BIOCHAR AND ASH AMENDMENTS TO IMPROVE SOIL PHOSPHORUS FERTILITY, WATER RELATIONS AND RETENTION

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ABSTRACT

Biochar and ash, both as separate products and including ash as a component of biochar[1], are produced as by-products from thermochemical decomposition and bio-energy generation processes such as combustion, gasification, or pyrolysis. The addition of biochar to improve nutrient uptake and retention has been studied in various settings and with a variety of crops. However, biochar, when applied without other treatments, has often been found to have limited impact on crop yields in Canadian prairie soils. This study aimed to determine the effects of biochar amendments, with and without added phosphorus fertilizer, on soils and crops in the Canadian prairies as related to crop yield, phosphorus uptake and recovery, soil phosphorus retention, water dynamics and phosphorus loss in leachate and runoff. This thesis reports on studies undertaken in 2022 with biochar and phosphorus fertilizer amendments on nutrient poor soils from the brown and black soil zones in southern Saskatchewan (controlled environment study) and from the brown soil zone at a site near Central Butte, Saskatchewan (field study). Under optimal conditions of the growth chamber, biochar derived from canola hull, manure and willow feedstocks were shown to contribute some available P for plant uptake, with observed recovery of applied biochar P being at best about 50% of Triple Superphosphate fertilizer. The biochars increased residual P in soil in both chamber and field depending on feedstock, with manure and willow biochars as well as the meat and bonemeal ash being the most effective, but the effects of biochar amendments on crop yield were variable, leading to the conclusion that the effects are at least partly related to the biochar feedstock and production conditions, as has been shown in many other studies on biochar. An important benefit of biochar amendment observed in the study was increased phosphorus retention in soil that contributed to increased post-harvest labile P as well as reduced leaching and snowmelt runoff export. To a lesser extent the biochars contributed to increased water holding capacity and water infiltration. The results of this study indicate that biochars and ash can potentially benefit canola and wheat production, by enhancing P nutrition and recovery, and that a balance may be obtained between biochar supplying P during the growing season while at the end of the season reducing P loss in the spring snowmelt runoff or during leaching events. Biochar added at 10 tonnes per ha showed the best performance in

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[1] Reference to biochar in this abstract includes ashes.

terms of agricultural improvement potential under both controlled environment and field conditions when applied to brown and black chernozem soils from southern Saskatchewan.

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I would like to take this opportunity to express my heartfelt gratitude to the following people who have been instrumental in the completion of this thesis. Without the collective efforts and support from each of these individuals and organizations, this thesis would not have been possible.

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DEDICATION

I would like to dedicate this thesis to my husband Vulco Viljoen, without whom this whole endeavour would not have been possible. For all the little things and the big things.

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
C	Carbon
CEC	Cation exchange capacity
CRD	Completely randomized design
EC	Electrical conductivity
F	F value used in statistics
GHG	Greenhouse gases
HSD	Honestly significant difference (Tukey)
K	Potassium
MBM(A)	Meat and bonemeal (ash)
MK	Modified Kelowna
N	Nitrogen
NUE	Nitrogen use efficiency
OC	Organic carbon
p	P value used in statistics
P	Phosphorus
PRS	Plant root simulator
PUE	Phosphorus use efficiency
RCBD	Randomized complete block design
rpm	Revolutions per minute
S	Sulphur
SE	Standard error
SK	Saskatchewan
(S)OC	(Soil) organic carbon
(S)OM	(Soil) organic matter
SSA	Specific surface area
TSP	Triple Superphosphate

1. INTRODUCTION

1.1 Background

Biochar and ash are produced as by-products from thermochemical decomposition and bio-energy generation processes such as pyrolysis, gasification and combustion. When organic matter such as wood, crop residues or animal wastes are subjected to pyrolysis, the nutrients present in the residues are largely retained in the biochar or ash and are available to be used as nutrient amendments in agricultural settings, depending on the solubility of the nutrient in the char (Alotaibi, 2014; Tenic et al., 2020). Most literature describes ash as the inorganic mineral component of biochar which typically forms about 0.5% – 5% of the solid product (Basu, 2018, Novak & Johnson, 2019). Ash can also result from gasification, where the temperatures and residence time is often too high to produce biochar. Where the term ash is used in this thesis, it refers to the latter except where specifically referred to as the ash faction of biochar. The terms biochar and char are used interchangeably in this thesis, mainly to describe the byproducts from pyrolysis processes, but are at times used as global terms to refer to all solid by-products produced during the thermochemical breakdown of biomass.

Biochar and ash have been promoted as soil amendments that can improve carbon sequestration and agronomic performance by increasing nutrient uptake and retention in agricultural settings. It has been studied extensively across the world using diverse crop types including vegetables, wheat, corn and beans to name a few (Lehman *et al*., 2006; El-Naggar *et al*., 2019; Schoenau, 2020; Tenic *et al*., 2020). Most biochar studies have been conducted using tropical or sub-tropical soils, with comparatively few studies in arid and semi-arid environments. Studies in mainly tropical soils showed significant improvement in some crops, especially under highly leached acidic conditions, while others have shown limited to no improvement with biochar amendments, and a small percentage showed a decline in yield after the addition of biochar (Tenic *et al.,* 2020), indicating the variability of outcomes from the application of biochar. Studies in the Canadian prairies have shown that biochar from agricultural feedstocks and waste by-products, when applied with or without other treatments, has limited impact on canola and wheat production, especially at low rates of application (Alotaibi, 2014; Ahmed, 2014; Hangs *et al*., 2021). However, limited information is available of the effect of biochar as a phosphorus fertilizer in the Canadian prairies.

In addition to agronomic performance, biochar may also help to reduce nutrient losses under conditions where loss potential for nutrients is high through leaching and runoff (Schneider *et al.,* 2019; Wiens *et al*., 2019). Of specific interest is phosphorus (P) – an important nutrient element in crop production. As P is a limiting factor to crop production in many prairie agricultural soils, it is commonly added as fertilizer, but with over-fertilization it can be a contributor to eutrophication of water bodies when it leaves the field in runoff (Grant & Flaten, 2019). Biochar reduces phosphorus losses during leaching and runoff events by adsorbing P ions and changing the phosphorus pools in soil (Schneider *et al*., 2019). However, limited research is available on the effect of biochar on the prevention of P losses in leachate and runoff, as well as the reduction of runoff by means of improved infiltration and water retention in the Canadian prairies.

This study looks at the short term (single growth season) impacts of adding different types of biochars that contain P in varying amounts on soils low in phosphorus to determine their effect on crop yields and soil P content and retention, as well as the char's effects on soil-water relations.

1.2 Research questions

The aim of this study was to investigate the following key knowledge gaps in the Canadian prairies through a series of controlled environment and field studies:

- Very few studies have included a comparison between biochars and fertilizer both applied alone, and chars co-applied with fertilizer.
- Limited research has been undertaken on the combined role of biochar both as a phosphorus source for crops and as a sink for reducing phosphorus losses in leachate and snowmelt runoff, especially in the Canadian prairies.
- Few studies have been undertaken to determine the capabilities of biochars in general to improve prairie soil's nutrient and carbon retention capacity and effects on water relations.

This study aimed to test the efficacy of biochars produced from different agricultural feedstocks for agronomic and environmental enhancement. Comparisons are made of biochar and commercial phosphorus fertilizer treatments alone and biochar co-applied with P fertilizer. The soils used are phosphorus deficient soils from the brown and black soil climatic zones in southern Saskatchewan.

Based on available research, the following assumptions were made, and research questions and a hypothesis developed accordingly to test these assumptions:

- Biochar and ash agricultural amendments in the Canadian prairies will improve soil available P, as assessed through plant P uptake and recovery, as well as P retention in the soil, as assessed through chemical extraction methods.
- Biochar and ash additions will improve soil productivity (availability of nutrients and increased soil health) and crop yield, however, the effectiveness of the amendments in enhancing crop uptake and recovery of added P would follow the pattern: commercial fertilizer > ash > biochar.
- Biochar will enhance soil-water relations by improving soil water infiltration and storage capacity.
- Biochar amended soils will retain more P and thereby reduce the P load in snowmelt runoff and during leaching events.
- Biochar will increase carbon sequestration.

Based on these assumptions, it is hypothesized that depending on the characteristics of the char as determined by feedstock and production conditions, it will provide phosphorus in varying amounts for crop utilization but less than that of commercial P fertilizer. It is also hypothesized that P losses in run-off and leaching will be less in char amended soils than in P fertilized soils due to the binding of P in the char materials.

The overall goal of this study is to investigate how separate and combined use of biochar, ash and P fertilizer on Saskatchewan soils can serve as a source and sink of P, increase crop yield, and affect other important soil properties, including pH, organic carbon and water infiltration and storage.

1.3 Thesis organization

This chapter and the following literature review provides a general introduction and overview of the research topic, with overall hypotheses and objectives of the study introduced. The following two chapters report on the specific research studies to address objectives while the last chapter provides an overall synthesis and conclusion.

Chapter 1 provides a general introduction to the thesis and research hypotheses and objectives.

Chapter 2 provides background literature review on production, uses and characteristics of chars derived from combustion of organic feedstocks and its use as a soil fertilizer amendment.

Chapter 3 reports on evaluations of the effect of biochars developed from different sources and under different production conditions, including commercially produced biochar and experimental biochar products produced on a pilot basis by a USask chemical engineering laboratory[2] on crop yield, nutrient uptake and soil residual available nutrients, organic carbon (C), pH, nutrient retention in leachate and water holding capacity in controlled environment and field conditions.

Chapter 4 presents the results from a second large plot field study using a single source of biochar to investigate the effects of the biochar amendment on crop yield, nutrient uptake, and retention, losses in snowmelt run-off water and water infiltration under field conditions.

Chapter 5 provides an overall synthesis of the research project, integrating the key findings of the two studies and provides recommendations for future research.

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[2] Biochar obtained from Dr. Dalai's Catalysis and Chemical Reaction Engineering Laboratories (CCREL) at USask.

2. LITERATURE REVIEW

2.1 Thermochemical processes to produce biochar and ash

Thermochemical processes are used to convert biomass to generate energy, biofuels and other biomaterials such as char (Trubetskaya & Matsakas, 2021). The three thermochemical processes, in order of heat application, are pyrolysis, gasification and combustion (Jameel *et al.,* 2010). Each of these processes produce different bioproduct fractions as can be seen in Fig. 2.1. This thesis project and literature review is focussed on bioproducts produced using pyrolysis and gasification.

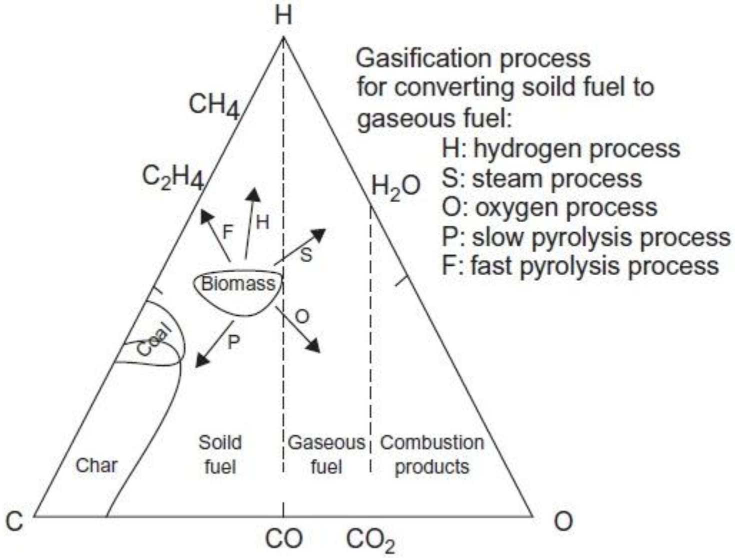

Fig. 2.1. C-H-O ternary diagram of biomass alteration during thermochemical processing. Credit: Basu, P. (2018). Chapter 5 - Biomass Gasification, Pyrolysis and Torrefaction (3rd Edition) (p155-187). Academic Press.

Pyrolysis is a thermochemical process used to break down biomass in the absence of oxygen. This process produces three product fractions: solid (biochar and ash), liquid (biofuels, heavy hydrocarbons) and gas (Basu, 2018). Biochar and ash can be produced via slow (minutes to hours) or fast (seconds) pyrolysis at temperatures ranging between 300 and 650°C, with some literature reporting temperatures as high as 1200°C (Mohan *et al.,* 2006; Novak & Johnson, 2019; Rajendran *et al.,* 2019), although this temperature is mostly used for gasification. Pyrolysis, compared to gasification or combustion produces a greater yield of solid product, using a process that does not release harmful volatiles and smoke while retaining a relatively high amount of carbon (Basu, 2018). When done under high vacuum, potentially toxic hydrocarbons are eliminated.

Gasification is undertaken at higher temperatures, typically in the range of 500^oC to 1200^oC and in the presence of a small fraction of air (Novak & Johnson, 2019). The main purpose of this process is to produce carbon and hydrocarbon gases (CO, CH_4, CO_2, etc.) while ash is produced as a by-product. The process is effective in reducing mass of waste material and in concentrating non-volatile elements in the remaining ash. The yield of the solid component by weight, produced through gasification, is around 10% or less compared to pyrolysis which produces between 12% (fast) and 30% (slow) yield (Ramola *et al.,* 2021).

Fig. 2.2 presents a flow diagram of the pyrolysis process in the Catalysis and Chemical Reaction Engineering Laboratories (CCREL) at the University of Saskatchewan, headed by Dr. Ajay Dalai. The CCREL produced some of the biochars used in this study.

The production of biochar and ash depends on the temperature, production rate (or residence time) and feedstock material. Processing biomass at lower temperatures and at a slower rate produces more solid materials while a higher temperature and shorter residence time results in higher biofuel and gas levels (Arni, 2017; Basu, 2018). Both temperature and feedstock influence the grain size or chunkiness of the biochar and/or ash, with higher temperatures resulting in a finer grain. For the project described in the following chapters of this thesis, chars were produced using fast pyrolysis (willow biochar at 400^oC), slow pyrolysis (canola hull, canola meal and manure chars at 300^oC to 600^oC) and gasification (meat and bonemeal ash (MBMA) at 650^oC to 800^oC). Both the manure char produced at 600^oC and the MBMA contained less oils with a resulting drier consistency. The plant-based feedstocks were a mixture of fine-grained powder and small (1-2cm) chunks, while the animal based feedstocks produced a much finer grained material.

