available P in both Mkushi and Kaoma, can be confirmed based on the theoretical biochar experiment (BL) that had a significant increase in P-AL from N samples (Kaoma p<0.001 and Mkushi p<0.01). However, for samples from biochar field (BF) in Mkushi a significant increase in P-AL (at p<0.01) was partly due to fertilizer application which made up almost as much plant available P as biochar did. As the results for Tot C implied did little biochar end up in the sample, a controlled experiment will not be transferable to field.

#### 4.2.2 The effect of biochar and fertilizer

Sorption isotherms for Mkushi biochar samples (BF) showed even lower  $Q_{max}$  (94 ±18 mg/kg) than pigeon pea (PP) samples did (Table 4).  $Q_{max}$  decreased significantly (p<0.05) from N to BF. The lower adsorption potential in BF samples than in BL samples can be explained by the significant increase in DPS from N to BF (p<0.05) due to P supply. No significant increase in pH showed that biochar's capability to increase pH thus weaker bonds of P, did not seem to have been the cause of increased P-AL. An increase in P content seem to have affected more. As mentioned, earlier research has reported varying reasons for biochar's effect, if it is mostly pH, P content or other mechanisms.

The overall goal of increased P availability is the anticipated increase in yield. In Mkushi, Martinsen et al. (2014) found yields to increase more than in Kaoma with biochar and fertilizer application than fertilizer alone. To compare this to P availability, their results coincides with Mkushi N samples having lower DPS, higher Q<sub>max</sub>/adsorption capacity and lower P-AL than Kaoma, thus the effects of available P will be higher. To have biochar field data from Kaoma to compare to both BF samples from Mkushi and the results of Martinsen et al. (2014) would be interesting. Further, the authors concluded that the effect of combining fertilizer and biochar was due to increased cation exchange capacity (CEC) and pH which improved to nutrient retention, thus stating that biochar probably is most effective together with fertilizer. Therefore, one could predict significant positive effects of biochar application in Kaoma in terms of yield increase as supported by literature and P availability supported by both literature and the positive effects seen in Mkushi.

Based on what has been discussed, it seems that biochar from pigeon pea feedstock can continue to be a crop favourable to make biochar of its residues in regards to supplying the soil with P in both Mkushi and Kaoma where P-AL is low. Also, the effect of fertilizer will increase with application of biochar as well due to increased DPS and lower adsorption in high P sorbing soils. So even though the soil has a high P adsorption, P-AL may still be relatively high if enough fertilizer has been added to increase DPS sufficiently.

#### 4.3 Study limitations and future work

Limitations of this study would be the lack of samples for biochar application in Kaoma as controlled lab experiments does not necessarily transfer to the field. The difference between biochar lab samples and field samples was illustrated in Mkushi. Further, this thesis had only one sample for each farm, and as there are local variations between farms, several replicates would increase the results' accuracy.

Further, it is suggested to do studies on multiple seasons with pigeon pea crop rotation and biochar application to fully understand the soil P mechanisms of pigeon pea in these fields. Maybe similar experiments could show different results after two or three seasons with pigeon pea possibly due to a more steady system. Also, it would be interesting to examine how long the biochar will "fuel" the soil with P as these results are based on samples taken within a year after biochar application. As this thesis only covers two regions of Zambia, these results may be not be transferable to other regions with different soils.

### 5 Conclusion

Crop rotation with pigeon pea did not increase the plant available P (H1), however, since the uptake of P by the pigeon pea plant is high, the P content in the biochar applied next season lead to a significant increase in plant available P. Based on BL samples, the second hypothesis (H2) could be confirmed, however not confirmed based on BF due to that little BC ended up in the sample and that almost half of the P content was from fertilizer input. Data implied that higher P-AL was connected to higher C:P ratio and higher DPS. DPS was negatively correlated with Q<sub>max</sub> (p<0.05) in Mkushi, however some samples did not imply such correlation which may be due to precipitation of Ca- or Al-P. Furthermore, application of fertilizer together with biochar will be advantageous due to a higher DPS and thus higher plant available P. So even though the soil has a high adsorption capacity, P-AL may be relatively high if enough fertilizer has been added to increase DPS sufficiently. A significant increase in pH was observed for BL samples and not BF samples. Increased pH was not concluded to be the main explanation for the significant increase in P-AL for field samples. Rather the P content in the biochar and increased DPS was reported here as the main effects.