The need for converting biomass using thermochemical processes links to the global requirements for waste reduction, reducing harmful greenhouse gas production resulting from decomposition and sustainable energy production to name a few (Patra *et al.,* 2021). Methane and other greenhouse gases (GHG) resulting from the breakdown of organic residues, including food and other agricultural waste products, has been shown to influence climate change and lead to an increase in global temperatures (IPCC, 2023). Investigations into reducing agricultural waste products and generating bioproducts which can be used to replace fossil fuels are being undertaken by the chemical

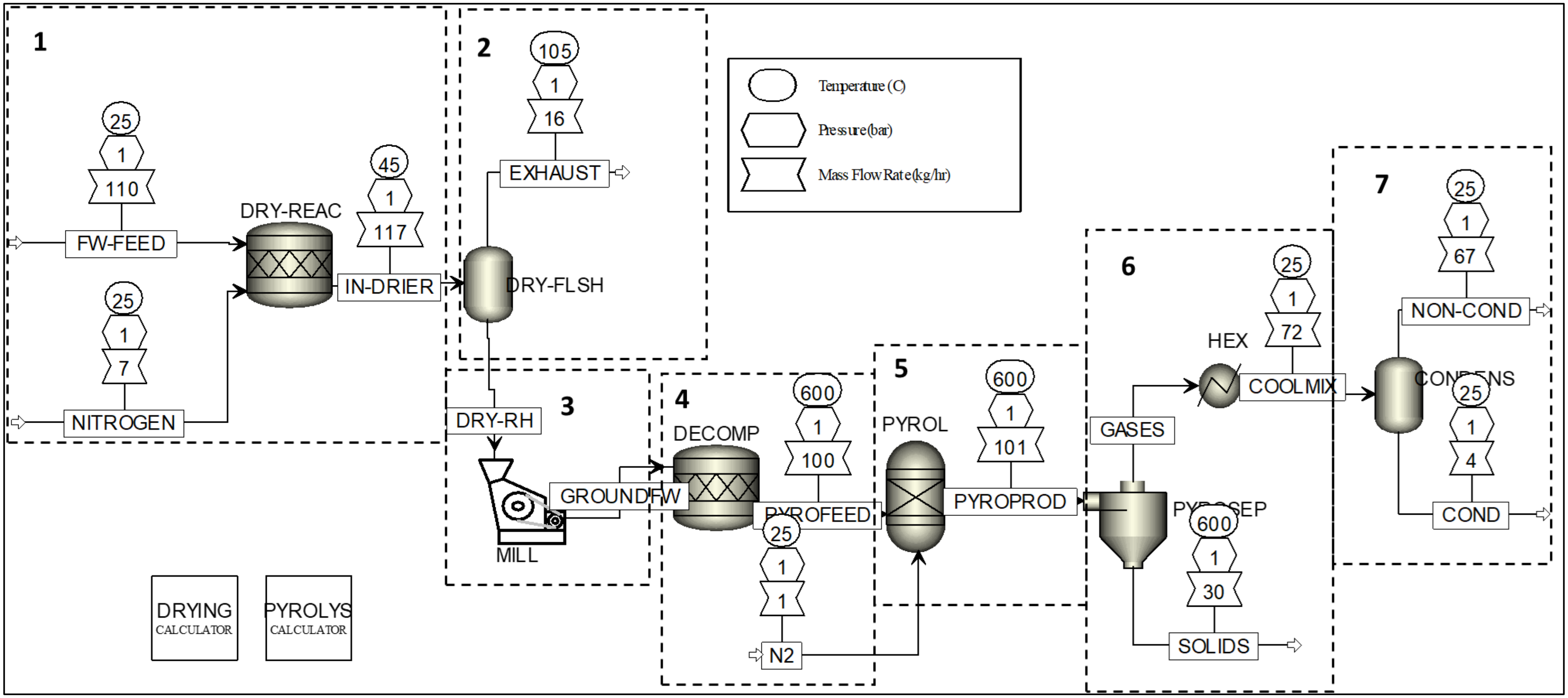

Fig.2.2. ***Flow diagram of the biochar production process in Dr. Dalai's Catalysis and Chemical Reaction Engineering Laboratories (CCREL) at the University of Saskatchewan as developed using the ASPEN process simulation software. The diagram shows the temperature in centigrade (circle), the pressure in bars (hexagon), and mass flow rate in kg/hr (concave hexagon). 1. The feedstock along with Nitrogen gas enters the drying reactor. 2. Nitrogen and moisture is off gassed. 3. Dried feedstock is ground. 4. The feedstock enters the pyrolysis chamber. 5. Nitrogen is added to the feedstock and the pyrolysis process commences. 6. Pyrolysis products are separated into gases and solids. 7. Gases are separated by means of condensing the gas into the bio-fuel liquid and remaining gas components (unpublished diagram courtesy of Dr. Venu Borugadda and Biswa Patra).***

engineering department at the University of Saskatchewan (Patra *et al.,* 2021). A component of this MSc. study is linked to the research being undertaken by the chemical engineering department and makes use of biochars produced in the CCREL.

While biofuels are commonly used, the solid by-products (char and ash) are not necessarily used in large scale or commercial applications and may end up on a landfill if no profitable use is found for it. The thesis research investigates the application of biochar in an agricultural setting to determine its production and environmental value.

2.2 Biochar and ash

Biochar, along with other organic matter has been used by various cultures for around 2 000 years as a soil amendment (Farm Energy, 2019; IBI, 2021a). Research on thermochemical decomposition products as soil amelioration has been ongoing for the past few decades.

Even though biochar research is still relatively new, a fairly large number of review papers have appeared over the past decade. These papers caution that although biochar can be beneficial as a soil additive, the potential risks associated with the use of biochar should not be overlooked, and recommended that further longer-term field studies be undertaken (Lehmann *et al.,* 2011; Spokas *et al.,* 2012; Mukherjee & Lal, 2013, 2014; Kuppusamy *et al.,* 2015; Shabaan *et al.,* 2018; El-Naggar *et al.,* 2019; Gao *et al.,* 2019; Zhang *et al.,* 2019; Tenic *et al.,* 2020). This section describes the general properties of biochar applicable to this study as highlighted by these and other authors.

The characteristics of biochar important for this study include its ability to release and sorb nutrients, specifically phosphorus, in nutrient deficient soils, a char's recalcitrance in soil, and its ability to alter soil-water relations.

2.2.1 General characteristics of char and ash

Feedstocks used in pyrolysis have a great influence on the composition of the chars produced. Lignocellulosic feedstock such as the willow and canola meal and hull used in this thesis research tend to have higher levels of carbon (C), hydrogen (H) and oxygen (O) than manure or other animal-based feedstocks (Novak & Johnson, 2019). Although feedstocks of higher mineral element content generally produce chars of higher mineral concentrations, the exact mineral content will depend largely on the feedstock and the thermochemical process and temperature used. Shabaan *et al*. (2018) noted that slow pyrolysis with higher temperatures resulted in more ash with associated greater nutrient concentrations.

The surface area of solid pyrolysis by-products is also dependent on the feedstock material and the pyrolysis temperature. Biochar surface areas increase from low temperatures (300^{o}C – 600^{o}C) to intermediate temperatures (650^{o}C – 850^{o}C) and thereafter decrease with continued rise in temperatures (Mukherjee & Lal, 2013). Cation exchange capacity (CEC) follows a similar increase-decrease pattern. This is explained by Antal & Grønli (2003) who noted that increasing temperatures in thermochemical decomposition processes result in the loss of alkyl aromatic units and O functional groups (e.g. hydroxyl, carbonyl, lactone, etc.) in biochar and ash. The authors indicated that the OH, C=O and aliphatic C-H groups disappear by 650^{o}C, the aromatic C-H groups disappear by 750^{o}C and by 950^{o}C the chemical spectra of biochar is similar to graphite. Thus, biochar and ash created at higher temperatures have less open C rings and chains available for oxidation, which in turn is linked to a decrease in specific surface area (SSA) and CEC (Mukherjee & Lal, 2014).

Through soil-biochar interaction, the high surface area of the biochar increases sorption capacity of soil by providing anion and cation exchange sites, which in turn increases a soil’s ability to retain nutrients (Mukherjee & Lal, 2013). The authors note in a 2014 paper that as nutrient availability and retention is linked to the CEC, higher temperature char and ash may be less effective at nutrient retention. While it may still be possible for higher temperature chars and ash to affect soils in terms of sorption, it is likely that a longer period will be required to develop sufficient sorption sites and associated soil-biochar interactions (Mukherjee & Lal, 2014).

A review study from 2020 showed that several studies have been done at varying rates of biochar application on various soil types/textures (Tenic *et al.,* 2020), most of which showed an improvement in the physical characteristics such as pH, available water content, bulk density and porosity. Overall, these studies showed that char addition increased soil pH (liming effect) and reduced or inhibited re-acidification. It was also noted that in general, biochar has a positive effect on the abundance and availability of macro nutrients, specifically N and P, and more so in soils amended with chars produced at lower temperatures. Other studies have also shown that biochar, when added to acidic soils, raise the pH, likely due to the presence of Ca, Mg, K and other cations, however, the alkalizing effect of biochar on soils with a higher pH, such as those found in SK is limited (Van Zwieten *et al.,* 2010; Mukherjee & Lal, 2014; Ahmed & Schoenau, 2015; Sarfaraz *et al*., 2020). These authors also note that the ability of biochar to affect soil pH is linked to increased CEC in more acidic soils treated with biochar. However, biochar has limited ability to raise the pH of calcareous soils and as such, it is expected that the soil-biochar interaction in these soils will not lead to a large increase in CEC. The alkalizing effect as well as the pH of biochar has been shown to decrease with age, likely due to oxidation and leaching (Shabaan *et al.,* 2018). Hangs *et al*. (2021) recommended that soil-biochar interactions be investigated over the longer term for their effects on sorption capacity as this is likely linked to N and P activity in soil.

Lehman *et al*. (2011) in a review looking at the effects of biochar on soil biota surmised that in general, biochar added to soil leads to an increase in soil biota. Significant changes in the makeup of the microbial community and enzyme activities were noted. At the time of the study, no negative impacts on soil biota had been observed. DeLuca *et al*. (2006) showed that wildfire-produced charcoal did not appear to have an influence on microbial biomass or activity, however, the charcoal may be able to change the activity and/or presence of specific microbes. El-Naggar *et al*. (2019) noted that biochars produced at a lower temperature increased the size of microbial communities, as opposed to supressing these communities by char produced at a much higher temperature. They ascribed it to lower temperature biochar having more volatiles which supplied the microbial community with available nutrients. Mukherjee & Lal (2014) reported a variety of results regarding the interaction of biochar and soil microbes, most notably, the potential for higher temperature char and ash to cause toxicity in mycorrhizal fungi and earthworms due to the higher pH and metal content, and the excessive sorbing of micronutrients leading to nutrient deficiencies which could create adverse conditions for soil fungi and bacteria. Yang *et al*. (2022) showed that the changes in soil porosity, as well as the different pore structures of biochar influenced the structure and abundance of the microbial community. The microbial community in turn affects the decomposition of soil organic matter (SOM) which determines the rate at which nutrients mineralize and become plant available.

Mineralization of nutrients is in part dependent on the rate at which biochar is applied (Karer *et al.,* 2013; Tenic *et al.,* 2020) while priming is defined as the changes occurring in C cycling and mineralization as a result of adding biochar to soils (Tenic *et al.,* 2020). The authors describe positive priming as increased mineralization while negative priming is linked to biochar binding organic matter and making it unavailable for microbial use. In their review paper, results regarding priming varied widely with many studies showing an increase in carbon sequestration while some studies showed enhancement of mineralization such that a net carbon loss was observed, necessitating the reapplication of biochar.

2.2.2 Biochar as a nutrient source and agronomic benefits

Biochar and ash can serve as nutrient sources, the effectiveness of which depends on the thermochemical decomposition process used. Ash is typically low in C and N but high in P and other minerals while biochar is rich in C (El-Naggar *et al.,* 2019; Schoenau, 2020). Biochar may also contain N and P in various proportions of varying bioavailability, depending on the feedstock material, and pyrolysis rate and temperature (Ippolito *et al.,* 2014; IBI, 2021b). These authors also note that biochars from wood feedstock are typically high in C and low in other nutrients while biochar from animal manure is also high in C but has higher mineral content such as P and K. Linked to this, Novak & Johnson (2019) note that manure and other animal-based feedstocks typically have a higher ash content associated with higher mineral content. This supports the composition of the biochars and ash used in this study as related to feedstocks (refer to Table 3.1).

Biochar as a slow-release nutrient source can improve the nutrient availability in soils and possibly reduce fertilizer requirements (Tenic *et al.,* 2020). Nutrient release and/or retention to and from biochar and soil is dependent on the sorption affinity of each nutrient with these substances (El-Naggar *et al.,* 2019). To facilitate the development of biochars with both nutrient retention and release capabilities suited to agronomic requirements, Tenic *et al*. (2020) noted that feedstock material can be blended to provide custom-made mineral profiles to address specific application requirements. Such blending would also improve the overall porosity and surface area profile of the char to enable improved chemical and physical interactions with nutrients. Linked to this are a few studies that have been done on char loading, which is the process in which a char is treated with a substance to have a specific effect. This can be achieved either through enriching the feedstock prior to pyrolysis, adding the required material with the feedstock prior to pyrolysis or immersing the char in a saturated liquid (Bolton *et al.,* 2019; Li *et al.,* 2020; Ghodszad *et al.,* 2021). Overall, these studies indicate that the loading effect improves a char's ability to adsorb nutrients. Unfortunately, these studies do not include information on the effect enhancement has on a char's capacity to act as a nutrient source in soils in the field.

The agronomic benefits and the capacity of biochar to improve soil fertility has been widely studied. While many papers indicate agronomic benefits, some studies have shown no benefits of biochar on soil fertility while others indicated negative crop responses – these studies have largely focussed on soils in tropical or temperate climate zones, with fewer studies on soils higher in pH such as those found in SK (Van Zwieten *et al.,* 2010; Karer *et al.,* 2013; El-Naggar *et al*., 2019). Hangs *et al*. (2021) noted that biochar added to prairie soils showed little to no agronomic benefit to canola except insofar as it increased N recovery to some extent. The study also showed that in some instances the addition of biochar in conjunction with manures decreased crop yield.

The age of the biochar (fresh vs weathered) has been shown to affect soils and crops differently. Mia *et al*. (2019) noted that chemically oxidized biochar, similar to naturally aged biochar likely contains more cation exchange sites, which is linked to greater retention of N and availability of P for plant uptake. The authors noted that P availability and uptake was not significantly affected by biochar applications alone, but rather in combination with N applications. Weathering may also increase oxidised functional groups along the char surfaces thereby increasing soil-biochar interactions (El-Naggar *et al.,* 2019). Hangs *et al*. (2021) found that a single application of biochar, in combination with liquid hog manure as a N source resulted in immobilization of N after four years, compared to the separate liquid hog manure and biochar applications. Although not investigated by the authors, the immobilization could be linked to the aging of the biochar.

Based on the finding of studies in temperate zones, crop yield and soil fertility effects depend greatly on biochar quantities added, with very high levels of biochar sometimes observed to decrease crop yield, as well as the type of biochar (feedstock and pyrolysis process) (Karer *et al.,* 2013; Ahmed & Schoenau, 2015; Hangs *et al.,* 2021). In addition, biochar appears to be most beneficial in these zones when combined with repeated applications of N, as per the agronomic N requirements in the region (Karer *et al.,* 2013). This is corroborated in the findings of a multi-year study which showed that fertilizer nitrogen, added in conjunction with biochar was largely taken up by crops in the first year, with decreased recovery in the following years, likely due to a mineralizing effect from the biochar (Hangs *et al.,* 2021).

A large portion of the literature focuses on how the C contents of biochar in soil affects nitrogen (N) mineralization. The available research is not detailed here as this thesis focusses on P. However, the following is noteworthy as it regards this study. Shabaan *et al*. (2018) indicated that feedstocks with higher lignin contents results in chars with higher C contents, with a high C:N ratio and associated reduced mineralization rates. Such decreased mineralization is not just linked to N, but also to other nutrients. Conversely, biochars with lower C contents result in increased mineralization potential and is thus able to release nutrients to the soil (Spokas *et al*., 2012).

A smaller portion of the literature focusses on the interactions of biochar and P. In a study on the use of P laden biochar, involving char treated with liquid KH_2PO_4 to increase the P content, the enhanced char was able to maintain soil available P over a longer period compared to the unimproved chars and the mineral P fertilizer (Li *et al.,* 2020). The improvement is linked to the homogenous and slow-release delivery of P from the P-laden char. A study on the use of biochar in a low pH red soil from Guangdong Province, China explored P sorption mechanisms using spectroscopy (Wu *et al.,* 2022). The study found that biochar decreased the soil’s capacity for P sorption thereby increasing bioavailable P, and increased the pH and dissolved organic carbon content of the soil. The increase in bioavailable P is attributed to the humic acid-like substances from what the authors termed the dissolved black carbon, which competes with phosphate in the soil for P sorption sites.

A study on the addition of varying proportions of manure char as a P source showed a slight rise in soil pH, an increase in CEC by 16-32 % and an increase in soil P by 82% (Jin *et al.,* 2016). Additionally, orthophosphate and pyrophosphate increased bioavailable soil inorganic P. Another study on acidic soils using different chars produced from diverse feedstocks under varying conditions found that the chars weakly adsorbed phosphate and that dissolved organic matter may inhibit P sorption, depending on the soil acidity levels (Schneider & Haderlein, 2016). As found by Wu *et al*. (2016), the dissolved organic matter competes with P for sorption sites, thereby potentially increasing P use efficiency. A four-year multi-crop field study from Brazil using wastewater sludge derived biochar on acid soils found that all P fractions were increased in the soil for at least two years after application (de Figueiredo *et al.,* 2020). The authors noted that the production conditions of the char did not affect the soil P fractions, but lower temperature-produced char resulted in greater crop yields. They concluded that biochar could replace mineral fertilizer for corn production.

A meta-analysis on the effect that biochar has on P availability in agricultural soils showed that while biochar can increase available P in acidic soils, there was no significant effect in alkaline soils (pH>7.5) (Glaser & Lehr, 2019). This said, biochar that was effective in raising available P levels did so in the short-, medium- and long term. Effectivity of the chars and the availability of P was linked to the feedstock and production conditions.

While biochar could act as a direct nutrient source and also improve the bioavailability of existing nutrients in the soil, when adding biochar to soil the purpose thereof must be clearly defined to determine which type of biochar (feedstock and production conditions) will potentially be most beneficial. This thesis looks at the use of biochar as a P fertilizer to increase soil available P and plant uptake as well as increasing P retention in the soil. Effects may be associated with an increase in soil available P originating directly from the additional P added as char as well as the impact of the char on processes affecting P availability in the soil such as sorption-desorption and mineralization as described previously. To this end, a variety of biochars and ash with varying P contents were used and compared to commercial P fertilizer.

2.2.3 Carbon sequestration

Biochar has been touted as one of the best methods of carbon sequestration in recent decades as it is recalcitrant when added to soil, leading to carbon retention (Lehman *et al.,* 2006; Alotaibi, 2014; House & Bever, 2019; Tenic *et al.,* 2020). As described in literature, the ability of biochar to increase carbon sequestration is a two-fold process:

1. Concentration of C in biochar through thermochemical decomposition[3] allows the C to be available for further use, whether as a fuel resource or soil amendment, instead of releasing the C into the air as CO_2 or other GHG. Pyrolysis can result in the retention of as much as 50% of C from the original biomass, depending on temperature and oxygen conditions (Basu, 2018). Comparatively, gasification and combustion of biomass under oxygenated conditions could retain as little as 3% of the original C (Adeyemi *et al*., 2017). Pyrolysis is thus the preferred method for producing high-C biochars.
2. Biochar is considered a stable and recalcitrant form of C. When crop residues are converted to char, the recalcitrance of the carbon is greatly increased. Through application of the char, it is widely believed that biochar placed in soil can sequester the C for hundreds to thousands of years. Not only does this allow for the C to be removed from the atmosphere via photosynthesis and reduce the recycling from plant material back to carbon and oxygen in decomposition, but it also increases the sorptive capacity of the soil (Sarfaraz *et al.,* 2020) and may reduce the bioavailability of remaining C (Cayuela *et al.,* 2013; Kerré *et al.,* 2016) which in turn will reduce the emissions from decomposition of soil organic carbon (SOC). Although ash is low in C, it has other benefits as a soil amendment and when used as such, the small percentage of C in the ash will be sequestered with a similar effect as described for biochar.

Notwithstanding the above, it should be noted that the recalcitrance of C in soil is highly variable, depending on the char feedstock and production conditions, the characteristics of the soil to which it is added, and whether it is used in actively managed agricultural settings or more passively managed areas such as nature reserves (Mukherjee & Lal, 2013, 2014; Tenic *et al*., 2020). Thus, in contrast to the optimism around biochar as a climate change miracle tool, some studies have been published indicating neutral impacts as well as GHG emissions from soils amended with biochars (Mukherjee & Lal, 2013, 2014). The authors noted that at the time of publishing, the majority of studies regarding biochar amendments in soil had been conducted in a laboratory or greenhouse setting, with very little field data available. Since then, additional studies have been undertaken and various review papers published. El-Naggar *et al*. (2019) noted in this regard that effects of biochar as a soil amendment, or

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[3] This is in contrast to the release of GHG through natural or other methods of decomposition of the organic feedstock materials.

otherwise, cannot be generalized as the characteristics of each biochar is uniquely dependent on the feedstock material, production process and temperature.

Although biochar is a stable form of C, the stability of the carbon is a function of the feedstock material, and materials with more lignin tends to be more stable. As well, higher pyrolysis temperatures result in more stable C (El-Naggar *et al*., 2019). As noted by Shabaan *et al*. (2018), biochar has a molar H:C ratio lower than that of the feedstock material, indicating polymerization. It is this characteristic that results in biochar being recalcitrant in soil. The authors also linked high lignin wood feedstock biochars to increased resistance to biodegradation when compared to animal by-product and crop residue chars. The rate at and direction in which biochar affects decomposition of SOC is related to the stability of the biochar. While on the one hand biochar could sequester SOC in its pore structure, reducing the availability of SOC for degradation and mineralization, the biochar could also promote microbial activity which would increase mineralization. Similarly, biochar may provide microbes with nutrients which will stimulate microbial growth and related SOC mineralization. The authors further state that the length of time during which biochar will influence C sequestration will depend on the stability of the biochar.

Weng *et al*. (2022) showed that in a tropical soil under some circumstances, biochar can be used to increase the SOC ceiling by changing the mechanisms in soil that affect mineralization. Zhang *et al*. (2019) reports the positive effects of C sequestration as demonstrated in short term incubation or field studies. However, Spokas *et al*. (2013) noted that three-year aged biochar increased microbial activity and resultant GHG emissions. The authors came to similar conclusions as El-Naggar *et al*. (2019), in that the biochar C:SOC ratio is the best indicator of CO_2 emissions in biochar amended soil, and that a ratio of greater than 2 will result in significant increases in CO_2 emissions.

The ability of biochar to sequester carbon in the long run is dependent on the soil used, the type of biochar added, climate and other external effects. As such, when adding biochar to soil with the intention to sequester carbon, various factors should be considered. These aspects should also be investigated when adding char for other purposes, to ensure that the site(s) remains carbon neutral or negative.

2.2.4 Biochar as a means to enhance soil-water relations

Soil hydrological properties, including water retention and water holding capacity, moisture content and infiltration rates, are linked to soil physical properties such as the bulk density and porosity, surface area and aggregate stability (Mukherjee & Lal, 2013, 2014). The authors noted that several studies reported improvements in water holding capacity and water retention due to amendment of soil with biochar. This is linked to the potential of biochar to form complexes with soil, leading to soil aggregates and resultant aggregate stability over longer periods. However, some studies reviewed by the authors indicated contrasting results.

Overall, biochar has been reported to increase infiltration and improve the soil's water storage (water holding) capacity, especially in dryland systems (Tenic *et al*., 2020). The authors note that the highest overall benefits may be seen in clayey soils, with diminishing returns in silt-loam and sandy soils. It was also noted that smaller biochar particles contribute more to water holding capacity than chunkier char due to increased microporosity associated with higher pyrolysis temperatures. Biochar amendments provided greater water holding capacity in coarser soils compared to medium textured soils and decreased the water holding capacity in fine textured soils (Tenic *et al*., 2020). Barnes *et al.* (2014) had similar results in a laboratory study. They proposed two hydrologic pathways for this: i) the first pathway is through the interstitial biochar-sand space as well as through the biochar pores; ii) the second is an overall increase in soil porosity through biochar addition. Hussain *et al*. (2020) showed that biochar increased the infiltration rate and decreased the desiccation crack potential due to char pores retaining water for longer periods than surrounding soil pores as well as the changes in size and dispersal of soil pores. The authors concluded that by preventing the development of cracks and associated pore pressure, biochar could reduce the need for irrigation as well as the effects of drought stress on vegetation.

As with other functions of biochar, the ability of biochar to improve or worsen soil-water relations are highly dependent on the biochar and soil properties. Part of this thesis work examines the effect of differently produced biochars applied at differing rates on water holding capacity and infiltration rates of prairie soils.

2.2.4.1 Infiltration

Infiltration has been studied for well over 100 years. It is defined as the *'process of entry into the soil, and subsequent movement, of water made available (under appropriately defined conditions) at its surface'* (Philip, 1998). Buckingham (1907) described the 'capillary potential' and 'capillary conductivity' of soil noting that after saturation of a soil is achieved, only some of the water will gravity drain from the soil while the remaining water will be retained through capillary action. Saturation is achieved once the larger soil pore spaces, which allows water to drain quickly through the profile, have been filled. Smaller interstitial pores are responsible for the retention of remaining water (Gargouri-Ellouze *et al.,* 2017). Philip (1957[1] & 1957[2]) expanded on this definition and gives an overview of infiltration research development through a series of published papers on the theory of infiltration (Philip, 1953 through to 1998). The capillary conductivity is the capacity of soil to allow further water movement due to external pressures (vertically or laterally) and is also referred to as hydraulic conductivity (or K). As much of the initial research on infiltration was done in laboratories under controlled conditions, research has been expanded to allow for field conditions, with a resulting

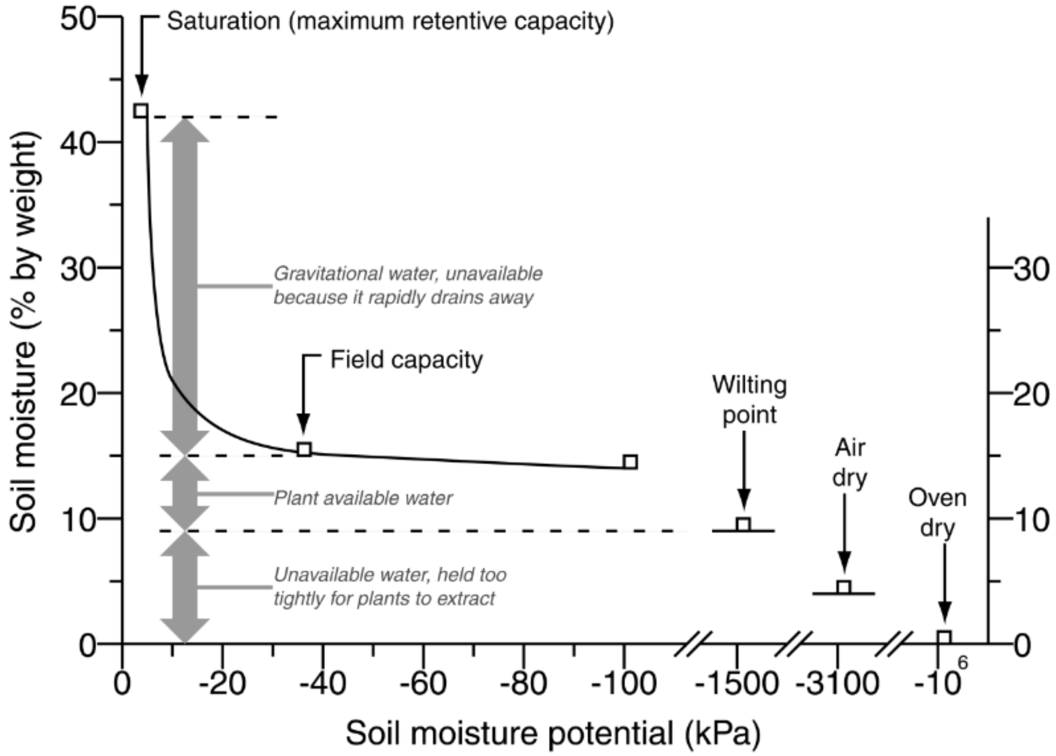

Fig. 2.3. Soil moisture curve showing the initial gravity infiltration, field saturated hydraulic conductivity (field capacity) and the permanent wilting point. Credit: Moorberg, Colby J. and Crouse, David A., "Soils Laboratory Manual: K-State Edition, Version 2.0" (2021). NPP eBooks. 39.

definition of field saturated hydraulic conductivity (or K_{fs}). K_{fs} allows for the calculation of hydraulic conductivity that takes into account air trapped within the soil, as is often the case under natural conditions (Elrick & Reynolds, 2002). Field capacity is illustrated in Fig. 2.3 as associated with gravity infiltration.

To determine which infiltration analysis method should be used in this thesis study, the author considered that an approach of more interest to farmers and agricultural managers would be knowing the infiltration rate of the soil before ponding occurs as it is related to runoff potential, otherwise known as sorptivity. One of the most commonly used equations for measuring infiltration rates, and the one used in this study, was developed by Philip in 1957. As part of his series on the theory of infiltration, he described field methods for measuring infiltration and further developed the sorptivity equation (Philip, 1957[2]).

The infiltration study also links up with the snowmelt runoff experiment in this thesis work which measured the loss of nutrients in snowmelt runoff.

2.2.4.2 Water holding capacity

Closely linked to infiltration is a soil's capacity to hold water. Cassel & Nielsen (1986) provides an overview of field capacity and available water capacity. They note that a soil's capacity to hold water is dependent on many factors, especially those that influence the pore size distribution. They also note that the water holding capacity may vary between soil horizons within the same soil, and that different soils have differing capacities. They define available water capacity or plant available water as the capacity of a soil to hold water between the field capacity and the wilting point (Fig. 2.3). Soil textures are linked to a range of volumetric soil moisture values, with plant available water increasing as clay content and microporosity increases and overall pore volume decreases (Fig. 2.4).