The results of this thesis contributes to knowledge gaps concerning how soil P properties change with pigeon pea crop rotations as no studies have addressed P sorption characteristics. As such, the findings of this thesis contribute to knowledge concerning mobilization of strongly bound P with pigeon pea, as just a few studies have looked at previously. Furthermore, assessment of the P content of biochar from pigeon pea feedstock have not been done prior to this. Thereby, this thesis can be of relevance to further research regarding nutrient availability and yield increase connected to pigeon pea.

We still do not know the long term effects of maize – pigeon pea crop rotation in Kaoma and Mkushi on P availability. Also, the effect of pigeon pea biochar application in Kaoma is uncertain, however significant positive effects there was predicted based on these results and earlier research. A recommendation to the farmers in Mkushi and Kaoma based on this thesis' results will be to use pigeon pea as a crop rotator and as biochar feedstock due to its great potential to increase plant available P. The effect of fertilizer increase when applied with biochar, thus less fertilizer will be necessary to increase yield. This is of high relevance as increased fertilizer prices causes a major challenge for small-scale farmers.

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# Appendix

## Appendix A

 Table: Coordinates of the farms where soil samples

 were taken, soil texture, and HWEC, HWEP and

 C:P ratio for each soil sample with SE

Farm	South	East
	coordinates	coordinates
M.2	13°43'48.6"S	29°06'31.1"E
M.3	13°43'38.3"S	29°06'19.4"E
M.6	13°44'08.1"S	29°06'10.2"E
M.8	13°44'32.7"S	29°05'48.14"E
M.9	13°44'45.0"S	29°05'57.4"E
K.2	14°51'16.9"S	24°49'01.8"E
K.3	14°52'51.3"S	24°49'51.2"E
K.6	14°44'41.8"S	24°33'28.0"E
K.7	14°43'37.8"S	24°34'10.6"E
K.9	14°42'03.5"S	24°32'25.2"E

Soil ID	Texture	Sand	Silt	Clay
	USDA			
		%	%	%
M.2.N	Sandy Loam	73.2	22.4	4.4
M.3.N	Sandy Loam	69.2	26.4	4.4
M.6.N	Sandy Loam	69.2	26.4	4.4
M.8.N	Loamy Sand	81.2	14.4	4.4
M.9.N	Loamy Sand	79.2	16.4	4.4
K.2.N	Sand	93.2	4.4	2.4
K.3.N	Sand	91.2	6.4	2.4
K.6.N	Sand	93.2	4.4	2.4
K.7.N	Sand	93.2	4.4	2.4
K.9.N	Sand	93.2	4.4	2.4

Soil ID	HWEC	HWEP	C:P
	mg/kg	mg/kg	
M.2.N	240	1.10	0.005
M.3.N	360	2.25	0.006
M.6.N	290	3.55	0.012
M.8.N	230	1.25	0.005
M.9.N	220	1.00	0.005
M.N	268	1.83	0.007
	(±120)	(±0.82)	(±0.001)
M.2.PP	260	2.45	0.009
M.3.PP	390	3.15	0.008
M.6.PP	300	3.15	0.011
M.8.PP	230	1.65	0.007
M.9.PP	330	3.65	0.011
M.PP	302	2.81	0.009
	(±135	(±1.26)	(±0.001)
K.2.N	300	13,5	0.045
K.3.N	280	9.5	0.034
K.6.N	320	8.5	0.027
K.7.N	300	8.5	0.028
K.9.N	280	6.0	0.021
K.N	296	9.2	0.031
	(±132)	(4.1)	$(\pm 0.0040)$
K.2.PP	320	7.5	0.023
K.3.PP	280	9.5	0.034
K.6.PP	290	9.5	0.033
K.7.PP	310	11.0	0.035
K.9.PP	240	8.0	0.033
K.PP	288	9.1	0.032
	(±129)	(±4.07)	(±0.0020)