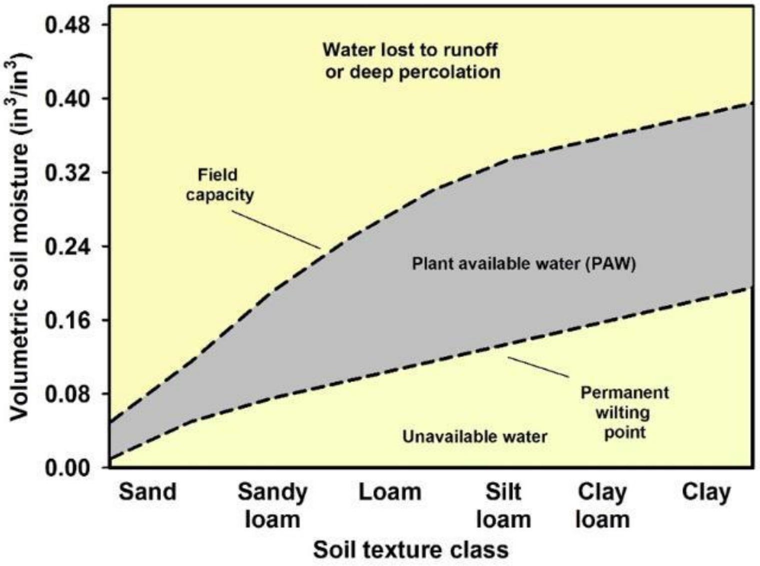

Fig. 2.4. Field capacity, available water capacity and wilting point shown in terms of soil texture. Each texture has a different soil moisture content range. Credit: University of Florida's Institute of Food and Agricultural Sciences (UF/IFAS) (2019). In Zotarelli, L., Dukes, M.D. & Morgan, K.T. (2019). Interpretation of soil moisture content to determine soil field capacity and avoid over -irrigating sandy soils using soil moisture sensors. UF/IFAS Extension publication # AE460.

2.2.5 Biochar as a method to reduce nutrient loss in leachate and snowmelt runoff

Biochar has been widely shown to positively affect N, P and sulfur (S) nutrient retention in a variety of laboratory and field settings, preventing loss of nutrients through leaching (Ding *et al.,* 2010; Knowles *et al.,* 2011, Troy *et al.,* 2014; Bradley *et al.,* 2015; Ghodszad *et al.,* 2021; Huang *et al.,* 2021). However, there is a need to determine whether the nutrient retention extends to the prevention of nutrients entering snowmelt runoff when biochar is applied to a soil, with or without the addition of fertilizer. Limited research has been done on the use of biochar in reducing nutrient loss in runoff, especially in prairie settings. Nutrients in runoff from agricultural fields have a negative environmental impact on water sources such as streams, rivers and lakes where the overland flow accumulates (Schneider *et al.,* 2019). The accumulation of phosphate, ammonium and nitrate in surface water bodies contributes to eutrophication and deterioration of water quality.

In the Canadian prairies, snowmelt water is the major source of runoff, with resulting loss of nutrients from croplands to surface water (Schneider *et al*., 2019; Wiens *et al.,* 2019). Phosphorus is transported in snowmelt in two forms – dissolved P and particulate P (King, 2015). Schneider *et al*. (2019) reported on a long-term study to determine the effects of various management systems in reducing nutrient loss in runoff. Their findings indicated elevated concentrations of P above previously established environmental thresholds for all sites under various management practices. A study by Wiens *et al*. (2019) focussed on the placement of P fertilizer to minimize P in runoff in the Canadian prairies and found that broadcasting P fertilizer without incorporation resulted in increased P runoff compared to in-soil placement. They concluded that i) P fertilizer should not be broadcast, especially when used at higher than recommended rates, and ii) methods placing P fertilizer below-ground will reduce the risk of runoff. Linked to this, a study by King *et al*. (2017) found that the placement of manure fertilizer did not greatly affect the nutrient load in snowmelt runoff, rather the rate of application and type of manure appears to be determining factors in this regard. Literature on snowmelt runoff in the Canadian prairies indicated that fertilizer and land management should be complemented by alternative methods to reduce nutrient runoff in snowmelt.

Nutrient retention can be increased via electrostatic cation adsorption on biochar surfaces (Van Zwieten *et al*., 2010; Ippolito *et al*., 2014). Studies have shown that biochar with high CEC can preferentially sorb and retain P on its surface, thereby reducing the availability of P in the soil-water solution (Mukherjee & Lal, 2014) due to sorption of P (Soinne *et al.*, 2014). The authors also found that in certain biochar amended soils, sorption of P may also be decreased. This was observed in coarse textured sandy soils and in soils with higher organic matter, which could result in either leaching or overland loss via runoff. Studies have shown that biochar positively affects aggregate stability (Soinne *et al*., 2014). The authors tested both wet and dry aggregate stability and found increased structural stability with the use of biochars. It was noted that the increased aggregate stability in clay soils specifically could reduce particulate P in runoff.

Research conducted in this thesis research examined whether biochar could affect prairie soils' ability to retain nutrients, specifically P during runoff, both from added P sources as well as using biochar high in P, as a means to reduce contaminants in run-off.

2.3 Phosphorus in agriculture and the environment

Phosphorus is a vital nutrient in agricultural practices, forming one of the four main macronutrients (N, P, K & S) required for plant growth and specifically crop production. Macronutrients are required at or above critical levels, defined as the limit below which the soil will require nutrient inputs to improve soil fertility and crop production (IPNI, 2015). The IPNI soil test report for North America, inclusive of the Canadian prairies, showed that in 2015, 81% of samples in SK tested below the critical P level (25ppm, or mg P/kg soil, Bray P1 equivalent), with a median P level of 14ppm.

To understand the positive and negative impacts of P as it regards agroecology, it is important to understand the different P fractions in soil. Between 30% and 65% of total soil P is organic, retained in the decomposing plant and animal residues, and thus, unavailable for uptake by plants (White & Hammond, 2008). The other 35 – 70% constitutes inorganic P which may be in primary mineral form, as secondary P bearing minerals derived from weathering of primary minerals, fertilizer P reaction products, and having originated from organic material which has sufficiently decomposed to be plant available. P cycles or transforms between these forms in various pools. The inorganic P fraction is divided into the readily- or plant available pool which occurs in soil solution, P that is loosely sorbed onto clay or other soil surfaces or in slightly soluble precipitates (labile pool), and strongly sorbed as well as relatively insoluble mineral P, which consists of primary and secondary phosphates. Both the sorbed and mineral P fractions slowly releases P into the plant available pool, with mineral P released more slowly as it requires weathering and dissolution. P cycling in soil take place through various pathways including mineralization/immobilization, adsorption/desorption, precipitation and dissolution (White & Hammond, 2008; Prasad & Chakraborty, 2019). Figure 2.5 shows the P cycle in soil with the different fractions of inorganic P detailed in terms of their interactions.

Various laboratory methods are used to measure P fractions. In this thesis research study, P forms analyzed include inorganic phosphate using the Modified Kelowna method (Qian *et al.*, 1994, Ashworth & Mrazek, 1995), water soluble P using a Millipore filtration (Carlson & Simpson, 1996), available P using a resin membrane method (Qian & Schoenau, 2002), and total P using a sulphuric acid digestion method. The phosphate component represents the inorganic bioavailable P as both the soluble and the particulate (labile) fractions. Water soluble P is the P fraction that in water is small enough to pass through a 0.45 µm filter. Although this fraction is very small, it is not necessarily fully dissolved and it may still contain very small organic P molecules (Carlson & Simpson, 1996). The resin P measurement provides a supply rate or flux of P ions, in contrast to the other methods which

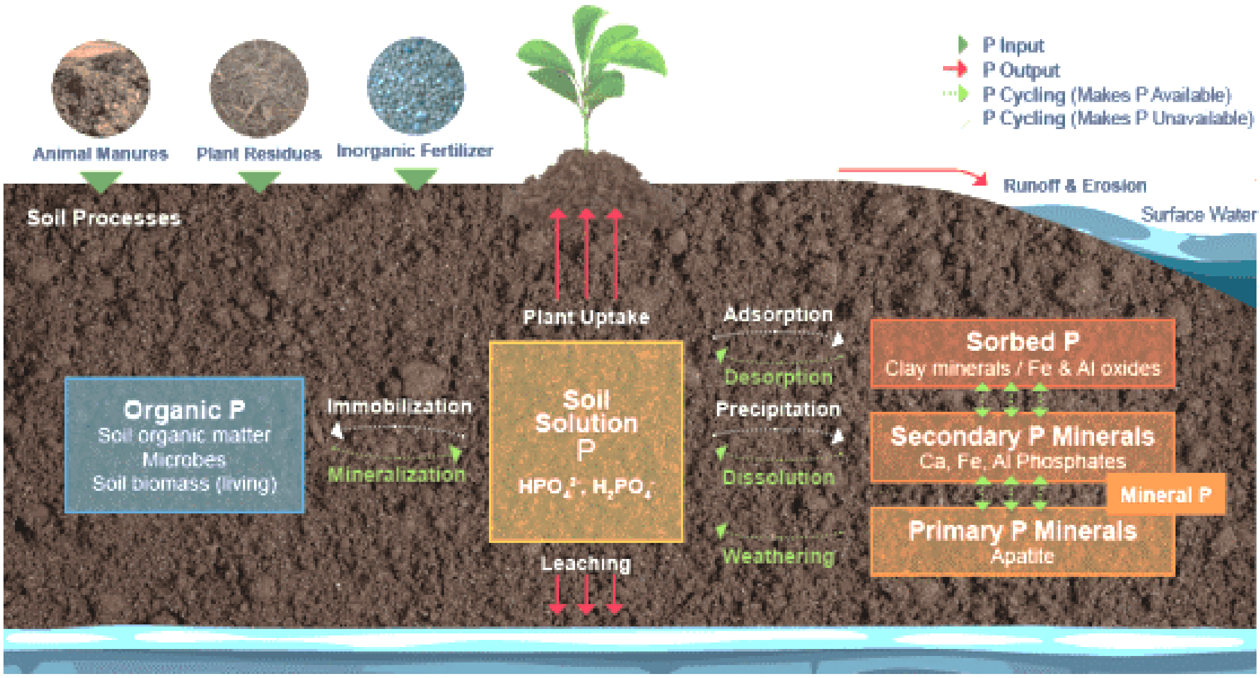

Fig. 2.5. Soil phosphorus cycle showing P inputs, pools in the soil and losses to the environment. Credit: Prasad, R. & Chakraborty, D. (2019). Understanding phosphorus forms and their cycling in the soil.

measures the concentration of P (Qian & Schoenau, 2002). Resin P is thus considered a relative indicator of the labile P which can be exchanged to become plant available. Organic P can be calculated by subtracting the inorganic phosphate component from the total P.

When discussing P losses through runoff or leaching, it is the inorganic fraction which is of most interest as it is directly available for uptake by aquatic organisms like algae, while the organic fraction is bound up in soil organic matter. Organic phosphate may still be lost in high-energy flood or runoff events where soil erosion occurs. As high-energy events are not of interest in this study, the focus remains on the inorganic P component.

The subsections below provides a discourse on the various methods through and rates at which P fertilizer is applied, and the effect it can have on the environment, followed by a discussion on the interactions between P and biochar, and how biochar can potentially be used to reduce P losses.

2.3.1 Phosphorus fertilizer application methods

Application methods used in the Canadian prairies are briefly discussed here to highlight best practices and how these compare to the methods used in this study, as well as the potential effect that the application methods could have on the outcomes of the study. It should be noted that the methods as applied in this study were chosen as the best option for the experimental design but was not assessed as an influencing factor.

The most common methods of application include seed-placed, banded placement near the seed (e.g. in a parallel row), and broadcasting and incorporating, with each method providing benefits and drawbacks for certain soil types and cropping methods (Wiens *et al.,* 2019). Broadcasting and incorporating can result in rapid transformation of the P into plant unavailable forms, especially in calcareous soils with a high pH such as many of the soils in SK, due to binding with calcium ions. As such, it is typically not recommended for low fertilizer application rates (Ministry of Agriculture, SK). In a 1994 producer's guidebook by Agriculture and Agri-Food Canada (Campbell *et al*., 1994), a recommendation was made to not use the broadcasting and incorporating method at all except on perennial forage crops. Despite this, broadcasting and incorporating are used in this thesis research due to the very fine nature of biochar and associated difficulties in incorporating it into soil. It is also anticipated that this method would maximize the interaction of the biochar with the soil and the potential benefit of the char on reducing P run-off losses.

P is relatively more available to plants when using a banded fertilizer method due to a reduction in contact surfaces and associated reduction in adsorption and immobilization (Campbell *et al*., 1994). Banding the fertilizer a short distance from the seed also prevents toxicity and 'seed burn'. The single row field component used in this thesis research made use of banding, as this method was deemed to provide the optimal uptake and yield with the least possible soil disturbance. As the effects of the application method is not the focus of this study, it was not specifically assessed.

2.3.2 Phosphorus fertilizer application rates

P fertilizer has been used in the Canadian prairies for around 100 years with varying application methods and rates (Grant & Flaten, 2019). Several improvements have been made over this period, especially in the past few decades to improve soil health in the prairies. One of these improvements is the development of the 4R Nutrient Stewardship framework, which according to the organization's website, includes *'increased production, increased farmer profitability, enhanced environmental protection and improved sustainability'* (The Nutrient Stewardship, 2017). As part of precision agriculture, the 4R's promote using '*the Right fertilizer sources, applied at the Right rate, at the Right time and with the Right placement'* to reduce risks associated with over-fertilization (e.g. eutrophication and algal blooms) while maintaining or improving crop yields. These goals are promoted by various other organisations, including the Saskatchewan Ministry of Agriculture for use by growers. The benefits of this system, as stated in the 4R Nutrient Stewardship plan, are social, environmental and economic, as the principles are fully adaptable for site specific and changing systems. Where P levels are below the critical rate, such as in the soils used for this study, the 4R's can be used to improve productivity by optimizing P levels along with other macro- and micronutrients.

Agriculture and Agri-Food Canada provides a dedicated Phosphorus Indicator webpage noting that reducing the P inputs to the required nutrient levels will reduce the P levels after harvesting, which results in reduced P levels in snowmelt runoff. While overapplying P in agricultural settings has cost implications for farmers, it is not directly harmful to the agricultural system. However, it will inevitably result in losses through leaching and runoff, leading to downstream environmental contamination impacts in both freshwater sources (wetlands, farm dams, rivers and lakes) and the ocean (Carlson & Simpson, 1996; Ngatia *et al.,* 2019). In addition to water contamination and eutrophication impacts from excess P application, loss of P is also a concern as rock mineral P is a finite resource. It is thus necessary to preserve as much P as possible within an agricultural system, and to recover P wherever possible to both reduce downstream impacts and retain a vital resource for future use. With this in mind, many studies have looked at biochar as a possible solution.

2.3.3 Phosphorus and biochar

The research in this thesis focuses on P in agricultural settings and aims to determine whether biochar can be used to increase plant available P while also reducing P losses through leaching and runoff. Numerous studies have been done on the interactions of biochar and phosphorus, but few of these studies have been done in a prairie setting. Three previous studies have been done at the University of Saskatchewan on the agronomic use of biochar to improve crop yield, including comparisons of biochar to other agricultural by-products (Stefankiw, 2012; Ahmed, 2014; Alotaibi, 2014). While these studies reported on P uptake and recovery, the focus was not on P interactions with biochar. A further study was undertaken at USask to investigate the impact of biochar, alone and in combination with manure, on soil P dynamics (Hangs *et al.,* 2021). The authors found that neither manure nor biochar or their combination had a great impact on soil P dynamics. This was ascribed to sufficient P levels and P-fixing capacity in the soils. Phosphorus availability and uptake could be increased when applied in concert with N sources, and by aging the biochar chemically or naturally (Mia *et al*., 2019).

Phosphorus species retained in biochar varies based on the feedstock used. While P speciation did not form a part of this study, it is important to note that P speciation is the driver for plant availability and the mobility of P in the soil (Huang *et al*., 2017). These authors also note that P speciation in biochar and ash is strongly linked to the type and richness of metals, especially those metals that easily bind to P. During pyrolysis and gasification of dry biomatter, P is usually retained in the solid component (biochar or ash), however, feedstocks high in organic matter and biomatter treated at higher temperatures tend to volatilize more P. The paper also noted that typically, organic P is decomposed at lower temperatures (~250°C), followed by the formation of pyrophosphates at mid-range temperatures (300-600°C) and at higher temperatures more P exists as orthophosphates (Huang *et al*., 2017). Other studies had similar findings, with Sun *et al*. (2022) reporting the presence of stable calcium phosphates from sewage sludge biochar, and Li *et al*. (2018) noting that organic P from poultry litter was transformed into inorganic P with water soluble forms such as hydroxy-apatite and oxy-apatite. Rose *et al*. (2019) noted that biochars from various plant- and animal-based agricultural wastes mainly retained Ca, K, Na and Al phosphates after pyrolysis. The P species along with the P load present in the biochar and ash will thus determine the soil-P and crop-P interactions which will drive the related agronomic and environmental performance as it relates to P.

Inorganic P, especially in the form of orthophosphate, sorbs onto positively charged binding sites found on organic matter surfaces such as biochar (Spohn, 2020). A potential mechanism for a char's sorption capacity is the presence of positively charged metal ions such as Ca, Al and Fe that are attracted to negatively charged biochar surfaces, which in turn creates a positively charged surface for PO_4 attraction, forming cation bridges (Weng *et al.,* 2022). This in turn leads to the reduction of P in leachate and runoff. The authors also note that the same mechanism attracts negatively charged organic molecules which increases porous clusters on the biochar surface (i.e. increased SSA and CEC) which leads to carbon deposition. It is noted that the Weng *et al.* study was done on tropical soils which may react differently to calcareous prairie soils. Shabaan *et al*. (2018) noted that P plant availability is linked to biochar's anion exchange capacity, which is limited, and by providing cations interacting with P. The study also found that the interaction of phosphate with various cations depends on the soil pH – as a result of pH changes that can occur due to soil-biochar interactions, biochar may be able to reduce precipitation of phosphate with the cations, thereby increasing the P plant availability. The authors looked at studies in both tropical and temperate climates and found an increase in plant available P with associated yield increases in both climates due to the addition of biochar. Another mechanism by which nutrient sorption/desorption occurs in biochar was examined by Hagemann *et al*. (2017). They found that biochar, when co-composted and aged with nutrient dense organic matter (OM) in soil resulted in the formation of a nutrient rich organic coating on the biochar surface. They concluded that this coating, rather than surface oxidation as noted in other literature, is responsible for biochar's functioning in soil, although oxidation still plays a role where the coating does not fully cover the biochar surface. They also noted that the protective coating may account for biochar's recalcitrance in soil. The study didn't specify whether this coating can also be found in environments with lower organic matter levels, however, the mechanism by which the coating forms should allow it to form even under lower organic carbon conditions such as in the prairies.

Ghodszad *et al*. (2021) undertook a meta-analysis of biochar as a nutrient source and nutrient sink. The study showed that biochar alters the soil P cycle through shifting the soil P pools and changing the soil's capacity to sorb/desorb P. The study further showed that the mechanism through which this occurs is linked to changes in the microbial population and associated enzyme activity, and concluded that high SSA, porosity and charged surface areas (CEC) is responsible for a char's ability to act as a nutrient sink, effectively removing certain nutrients from either soil or water. Direct contributions of P from the char to the bioavailable pool are variable. Glaser & Lehr (2019) in another review paper noted that biochar's ability to act as a P source was not linked to the feedstock material, but that the production temperature and application rate were the biggest factors in determining a char's effectivity as a fertilizer. They did note that very little information was available regarding the chars' P content and the correlation thereof with plant available P in soil. The authors highlighted a few knowledge gaps, one of which this study in part aims to fulfil, namely the effects of different amounts of char added to soil as a P fertilizer.

This study investigated the interaction of biochar with a commercial phosphorus fertilizer. To increase the plant available P in agricultural soils, P fertilizer in SK is added typically in the form of granular mono-ammonium phosphate (MAP) or liquid ammonium polyphosphate (APP) (Ministry of Agriculture, SK). Both of these contain nitrogen. To allow for control of the level of added nitrogen in this thesis study, separately from the added P, this study instead made use of Triple Superphosphate (TSP), which contains no nitrogen, and supplemented nitrogen using urea.

All the review studies assessed as part of this literature review note that the underlying mechanisms of the effect chars have on P bioavailability as well as the interaction of P with living organisms requires further study as it its poorly understood. These studies further list the need to undertake long term studies, as most of the available data is limited to a few years at most. Ghodszad *et al.* (2021) added that economic aspects of biochar usage should be included in studies as without this data, biochar use efficiency cannot be fully determined. A part of the data from this study will be used by the USask chemical engineering department to do an economic cost-benefit analysis. It is anticipated that collaborative research between scientists and engineers will be required to address this specific knowledge gap.

2.4 Linked studies at USask

Three previous theses/dissertations have been undertaken at USask looking at the interactions of biochar and other bio-energy by-products in SK agricultural field soils (Stefankiw, 2012; Ahmed, 2014; Alotaibi, 2014). This study follows upon various aspects of these studies. The most notable findings of each study as it relates to this study is as follows:

- Stefankiw, J.J., 2012: the willow-based biochar (used in both the controlled environment and field trials of this study) did not significantly improve crop yield or P recovery in a growth chamber study. Of all the novel amendments, biochar was the least effective at improving crop yield. High rates of biochar application (50-100t/ha) are not considered feasible in the Canadian prairies and further long-term field studies using practical low biochar application rates are required.

- Ahmed, H., 2014: This study tested the use of various biochars at rates of 1 and 2t/ha on two contrasting SK soils – a black chernozem and a brown chernozem. The latter had a lower level of organic matter and showed fewer significant responses to the biochar additions. Overall, canola showed a positive response to the biochar additions while subsequent wheat crops showed little response to the char on either soil. The fast pyrolysis biochars were more effective than the slow pyrolysis chars in terms of crop yield and N and P recovery.
- Alotaibi, K.D., 2014: Meat and bonemeal ash (used in the single row field trial part of this thesis study) had less effect on crop yield compared to mineral fertilizer in P deficient soils in a pot study. Biochar improved crop yield in combination with N fertilizer – this was noted to indicate biochar providing an improvement of N use efficiency. However, the study yielded a smaller response than similar studies undertaken using tropical soils and indicated that increased biochar application rates may be required for a better response.

3. DIFFERENT BIOCHAR AMENDMENTS AS SOURCES OF PHOSPHORUS FOR IMPROVED SOIL CONDITIONS, CROP NUTRITION AND GROWTH

3.1 Preface

This chapter (Chapter 3) describes the research undertaken to assess and compare the performance of various biochars and ashes as phosphorus sources for crops. An initial growth chamber study was undertaken examining the response of canola to four different chars and commercial P fertilizer. This was followed by a small-scale field component evaluating the response of canola using three different biochars and two ashes along with a commercial P fertilizer source. Due to grasshopper infestation and subsequent canola crop failure in the field in 2022, the soils and related treatments used in the field were collected in intact cores and used in a follow-up growth chamber study examining the effect of the treatments on wheat, which is a common crop grown following canola in rotation. Biomass for the first two components as well as grain and straw yield in the second growth chamber study were evaluated together with the uptake and apparent recovery of phosphorus by the crops, and residual soil phosphorus. In Chapter 4, one of the biochars (willow) used in the studies described in this chapter (Chapter 3) is used in a larger scale field component to evaluate the char as a source and sink for P when applied alone and in combination with P fertilizer for field-scale canola production.

3.2 Abstract

Biochars, which are by-products of thermochemical decomposition, have been shown to be beneficial in agricultural settings, especially in tropical environments. This study was undertaken in response to limited knowledge in the Canadian prairies on the effects of biochar and ash produced from different feedstocks and under different production conditions as a source of phosphorus for crops, to improve soil phosphorus management, to improve a soil's water holding capacity to reduce nutrient losses in leachate. Feedstocks to produce chars used in this study included canola meal, canola hull, manure (fresh and composted), willow, as well as meat and bonemeal (MBM). Application rates for the first component of the study included biochars at 50kg P/ha, 10t/ha char and 10t/ha char plus added commercial Triple Superphosphate while in the second component of the study, the chars and ash were added at a rate of 25kg P/ha. The MBM ash (MBMA), willow char and manure char had the best overall performance in increasing the crop yield and supplying P to the crop and retaining P in the

soil. Canola hull char performance was variable and impacted by soil type, while canola meal char was almost consistently a poor performer. Canola meal has value as a feedstock, and based on the results of this study, it is not recommended that it be used to produce chars for agricultural soil enhancement. Although manure has agricultural value in its raw and composted forms, there are environmental, commercial and agricultural benefits to charring the manure. Overall, the crop recovery of P added in the best performing chars was about half that observed for commercial P fertilizer (Triple Superphosphate). Higher addition rates of char, especially when combined with commercial P fertilizer, had better performance. However, there remains a trade-off between optimizing crop production and reducing environmental impacts, and therein the chars alone provided a good balance between these two factors. Overall, chars at higher levels of application (10 tonnes per ha) showed agricultural improvement potential under both controlled environment and field conditions when applied to brown and black chernozem soils from southern Saskatchewan.

3.3 Introduction

Biochar and ash are produced as by-products from thermochemical decomposition and bio-energy generation processes such as pyrolysis. When organic matter (OM) is used in a pyrolysis process, the carbon along with nutrients present in the feedstock are retained in the biochar or ash to varying extents and in varying proportions. These nutrients are thus potentially available to be used as nutrient amendments in agricultural settings (Alotaibi, 2014; Tenic *et al.,* 2020), provided they are not immobilized in the production process. In addition, converting biomass using thermochemical processes links to the global requirements for waste reduction, reducing harmful GHG production resulting from OM decomposition and sustainable energy production to name a few (Patra *et al*., 2021; IPCC, 2023). A detailed review of biochar and its ability to act as a phosphorus nutrient source is provided in Chapter 2 of this thesis.

The OM feedstock material along with the thermal decomposition process temperature and residence time is responsible for the properties of the resulting char and ash (Novak & Johnson, 2019; Ramola *et al.,* 2021). Slow pyrolysis that results in longer residence time along with higher temperatures leads to a higher ash component in the solid by-product, which is associated with greater nutrient concentrations (Arni, 2017; Basu, 2018). The main factors determining a char’s ability to sorb nutrients are the specific surface area (SSA) and cation exchange capacity (CEC) (Mukherjee & Lal, 2014; Soinne *et al.,* 2014). When biochar is added to a soil, its inherent properties will alter the soil properties. This includes, in varying rates and proportions, the alteration of soil nutrient pools and associated plant responses, microbial distribution and activity, and water holding capacity, all of which can alter the transformation and flow of nutrients in soil and water (Karer *et al.,* 2013; Tenic *et al.,* 2020). In addition, chars and ash typically have low biodegradability in soil, leading to increased carbon sequestration, however, there may be circumstances where char additions can lead to increased release of greenhouse gases (GHG) (Karer *et al.,* 2013; Mukherjee & Lal, 2013, 2014; Basu, 2018; IPCC, 2023).

Changes to soil phosphorus pools depends greatly on the soil's characteristics such as pH levels, existing P pools, tropical vs temperate climatic influences and levels of soil organic matter (SOM) (White & Hammond, 2008, Prasad & Chakraborty, 2019). Typically, the proportion of total P in soil comprised of inorganic P forms ranges from 35-70% (White & Hammond, 2008). The inorganic component may be in stable, plant unavailable non-soluble mineral forms such as apatite, strongly adsorbed to mineral surfaces and unavailable, or in available forms termed labile P (Qian *et al.*, 1994, Ashworth & Mrazek, 1995). The labile forms are slightly soluble phosphate minerals, loosely sorbed phosphate, and readily mineralizable organic P (Qian & Schoenau, 2002). Both the stable and labile pools can be converted to P that is directly available for plant uptake in the form of orthophosphate ions in solution (Carlson & Simpson, 1996). Mineral P is released more slowly as it requires weathering and dissolution, and P in solution can precipitate or otherwise be immobilized to the non-available forms (White & Hammond, 2008, Prasad & Chakraborty, 2019). The addition of biochar can lead to increased bioavailability by increasing microbial activity which leads to faster mineralization of organic phosphorus (Ghodszad *et al.,* 2021). It can also increase a soil's anion and cation exchange capacity by increasing the surface area (Mukherjee & Lal, 2013). The ion exchange sites can hold phosphate and lead to an exchange of ions in soil solution with phosphate held in the char or ash being released to become bioavailable and can also exchange with phosphate ions to result in net sorption (Mukherjee & Lal, 2014; Shabaan *et al*., 2018). Soluble organic compounds released by the char may also affect P sorption-desorption processes. The research described in this chapter examines the effect of different chars on plant phosphorus availability as well as crop yield. Plant availability was assessed by determining the uptake and recovery of P in crops and comparing the residual bioavailable P in soil after harvest. The effect of chars on crop yield was determined by measuring resulting biomass or straw and grain yields following addition to soil.

A leaching study was included to determine the effect of different chars on retention and release of P to water, as movement of P off-site from agricultural fields in water is an environmental concern (Grant & Flaten, 2019). Soil hydrological properties, including water holding capacity and infiltration rates, are linked to soil physical properties such as the bulk density and porosity, surface area and aggregate stability (Mukherjee & Lal, 2013, 2014). The water dynamics in soil in turn influence nutrient transformations, transport and loss (King & Schoenau, 2009; Wiens, 2017; Tenic *et al.,* 2020). Various studies have been done that show improved water holding capacity and water retention due to amendment of soil with biochar (Hageman, 2017; Dai, 2020), resulting from the char's ability to form complexes with soil, leading to soil aggregates and resultant aggregate stability over longer periods. To determine if the same effect could be seen in prairie soils, the biochars produced from different feedstocks and production conditions evaluated in this study were used to observe the effect on improving the soils' water holding capacity.

The research in this chapter includes biochars and ash from both plant- and animal-based feedstocks. Of importance to this study is the phosphorus content of these chars, which is typically higher in the animal-based feedstocks than the plant-based feedstocks (Huang *et al*., 2017). It was anticipated that the animal-based feedstocks would thus be more beneficial to crop yield and aid in increasing the soil phosphorus content. However, as plant-based chars have a higher lignin content with an associated reduced breakdown rate (Glaser & Lehr, 2019), these chars were expected to perform better at longer term phosphorus retention, thereby preventing P losses from leaching events. All chars were expected to increase the soil carbon content due to the increased carbon load from the biochars, with the ash expected to contribute to a lesser extent because of the lower C content (El-Naggar *et al*., 2019).