Soil ID	pН	Tot C	Tot N	C/N	P-AL	Pox	Alox	Feox	DPS
		%	%		mg/kg	mg/kg	mg/kg	mg/kg	
M.2.N	5.2	0.42	0.05	8.06	4.7	27	360	310	0.040
M.3.N	5.5	0.48	0.07	7.12	5.0	32	500	340	0.038
M.6.N	5.1	0.53	0.05	9.72	11.0	59	320	350	0.088
M.8.N	5.1	0.53	0.05	10.17	3.7	26	320	170	0.053
M.9.N	5.1	0.46	0.05	8.71	4.7	31	380	250	0.049
M.N	5.2	0.48	0.06	8.75	5.82	35	376	284	0.054
	(±0.1)	(±0.02)	$(\pm 0.02)$	(±0.55)	(±1.31)	(±16)	(±168)	(±127)	(±0.009)
M.2.PP	5.3	0.57	0.04	15.09	3.7	27	400	310	0.038
M.3.PP	5.4	0.97	0.06	18.47	7.6	34	460	330	0.043
M.6.PP	5.6	0.57	0.03	22.87	19.0	49	310	340	0.075
M.8.PP	5.4	0.46	0.02	17.33	4.3	20	270	130	0.050
M.9.PP	5.9	0.58	0.03	25.52	6.9	31	280	200	0.065
M.PP	5.5	0.63	0.04	17.88	8.3	32	344	262	0.054
	(±0.1)	(±0.28)	(±0.02)	(±1.39)	(±2.78)	(±14)	(±154)	(±117)	(±0.007)
M.2.BF	5.3	0.63	0.02	15.45	30.0	47	280	230	0.092
M.3.BF	5.2	0.95	0.06	18.13	10.0	42	550	330	0.048
M.6.BF	6.0	0.74	0.04	21.69	35.0	83	310	290	0.138
M.8.BF	5.1	0.58	0.03	17.62	22.0	63	300	160	0.137
M.9.BF	5.8	0.84	0.05	31.91	35.0	68	330	220	0.124
M.BF	5.5	0.75	0.04	19.68	26.4	61	354	246	0.108
	(±0.1)	(±0.33)	(±0.02)	(±1.77)	(±4.7)	(±27)	(±158)	(±110)	(±0.17)
M.2.BL	6.5	1.94	0.06	34.48	11.0	27	330	250	0.047
M.3.BL	6,5	2.20	0.06	45.73	13.0	34	460	290	0.045
M.6.BL	6.5	1.98	0.04	50.41	26.0	60	300	310	0.098
M.8.BL	6.6	1.85	0.04	43.95	13.0	34	310	150	0.074
M.9.BL	6.5	1.89	0.04	12.43	15.0	34	360	220	0.059
M.BL	6.5	1.97	0.05	41.30	15.6	38	352	244	0.065
	(±0.0)	$(\pm 0.88)$	$(\pm 0.02)$	(±3.49)	(±2.7)	(±17)	(±157)	(±109)	(±0.010)
K.2.N	6.0	0.71	0.06	11.91	16.0	20	95	42	0.146
K.3.N	6.1	0.62	0.05	11.09	14.0	24	140	50	0.126
K.6.N	6.2	0.54	0.05	12.85	12.0	19	100	48	0.128
K.7.N	6.0	0.65	0.05	11.24	9.5	25	130	85	0.116
K.9.N	5.8	0.52	0.05	15.38	8.6	24	230	110	0.071
K.N	6.0	0.61	0.05	11.90	12.02	22	139	67	0.118
	(±0.1)	(±0.27)	(±0.02)	(±0.34)	(±1.37)	(±10)	(±62)	(±30)	(±0.013)
K.2.PP	6.1	0.63	0.04	28.53	6.7	15	95	43	0.109
K.3.PP	6.4	0.64	0.02	48.06	16.0	32	170	50	0.145