While research has been conducted using biochar to address various individual aspects that are included in this thesis work, the majority of the existing work has been done on tropical or sub-tropical soils and with different sources of biochar to test the various aspects separately (Glaser & Lehr, 2019, Tenic *et al*., 2020; Ghodszad *et al*., 2021). Although research has been undertaken with biochar in the Canadian Prairies (Stefankiw, 2012; Ahmed, 2014; Alotaibi, 2014; Hangs *et al.*, 2016; Hangs *et al.,* 2021), there is a very limited body of knowledge on the capabilities of biochar and ash to improve prairie soil phosphorus fertility and retention capacity as well as the effects of biochar on prairie soil-water relations. The majority of studies using biochar in the Canadian prairies have been undertaken under controlled environment conditions and has found that biochar has a very small effect on canola crop production, especially at lower application rates (Stefankiw, 2012; Ahmed, 2014; Alotaibi, 2014). Field trials using a variety of biochars is needed to complement the controlled environment studies. This study addresses these gaps through a series of controlled environment and field studies assessing the efficacy of different biochars produced from agricultural feedstocks as a source of P for canola and wheat growth. Furthermore, this study evaluated the ability of biochar to retain phosphorus and reduce P export during leaching as well as the effects on soils' water holding capacity. This study compared biochar alone and in conjunction with commercial P fertilizer treatments on crop growth and soil properties in P deficient soils from the brown and black soil climatic zones in southern Saskatchewan (SK).

3.4 Materials and methods

3.4.1 Biochars

This component of the MSc project involved a growth chamber study using four different biochars and a small plot field study using five different chars/ashes applied to a soil in the field from which intact cores were taken at the end of the season and used in a growth chamber study. The biochars used in this study represent different production conditions and different feedstock material which affect the value of the char as a P fertilizer source. The chars described below were used for this study. Table 3.1 provides specific details on the composition of the biochars used in the study based on laboratory analysis in the chemical engineering and soil science departmental analytical laboratories at the University of Saskatchewan.

- Willow biochar was obtained by the University in 2011 from the Saskatchewan Research Council (SRC) in Saskatoon, SK, (SRC, 2012). While this biochar has the lowest P content of all the chars used, this was the only char available in sufficiently large amounts to be used in the large field plot study described in Chapter 4 as well as in the growth chamber studies described in this chapter. The char's particle size is very fine, and it has been used in previous research studies at

USask. The results from this study provide further information on the effectiveness of a wood-based feedstock biochar.

- Meat and bonemeal ash (MBMA) – this ash was created during the gasification of meat and bonemeal cracklings, provided by Saskatoon Processing Ltd., Saskatoon, SK, Canada. The MBMA was split into coarse (>600µm) and fine (<600µm) fractions for a previous pot study (Alotaibi, 2014, Alotaibi *et al*., 2014) as a high P content char/ash. The MBMA was not tested in the field.
- All remaining biochars were obtained from the USask chemical engineering laboratory specifically for this project:
    - Canola meal biochar – this char has the highest P content, obtained from pyrolyzing the canola meal left behind after oil extraction. This biochar is included to test the effect of a crop-based high-P biochar in nutrient deficient soils. However, it is unlikely that much biochar would be made from canola meal as the meal has a high commercial value for use as food and feed and is generally viewed as a co-product rather than a by-product.
    - Canola hull biochar – this char has a much lower P content than the canola meal as it is made from the hulls of the seeds. The hulls are a by-product and could feasibly be turned into a bio-energy product with biochar as a by-product of the process.
    - Manure biochar - two batches of manure were obtained from the Beef Cattle Research and Teaching Unit (BCRTU) at different times: composted manure in fall 2021 and fresh manure in spring 2022, as the initial volume was not enough for both the growth chamber and field studies. Although manure is already a beneficial agricultural additive, char produced from it has shown potential in agricultural settings in other studies. Pyrolyzing manure is also a good way to reduce transport costs through weight and volume removal, and to remove any potential pathogens, weed seeds, hormones or other unwanted biological side effects. Manure charring could thus be used on a commercial scale as an alternative to composting. The composted manure char (2021) had a higher P content than the fresh manure char (2022) due to the concentration of P during the composting process, as well as a higher sand content in the fresh manure char, further reducing the phosphorus in the 2022 batch.

Table 3.1. Selected characteristics of biochars used in this thesis research showing the feedstock material, pyrolysis temperature, specific surface area and total pore volume, percentages of phosphorus, carbon, nitrogen and sulfur in each biochar. Values that are not available are indicated by N/A.

Biochar feedstock	Pyrolysis (P) / gasification (G) temperature (°C)	Specific surface area (m^2/g)¶	Total pore volume (cm^3/g)	%P in biochar	%C in biochar	%N in biochar	%S in biochar
Canola meal†	P - 300	2.1	0.03	3.04	66.4	7.7	0.5
Canola hull†	P - 300	1.5	0.03	0.55	63.0	3.4	1.4
Manure 2021‡	P - 600	N/A	N/A	2.17	N/A	N/A	N/A
Manure 2022	P - 600	8.1	0.04	0.23	26.4	1.3	0.5
MBMA coarse§	G - 650-850	N/A	N/A	12.70	0.9	0.2	0.0
MBMA fine§	G - 650-850	N/A	N/A	17.70	0.1	0.2	0.4
Willow biochar	P - 400	3.0	NA	0.17	70.7	1.4	0.1

† The canola meal, canola hull and manure biochars were provided by Dr. Dalai's research group. Additional chars/ash were available at Dr Schoenau's laboratory and were used for comparisons and as follow up from previous USask studies.

‡ The 2021 manure char was not analyzed for any constituents except P at the time of production and no char remains to be analyzed.

§ Canola hull char was not available for the field study and was replaced by the meat and bonemeal ash (MBMA).

¶ Specific surface area, total pore volume and percentages of C, N & S were provided by Dr Dalai's lab, as per Patra *et al.* (2021).

3.4.2 Canola study

The first growth chamber study evaluated the effect of biochar treatments on canola under carefully controlled optimal water and temperature conditions for canola growth, with minimal effect of weather and soil variations. Use of homogenized field soils reduced variability and enabled small treatment effects on soil nutrient availability, and plant uptake and response to be more easily discerned. The study also allowed for the use of small amounts of biochar that were produced under laboratory conditions.

3.4.2.1 Phytotron component

Two soils were used for the canola study: 1) a brown chernozem loamy sand soil of the Haverhill Association, taken from the same region as where the field study was undertaken and located near Central Butte, in south-central Saskatchewan; and 2) a black chernozem sandy loam soil of the Oxbow Association, taken from the South-East Research Farm located near Redvers, SK. Both soils are relatively low in available phosphorus content (<15mg/kg Modified Kelowna (KM) extractable P) and are thus considered suitable to test the effectiveness of P-containing biochars as a P source. Both soils were air-dried and homogenised prior to use. Table 3.2 shows selected physical and chemical characteristics of the soils used in this component of the study. Both soils were slightly alkaline in pH and non-saline. The Haverhill soil, being from the brown soil zone, had lower organic carbon content than the black Oxbow soil.

Table 3.2. Selected nutrients, pH and electrical conductivity (EC) of the soils used in the first growth chamber study (results supplied by ALS and Western Ag laboratories).

Properties†	pH	EC (mS/cm)	N as NO_3 (mg/kg)	S as SO_4 (mg/kg)	MK‡-P (mg/kg)	MK-K (mg/kg)	Organic carbon (%)
Haverhill	8.1	0.33	17.5	5.7	14.6	148	1.32
Oxbow	7.9	0.36	7	10.5	5.8	357	3.14

† All measurements were above the associated detection limits of the instrumentation used.

‡ Denotes Modified Kelowna extractable available (soil test) P and K

Four biochars (canola meal, canola hull, manure (2021) and willow) of varying nutrient content were used in the canola study to compare the effect on the identified parameters: soil fertility, nutrient retention, carbon concentration and water holding capacity. The study was set up as a two-factor completely randomized design with 15 different treatments per soil, with 4 replications each in a Completely Randomized Design (CRD) configuration for a total of 120 pots (Table 3.3).

Table 3.3. Canola study– treatment configuration and rates with four replicates of each treatment for each soil type including the controls, basal applications, four biochars (canola meal, canola hull, manure and willow) and P fertilizer (Triple Superphosphate (TSP)).

Treatment per soil	Treatment application rate	Basal fertilizers
Control 1 (no amendment treatment, no fertilizer) – **4 pots**	No application	None
Control 2 (no amendment and basal N, K, S fertilizer) – **4 pots**	No application	Basal application of N, K & S fertilizer were the same for each treatment and applied at rates of 200mg N/kg of soil added as urea (46-0-0) and 40mg of S/kg and 110 mg of K/kg of soil added as K_2SO_4 (0-0-47-17).
Four biochars applied as a P source – **16 pots**	Biochar at a rate to add 50kg P/ha (25mg P/kg of soil) in the pot based on P content of the char.	
Four biochars at a flat product rate – **16 pots**	Biochar at 10t/ha (5g/kg of soil)	
Four biochars along with P fertilizer (TSP) – **16 pots**	Biochar at 10t/ha and P fertilizer at 50kg P/ha (25mg of P/kg of soil)	
TSP fertilizer – **4 pots**	TSP fertilizer at 50kg P/ha (25mg of P/kg of soil) calculated based on %P in TSP.	

Biochars was applied at a rate of 50kg P/ha of soil (25mg P/kg of soil) to determine how biochar can act as a P source in comparison to commercial P fertilizer. Biochars were also applied as treatments at constant rate of 10t/ha biochar to produce a variable P rate due to differences in P concentration of different chars, to compare the interaction of the chars with the soils at the same rate of product application. Basal applications of N, K and S were made at the same rate to all treatments except control 1 so that limitations of these nutrients did not occur and the effect of the amendments on P fertility and fertilizer response could be evaluated. Therefore, all treatments except control 1 received a basal fertilizer application. The N, K and S applications are typical of what is applied in the field, scaled to a pot study. Quantities of nutrients added and the nutrient content in each treatment which were used in the apparent nutrient recovery and nutrient use efficiency calculations are shown in Table 3.4.

Table 3.4. Quantities of char, N and P applied per treatment for the canola study.

Treatment	Char added	%N in treatment	N applied (mg/kg)	%P in treatment	P applied (mg/kg)
Control2	-	-	0.20	-	-
Canola meal 50kg P/ha	0.82	8.08	0.27	3.04	25.0
Canola hull 50kg P/ha	4.55	3.35	0.35	0.55	25.0
Manure (2021) 50kg P/ha	1.15	0.98	0.21	2.17	25.0
Willow 50kg P/ha	14.71	1.40	0.41	0.17	25.0
Canola meal 10t/ha	5.00	8.08	0.60	3.04	152.0
Canola hull 10t/ha	5.00	3.35	0.37	0.55	27.0
Manure (2021) 10t/ha	5.00	0.98	0.25	2.17	108.0
Willow 10t/ha	5.00	1.40	0.27	0.17	8.0
Canola meal 10t/ha & TSP	5.00	8.08	0.60	3.04	177.0
Canola hull 10t/ha & TSP	5.00	3.35	0.37	0.55	52.0
Manure (2021) 10t/ha & TSP	5.00	0.98	0.25	2.17	133.0
Willow 10t/ha & TSP	5.00	1.40	0.27	0.17	33.0
TSP fertilizer	-	0.00	0.20	24.60	25.0

Mean nutrient uptake in the control used of the calculation:	Haverhill soil (µg/kg)	Oxbow soil (µg/kg)
Control 1 – used for N uptake as no N was added to this control	7005.32	7562.61
Control 2 – used for P uptake as basal fertilizer was added to this and all treatments	2501.05	2864.38

Each pot (12.2cm in height x 15cm in diameter) was filled with 800g of soil. A further 50g of soil was mixed with the relevant treatments to resemble a broadcast and incorporate type of amendment application in the field and placed on top of the filled pot, followed by the N, K & S basal application, and deionized water to bring the soil moisture to field capacity moisture levels. Then each pot was topped with 150g of soil for a total of 1kg soil, and subsequently planted with 10 canola seeds (*Brassica napus* var. Liberty Link 233P).

Some reseeding was required as some seeds did not germinate initially in a few pots. This may be related to a slight inhibitory or salt effect from the amendments on germination. However, once germinated the plants grew well. After initial germination, the plants were thinned to three healthy seedlings per pot. Pots were maintained in a growth chamber at the University of Saskatchewan's phytotron facility for two months and periodically rotated to account for any uneven distribution of light and air flow within the chamber (Fig. 3.1). Conditions in the chamber included 18 hours of light at 22^{o}C (daytime) and 6 hours of darkness at 13^{o}C (nighttime), and 50% relative humidity. Moisture was maintained at field capacity throughout the study.

Fig. 3.1. Photos of the canola study showing the seedlings approximately 1 month after germination (left) and one week before harvesting (right).

After two months, above-ground biomass was harvested and dried in a drying chamber at 35^{o}C for two weeks. Total above-ground shoot dry matter biomass weight (yield) was determined prior to grinding and analyzing the plant material for total P and N concentrations. The digest was conducted using the sulfuric acid digest method as per Thomas *et al*. (1967) where after the total nutrient uptake and apparent nutrient recovery was determined. The apparent nutrient recovery in the plant material was used to determine the nutrient uptake efficiency and agronomic performance of the various treatments. Equations for nutrient uptake and recovery are shown below.

$$Nutrient\ uptake\ (\mu g) = Nutrient\ concentration\ (\mu g/g) * Crop\ yield\ (g)$$

Eq. 3.1

$$Apparent\ P\ recovery = \left[\frac{TPUTP - TPUC}{Total\ P\ applied}\right] * 100$$

Eq. 3.2

Where TPUTP = Total P Uptake in a given P source amended Treatment; TPUC = Total P uptake in the P Control treatment unamended with P source (control 2); and Total P applied = the amount of P added in the amendment application. The same formulae were used to determine N uptake and recovery using control 1 as the unamended treatment.

After canola harvest, soil from the pots was placed in a tray to air dry, after which it was homogenized, and a sub-sample was sieved using a 2mm sieve. The soil was analyzed for residual nutrients including inorganic N (NH_4^+-N & NO_3^--N), MK extractable inorganic P, resin exchangeable P, water extractable P and total P, pH, EC and organic carbon concentration (Carter & Gregorich, 2008) – refer to Section 3.4.3 for a detailed explanation of the analytical methods used for this study.

3.4.2.2 Water holding capacity experiment

Cassel & Nielsen (1986) noted in their description of small core water holding capacity experiments that any method other than in-situ field testing is an approximation of a soil's water holding capacity. The small core method requires the use of a pressure plate, and to determine the correct conditions for this experiment the soil water pressure should first be determined. These values typically range from 5kPa to 50kPa, with lower values corresponding to coarser textured soils. These authors note that through time, a generic value of 33kPa, a value used for medium-textured soils, has come to be used by most scientists, even though this may not always be applicable. To account for soil texture and pore distribution, they recommend that in-situ cores be taken from the field to measure water holding capacity. Cassel & Nielsen caution against the use of disturbed soil as this may skew results.

However, as the soil had been mixed during drying and sample collection for the nutrient analysis, the soil was not intact and had only a few large aggregates. Since the intention of this component of study was to compare the effects of the chars rather than obtaining water holding capacity measurements representative of undisturbed conditions, the use of this soil was deemed adequate. The water holding capacity was thus determined using a modified Cassel and Nielsen (1986) pressure plate apparatus procedure with disturbed instead of intact soil cores.

From the 10t/ha biochar treatments and the control with basal fertilizer (control 2), one sample of each was collected for both soil types (10 samples in total). The 10t/ha biochar treatments were used, as an equal weight of char was required for the comparison. A subsample of each soil sample was oven dried at 105°C for 24 hours. Using a bulk density of 1.2g/cm^3 for both soils (approximated from the bulk density of nearby fields) as an approximate of the pre-harvest compaction, the weight of the wet soil needed per core was calculated at 135.91g. Dry soil was mixed with a solution made from distilled water and calcium sulfate dihydrate to improve water uptake. Equations 3.3 and 3.4 provide the basis used to calculate the mass of soil needed.

$$Mass\ of\ dry\ soil\ needed = Volume\ of\ core * Bulk\ Density\ (\delta b) \tag{Eq. 3.3}$$

$$Mass\ of\ wet\ soil = Mass\ of\ dry\ soil * (weight\ of\ water + 1) \tag{Eq. 3.4}$$

The wet soil mixture was packed into moisture cans which were covered at the bottom with Whatman #4 filter paper and wrapped in cheese cloth to prevent soil loss (Fig. 3.2). The moisture cans were subsequently saturated over 3 days and placed on ceramic pressure plates at -0.33 bar (noted as an average field capacity pressure for medium textured soils, Cassel and Nielsen, 1986) for 2.5 weeks.

Fig. 3.2. Preparing soil moisture cans for the water holding capacity experiment (left) and moisture cans in the pressure plate apparatus (right).

After a week in the apparatus, the cores were weighed every few days until equilibrium was reached. Equations 3.5 and 3.6 were used to calculate the gravimetric and volumetric water content, the latter expressed as a fraction or percentage.

$$Gravimetric\ water\ content\ (\theta g) = \frac{Mass\ of\ water}{Mass\ of\ dry\ soil} * 100$$

Eq. 3.5

$$Volumentric\ water\ content\ (\theta v) = \frac{\mathrm{\theta g} * \mathrm{\delta b}}{\delta w}$$

Eq. 3.6

Where δb is the bulk density of the soil and δw is the density of the water.

3.4.3 Wheat study

3.4.3.1 Field component using canola

Small experimental plots[4] were located in a wheat stubble field ~6km south of Central Butte, in south-central Saskatchewan (50°44'29.98"N 106°25'42.84"W) in an area with no salinity or flooding concerns. Figure 3.3 shows the location of the site in relation to nearby towns and the soil zones (SKSIS, 2023). The field study evaluated the performance of various biochars under field conditions where environmental conditions are typically less desirable for growth than the optimal controlled conditions of the chamber and more closely represent actual conditions encountered by growers. This was true in the 2022 field experiment, as drought and grasshopper infestation led to destruction of the canola seeded plots in July 2022 and necessitated taking intact soil cores from the field back to the controlled environment chamber where wheat was grown on the cores to evaluate the treatment effect.

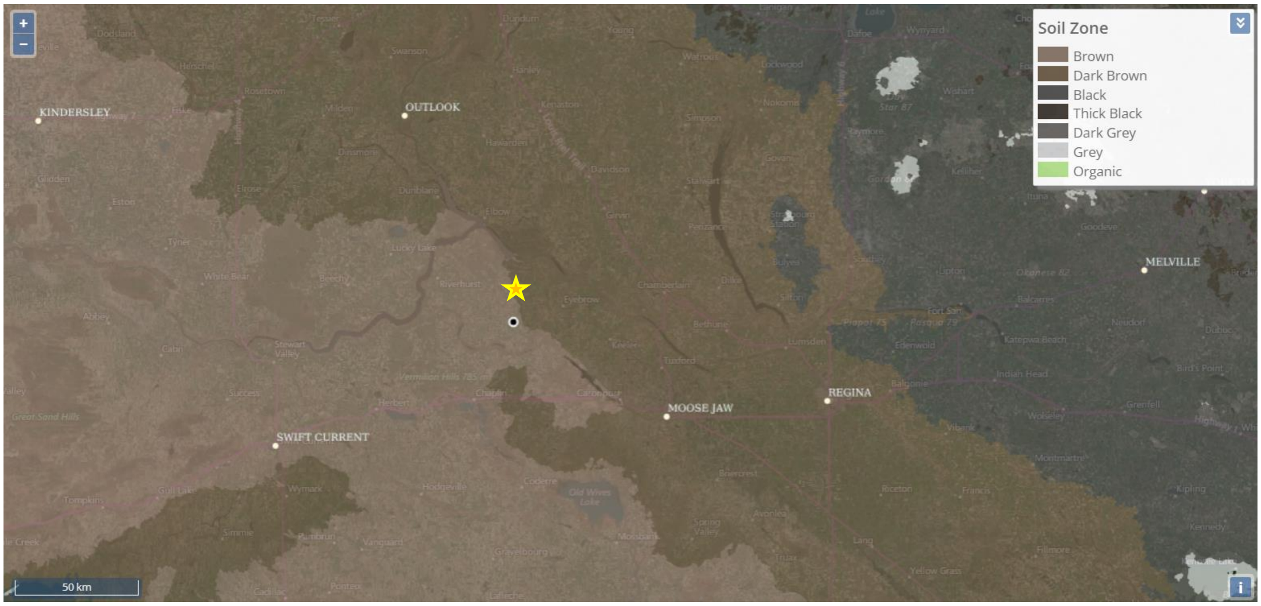

Fig. 3.3. Small row field study site location (yellow star) in relation to the soil zones of Saskatchewan (map extracted from the Saskatchewan Soil Information System, sksis.ca/map, January 2023).

The site was chosen due to the low existing P levels (10mg P/kg) in the soil to determine whether the biochar could act as a P source, and the effect of the biochar on the soil's nutrient holding and

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[4] Sometimes referred to as 'small plots' or 'single rows' to distinguish it from the larger plots described in Chapter 4, which are referred to as 'large plots' or the 'large plot site'.

releasing capacity. The study site consisted of a loamy brown chernozemic soil of the Ardill association (SKSIS, 2023). Although the site is within the prairie pothole region, the immediately surrounding topography in this field is almost flat. SKSIS indicates salinity class 2 for the broader area (slight effect on crops) – although the average surface electrical conductivity (EC) observed for the soil at this site (0.26mS/cm) is considered non-saline, other factors such as the extent of the salinity in the general area and the landscape play a role in determining the overall salinity class. Table 3.5 shows selected physical and chemical properties of the small plot soil. Refer to Table C1 in Appendix C for a detailed breakdown of the soil characteristics at different profile depths.

Table 3.5. Selected nutrients, pH and electrical conductivity (EC) of the soil (0-15cm) from the small plot study measured on soils collected in spring 2022.

Properties	**pH**	**EC (mS/cm)**	**N as NO_3 (mg/kg)**	**S as SO_4 (mg/kg)** †	**Available P (mg/kg)**	**Available K (mg/kg)**	**Organic carbon (%)**	**Textural class**
Analysis	7.8	0.26	21.6	5.9	10.2	305	1.28	Loam

† Analysis of Available S supplied by ALS Laboratory, April 2022

Climate data for the site was obtained from a weather station located approximately 1.7km south-east from the site (data provided courtesy of Dr. Ryan Hangs, 2022). Average surface soil temperatures ranged from 14.1°C in May 2022 (seeding) to a high of 23.2°C in August 2022 (harvesting). During the same time, average daytime air temperatures increased from 12.5°C to 21°C. Precipitation for the four-month period totalled 136mm with July 2022 seeing the highest rainfall during this period. Precipitation during this period is well below the historic average of 195mm for Central Butte (meteoblue.com, 2023) while the average daytime air temperatures were slightly lower than the historic average, resulting in drought conditions. See Fig. 3.4 for a summary of the weather data for the summer of 2022.

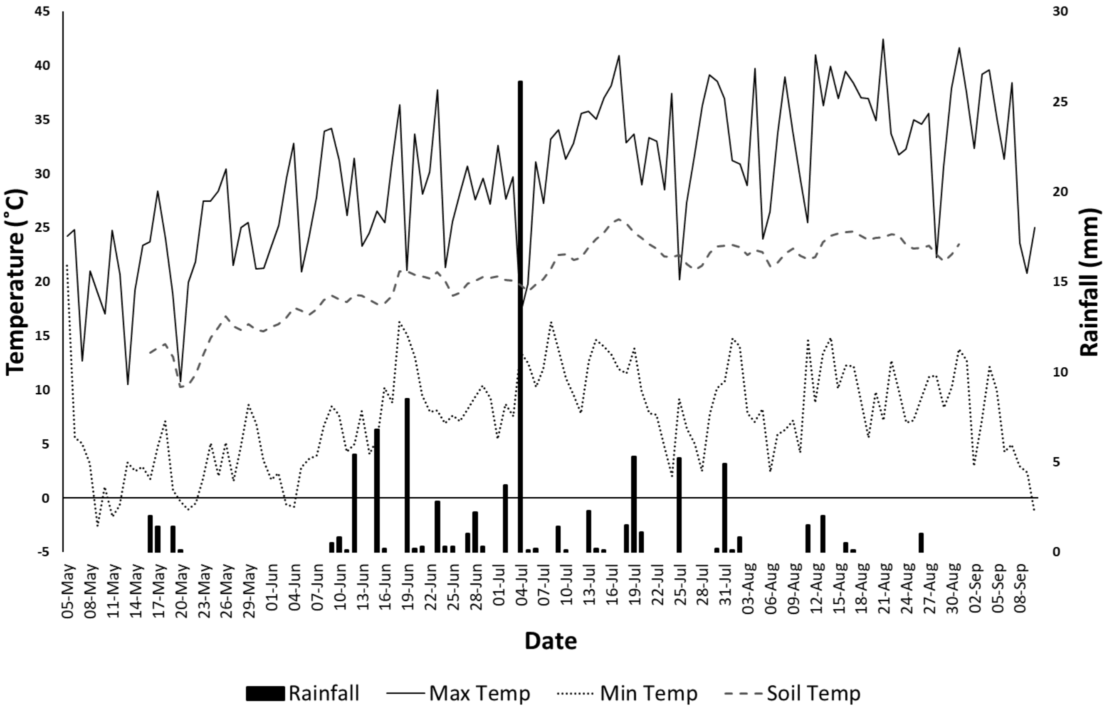

Fig. 3.4. Climate data for the field site near Central Butte for the period May to September 2022. Indicated on the graph are minimum and maximum air temperatures (measured between 5 May and 10 September 2022), average soil temperature for the 0-10cm soil depth and precipitation measured between 16 May and 31 August 2022 (data supplied by Dr. Ryan Hangs, 2022).

The field component was set up as a Randomized Complete Block Design (RCBD) consisting of 32 small plots (0.25m x 3m) with each single row serving as a replicate plot of a treatment (Fig. 3.5) using the following amendments: canola meal char from Dalai lab, manure char from Dalai lab (collected in 2022), meat and bonemeal ash (MBMA) – fine and coarse fractions, and willow char (refer to Table 3.1 for the char characteristics). Although very little variability was anticipated across the site, it was decided to block the experiment to compensate for any unknown variability. The experiment was set up as single rows in the field as there was a limited amount of char that could be produced in the lab from the desired feedstocks. Biochars were applied in the field in single rows in a band located approximately 5cm from the seed-row. This component served as a follow-up to the canola study.

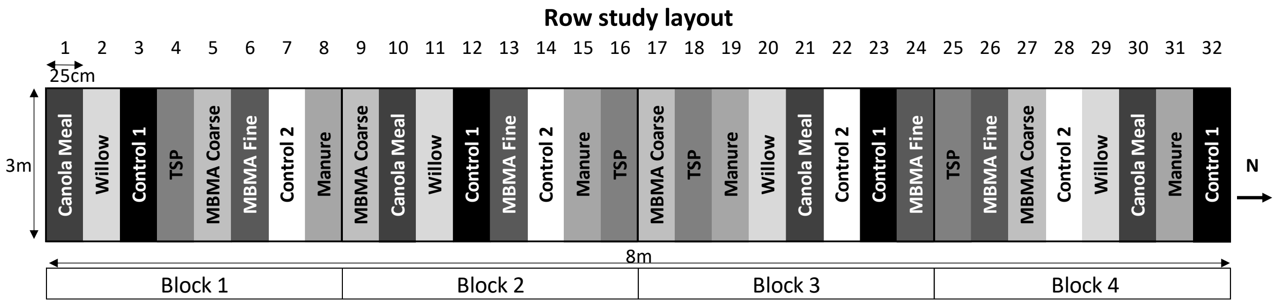

Fig. 3.5. RCBD layout for the field study. N indicates north. Key: control 1 - no treatments; control 2 - basal application of N, K and S only; canola meal biochar & basal application; manure biochar & basal application; willow biochar & basal application; meat and bonemeal ash (MBMA) coarse fraction & basal application; MBMA fine fraction & basal application; Triple Superphosphate (TSP) fertilizer & basal application.

The MBMA replaced the canola hull char used in the canola study, as canola hull char could not be produced in sufficient quantities in time for the field season. It was initially thought that the manure char produced from manure collected in 2022 would have a similar phosphorus concentration as the char produced from the manure collected in 2021, however, due to a much lower P concentration in the char produced from the manure collected in 2022, the amount produced needed to increase by a factor of 10. Quantities of nutrients added and the nutrient content in each treatment which were used in the apparent nutrient recovery and nutrient use efficiency calculations are shown in Table 3.6.

Table 3.6. Quantities of char, N and P applied per treatment for the wheat study.

Treatment	Char added	%N in treatment	N applied (kg/ha)	%P in treatment	P applied (kg/ha)
Control 2	-	-	100.00	-	-
Canola meal	822.40	8.08	163.00	3.04	25
Manure (2022)	5000.00	1.33	166.50	0.23	25
Willow	14705.87	1.40	305.88	0.17	25
MBMA coarse	196.80	0.20	100.39	12.70	25
MBMA fine	141.20	0.24	100.34	17.70	25
TSP fertilizer			100	19.40	25
Mean nutrient uptake in the control used of the calculation					**kg/ha**
Control 1 – used for N uptake as no N was added to this control					14.89
Control 2 – used for P uptake as basal fertilizer was added to this and all treatments					1.23

Due to the delay in obtaining the chars, seeding with canola (Liberty Link 233P variety) took place in early summer (7 June 2022) instead of the optimal late spring seeding time, and approximately 3-4 weeks after the surrounding fields were seeded. The rows received banded treatments of biochar and P fertilizer at rates of 25kg P/ha – banding was used to prevent cross contamination and loss of material under windy conditions. Canola was seeded in rows beside the hand applied banded treatments at a rate of 6kg/ha. Each treatment except control 1 received the following additional basal fertilizer in the treatment band: 100kg K_2SO_4/ha (0-0-47-17) and 217kg urea/ha (46-0-0); the urea rate was calculated based on adding 100kg actual nitrogen per hectare, at 46% N content in the urea. The nutrient rates are typical of what is applied in the field and ensured that crops were not deficient in any nutrient but P, to enable measurement of P uptake and recovery.