Table: Soil properties each soil sample and mean values with SE

K.6.PP	6.4	0.50	0.01	43.84	13.0	16	70	43	0.142
K.7.PP	6.1	0.61	0.01	25.41	12.0	30	130	90	0.136
K.9.PP	6.0	0,56	0.02	48.40	16.0	27	140	65	0.132
K.PP	6.2	0.59	0.02	32.24	12.7	24	121	58	0.133
	(±0.1)	(±0.26)	(±0.01)	(±6.04)	(±1.7)	(±11)	(±54)	(±26)	(±0.006)
K.2.BL	7.2	1.96	0.04	51.03	24.0	37	120	57	0.209
K.3.BL	7.4	1.98	0.04	66.30	26.0	42	220	170	0.108
K.6.BL	7.4	1.81	0.03	33.02	24.0	24	79	39	0.203
K.7.BL	7.3	1.75	0.05	82.25	22.0	38	170	120	0.131
K.9.BL	7.2	1.90	0.02	8.06	20.0	31	130	71	0.154
K.BL	7.3	1.88	0.04	56.20	23.2	34	144	91	0.161
	(±0.1)	(±0.84)	$(\pm 0.02)$	(±8.38)	(±1.02)	(±15)	(±64)	(±41)	(±0.020)
Biochar ·	- 75.2	0.878 85.62	500	470	320	250		0.825	

Table: Data for Langmuir sorption isotherms for Mkushi.							
Soil ID	Qmax mg/L	К <sub>L</sub> L/mg	R <sup>2</sup>				
M.2.N	0.296	0.090	0.98				
M.3.N	0.244	0.060	0.99				
C.6.N	0.164	0.030	0.94				
M.8.N	0.104	0.010	0.94				
M.9.N	0.181	0.030	0.98				
M.N	0.198 (±0.033)	0.044 (±0.014)	0.97 (±0.01)				
M.2.PP	0.127	0.016	0.98				
M.3.PP	0.159	0.030	0.98				
M.6.PP	0.081	0.007	0.95				
M.8.PP	0.116	0.013	0.96				
M.9.PP	0.055	0.003	0.98				
M.PP	0.108 (±0.018)	0.014 (±0.005)	0.96 (±0.01)				
M.2.BF	0.060	0.004	0.98				
M.3.BF	0.163	0.030	0.94				
M.6.BF	0.071	0.005	0.92				
M.8.BF	0.083	0.007	0.99				
M.9.BF	0.092	0.008	0.99				
M.BF	0.094 (±0.018)	0.011 (±0.005)	0.96 (±0.02)				
M.2.BL	0.286	0.080	0.92				
M.3.BL	0.350	0.120	0.95				
M.6.BL	0.267	0.070	0.93				
M.8.BL	0.275	0.080	0.90				
M.9.BL	0.319	0.100	0.85				
M.BL	0.299 (±0.015)	0.090 (±0.009)	0.91(±0.02)				

## Appendix B: Data and calculations from sorption experiments





Figure: Linear regression from the Langmuir isotherm for samples in Mkushi. Amount of P in solution is plotted against P in solution/P adsorbed. A  $R^2$  closer to 1.00 shows better linear relationship.



Figure: Linear regression from the Langmuir isotherm for samples in Mkushi. Amount of P in solution is plotted against P in solution/P adsorbed. A  $R^2$  closer to 1.00 shows stronger linear relationship.

#### **Appendix D: Calculations**

#### 1. <u>P content of biochar applied in the field</u>

For biochar, it was extracted 500mg P per kg biochar in the P-AL analysis, which equals 0.5g/kg. This means that plant available P (determined by P-AL) makes up about 0.05% of the biochar. Amount of biochar applied in Mkushi fields was 4 ton/ha which equals 4000 kg/ha, and if plant available P makes up 0.05% the biochar, plant available P applied in the field through biochar was approximately 20kg/ha.

#### 2. <u>P-AL contribution from fertilizer and biochar:</u>

Because fertilizer and biochar contributed with approx. the same amount of P (calculated above) the amount of P-AL that fertilizer and biochar both contributed with would be: P-AL of BF subtracted the P-AL of N and divided by two: 26.4 mg/kg (P-AL BF) - 5.82mg/kg (P-AL N)/2 = 10.29 mg/kg.



Norges miljø- og biovitenskapelige universitet Noregs miljø- og biovitskapelege universitet Norwegian University of Life Sciences Postboks 5003 NO-1432 Ås Norway