Spring rain and snowmelt water provided moisture for germination. However, the 2022 field season was dry, with less than average precipitation, and followed on from a drought year in 2021. As a result, water availability in early summer was much reduced and the germination of the canola was slower than that of the surrounding commercial crops. A week after seeding, the site was irrigated with approximately 1cm of water to compensate for the lack of moisture. Crop growth appeared average; but the canola was younger than the surrounding commercial crops. As adjacent crops ripened, a grasshopper infestation during the summer focussed on the younger, greener plants and ruined the crop despite applications of malathion and carbaryl insecticide[5] (Fig. 3.6). Consequently, seed growth was retarded/prevented and only biomass could be recovered during harvesting on 10 August 2022.

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[5] The small plots were pre-treated with pre-seed Roundup 540 (glyphosate) at 0.4 litres per acre plus Aim (carfentrazone) at 0.024 litres per acre in the last week of April 2022. A further application of Liberty (glufosinate) at 1.35 litres per acre was made post-emergence.

Fig. 3.6. Photos of the field study site showing the canola seedlings one month after seeding (left) and on the day of harvesting (right). Note the comparatively advanced growth stages of the surrounding commercial crops.

Harvesting was conducted by taking a 1m row length from each treatment. The canola biomass collected from the field was air dried and weighed for total biomass. Soil samples were collected at depths of ~0-15cm across the seed row (the soil was very dry and hard, and shovels were used instead of augers). Air-dried biomass and soil were ground and analyzed for the same constituents as for the first growth chamber study. The biomass was very low and uniform across the plot area due to extensive grasshopper feeding and therefore do not reliably reflect the influence of the treatments on plant growth and nutrient uptake. However, the nutrient uptake and recovery was still measured and calculated using equations provided in Section 3.4.1.

3.4.3.2 Phytotron component using wheat

As a result of the extensive above-ground feeding on canola by the grasshoppers that prevented meaningful evaluation of treatment effects on yield, it was decided to follow up the fieldwork by collecting intact cores of the aged field char treatments after harvest and using them in a controlled environment study with wheat grown as the crop that would typically follow canola in rotation. Intact soil cores were collected by hand across the seed rows for each treatment on 27 September 2022 to a depth of approximately 10cm. The soil cores were collected in 15cm long x 10cm diameter polyvinyl chloride (PVC) pipes. The soil was extremely hard and dry during collection – to prevent soil loss, the cores were placed in plastic bags during transport and stored therein for 8 days. On 5 October 2022, during preparation for seeding, the cores were covered with cheese cloth on the bottom and placed in saucers. The cores were moistened to field capacity using 200ml of deionized water per core as well as 50ml water containing dissolved urea at a rate to add the equivalent of 100kg N/ha. No other fertilizer was added to the cores. The cores were left to equilibrate for two days, after which six wheat seeds (*Triticum aestivum L.* – Hard Red Spring Wheat var. Connery) were seeded. The cores were moved to the University of Saskatchewan's phytotron facilities where they were kept under the same conditions as that used for the first growth chamber study (Fig. 3.7).

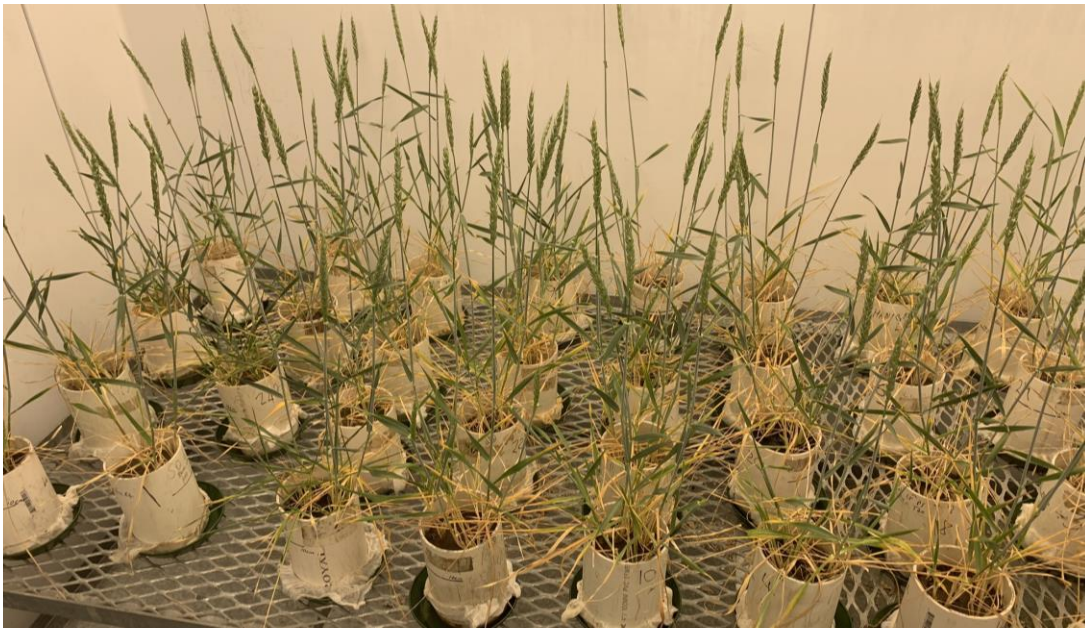

Fig. 3.7. Photo of wheat grown in the growth chamber showing the seedlings at the end of November 2022 after about six weeks of growth.

Two cores did not germinate well, and additional seeds were added. On 17 October, the plants were thinned to three seedlings per core in all cores. The cores were rotated twice a week for the first three weeks, thereafter weekly to ensure even exposure to light and air flow in the chamber. Additional urea at a rate to add the equivalent of 100kg N/ha was added on 4 November 2022. The cores were maintained at field capacity throughout growth until 23 December 2022 where, approaching maturity, they were left to ripen and dry out until 3 January 2023 when they were harvested.

Above-ground biomass was harvested and dried in a drying chamber at 35^{o}C for two weeks. Biomass was separated into seed and straw to determine grain and straw yield as well as nutrient uptake. Although seed yield data is available for the wheat in the chamber, it should be noted that due to different growing conditions and the use of pots (cores), this data cannot be compared to average yields obtained in the field. Apparent recovery could not be calculated for this component of the study due to the undefined loss of P from the field component. The soil was analyzed for the same residual constituents as for the first growth chamber study described in Section 3.4.1.

3.4.3.3 Leachate experiment

The leaching technique used in this thesis research is based on the methods described in King & Schoenau (2009) and Wiens (2017) using intact cores taken from the field, which retained the soil and pore structure, as well as the applied treatments in intact layers. Intact soil in cores, brought to field capacity, is treated with a simulated rainfall event and leachate water is subsequently collected and analyzed for orthophosphate concentrations.

After harvesting, the cores were leached as per the method developed by King & Schoenau (2009). The leaching compared the concentration of nutrients removed during leaching as a function of treatment, including the post-harvest soil residual nutrients. The cores were left for a week after the wheat was harvested, at which time they were brought up to field capacity by gradually adding deionized water to each core to the point where the water was just starting to drain. The cores were allowed to equilibrate for 24 hours whereafter they were placed on collection containers and a 5cm rainfall event was simulated by adding deionized water to each core. After approximately 36-hours, leachate from the collection containers was measured for volume (ml of leachate), homogenized and a sample collected for P analysis. The samples were vacuum filtered through a 0.45µm membrane using the Millipore vacuum system, where after the samples were analyzed using the SEAL™ Segmented Flow Automated Colorimetry System (AA3). Nutrient concentrations in leachate were calculated using equation 3.7.

$$Nutrient\ conc. leached\ from\ soil\ (\mu g/g) = \frac{Nutrient\ conc.\ in\ leachate * Volume\ of\ leachate}{Dry\ weight\ of\ soil} \qquad \textit{Eq. 3.7}$$

3.4.4 Laboratory analysis for canola and wheat studies

Nitrate and Nitrite as N in soil was determined using the 2M KCl Procedure as per Bélanger *et al*. (2008). 5.0g of soil was weighed into extraction bottles to which 50ml of 2M KCl solution was added, and the mixture placed on a rotary shaker at 142rpm for 1 hour. The resulting solution was filtered through VWR454 filter paper and analyzed in a SEAL^{TM} AA3 automated colorimetry analyzer.

Water extractable (soluble) P was extracted using a modified Tiessen and Moir (2008) procedure. This method consisted of weighing 2g of soil and adding 100ml deionized water to it, followed by shaking the mixture on a rotary shaker at 200rpm for 1 hour. The solution was vacuum filtered through a 0.45um membrane using the Millipore vacuum system and analyzed colorimetrically in the AA3.

Soil test extractable available P was determined using the routine soil P test Modified Kelowna (MK) method as per Qian *et al*. (1994). For P, this method removes the plant available slightly soluble solid phase P as well as adsorbed P in rapid equilibrium with soil solution, i.e., the labile pool as well as the phosphate in soil solution described in the previous paragraph. This method entailed measuring 3.0g of soil to which 30ml of the Kelowna solution was added and the mixture shaken on a rotary shaker at 142rpm for 5 minutes. The solution was filtered through VWR454 filter paper and analyzed using flame emission spectroscopy (Agilent 200 AA/FE).

The ion exchange resin membrane exchangeable "sandwich" P (as per Qian and Schoenau (2002) was determined by adding soil from each treatment into two small containers (16-dram vial snap cap lids), which were brought to field capacity (1.85ml for spring soils and 1.75 – 1.8ml for fall samples). A charged resin membrane was placed ('sandwiched') between the soil in the two containers which were then wrapped in Parafilm M™. The sandwiches were left to incubate for 24 hours, where after the membranes were removed, washed in distilled water and placed in vials to which HCl was added. After an hour of reacting with the HCl to elute the P from the membrane surface, the membranes were removed and the phosphate-P in the eluent HCl analyzed in the AA3 to determine the supply rate of P in the soil at the time of harvest. This method measures soil solid phase phosphate release and exchange with the counterion bicarbonate ions on the ion exchange membrane surface exchange sites.

Total N and P for the plants were measured using the sulphuric acid – peroxide digestion method as per Thomas *et al*. (1967). In this method, 0.3g of ground soil/plant material was weighed into glass tubes to which 5ml of 36N $H2SO_4$ was added. The tubes were placed on a heating block at 360°C for 30 minutes whereafter they were removed and allowed to cool for 20 minutes. 0.5ml of 30% (v/v) H_2O_2 was added to each tube, followed by vortexing. The tubes were then returned to the heating block for a further 30 min. The addition of H_2O_2 and further heating was repeated until all samples were colourless (i.e. the carbon had been removed). Samples were left to cool overnight. Deionized water was slowly added to cooled samples to just under 100ml. Tubes were again allowed to cool as the water caused an exothermic reaction. Once the tubes were cooled to room temperature, deionized water was added up to 100ml, the tubes were capped with a stopper and inverted 5-6 times to mix the content. A sub-sample of the extract was collected in a vial and analyzed using the AA3.

The soil pH and EC were measured as per Houba *et al*. (2000), in which 20g soil from each treatment was mixed with 40ml 0.01M $CaCl_2$ where after it was placed on a rotary shaker at 142rpm for 20 minutes. The soil was allowed to settle out of the solution for an hour, then filtered with Whatman #1 filter paper. The pH and EC were measured with the respective calibrated probes on a Beckman pH meter.

Organic carbon (OC) analysis required preparation of the soil by removing carbonates following the method provided by Skjemstad and Baldock (2008). 0.3g of ground soil was weighed into a nickel liner placed within a ceramic combustion boat. Samples were moistened with 0.5ml deionized water. Then 1.0ml of 6% (w/v) H_2SO_3 was added, and the boat placed onto a hot plate set at 70°C. The boats were monitored for a fizzing reaction and additional H_2SO_3 added in 1.0 mL increments until no further reaction was observed. Although samples were left to evaporate between H_2SO_3 additions, they were not allowed to dry out. When no further reaction was observed, samples were removed from the hot plate and placed in an oven set at 70°C to dry for 10 hours. Dried samples were analyzed using the LECO C632 determinator. The initial weight of each sample was used during calculation of the OC content.

Texture (sand, silt and clay content) for soil samples were determined using the hydrometer analysis method as per Bouyoucos (1962). A 40g sample of air dried and ground soil was weighed into a stirring cup to which was added 10ml of a $(NaPO_3)^{6-}Na_2CO_3$ dispersing solution. The mixture was left to sit for 10 minutes where after it was mechanically stirred for 3 minutes. The mixture was poured into a cylinder along with enough deionized water to fill it to the 1000ml mark then further agitated by moving a plunger up and down. A reading was taken from a soil hydrometer (ASTM No. 152H with Bouyoucos scale in g/l) which was released into the suspension for 40s, followed by a reading taken from a thermometer suspended in the solution. After two hours, the agitation, hydrometer and thermometer steps were repeated.

3.4.5 Statistical analysis

The data was analyzed using RStudio (version 2022.12.0). Outliers were identified using both the Grubbs test and the Tukey interquartile ranges. After outliers were removed, the data was tested for normality through Shapiro-Wilk tests, residual plots, quantile-quantile plots, kurtosis and skewness. Variance was established using the Levene Test. Where data was not normally distributed and/or had significantly different variances, it was subjected to a log or square root transformation.

Linear mixed effect models (lme, lmer, glmm and glmer) were used for the multi-variate analysis – for the model applicable to each parameter, refer to Table C6 in Appendix C. For the canola study both the main and interaction effects of the soil and treatments were assessed. Residuals were tested for normality using a Shapiro-Wilk test, histogram, scatterplot and quantile-quantile plots. The best model was chosen based on a combination of the lowest Akaike Information Criterion (AIC) and the Bayesian Information Criterion (BIC) value, along with the highest r squared value.

ANOVA Type III tests were used to determine model-wide significant differences. Multi-treatment comparisons were made with a post-hoc Tukey Honestly Significant Difference (HSD) test through estimating the marginal means (emmeans and cld functions). Statistical significance was set at 5%, (alpha=0.05) except in a few cases for soil residual or leachate nutrients where a 10% (alpha=0.1) was deemed necessary due to the highly heterogeneous nature of nutrient distribution in soil (Pennock, 2004).

Interaction effects between measured variables were determined using covariance, correlation, and principal component analysis. The output of these interactions is available in Appendix D. The data and analytical code for this thesis work is available at: https://github.com/AnelD13/BiocharAshAmendments_ImproveSoil_P_Fertility_WaterRelationsRetention (Dannhauser, 2023).

3.5 Results

Although both nitrogen and phosphorus were analyzed as part of this thesis, the focus is on phosphorus. Figures and tables related to nitrogen are included in Appendix A.

3.5.1 Canola study

3.5.1.1 Effect of char application on canola biomass

For amendment treatments made at 50kg P/ha (25mg P per pot with each pot containing 1 kg of soil) (Fig. 3.8A), the willow biochar and TSP commercial P fertilizer performed the best, followed by the manure char treatment. For the Haverhill soil, the canola meal char performed slightly poorer in increasing biomass compared to the manure treatment. In the Oxbow soil, both the canola meal char and canola hull char treatments yielded significantly lower biomass than the manure char and did not do much better than the control with basal fertilizer. For char treatments applied at 10t/ha (5g char per pot), with or without TSP, all treatments performed significantly better than the controls for both soils (Fig. 3.8B). Overall, the char plus TSP treatments produced the same or more biomass than the TSP alone. Both the chars and TSP as well as the TSP alone did similar or better than the chars alone.

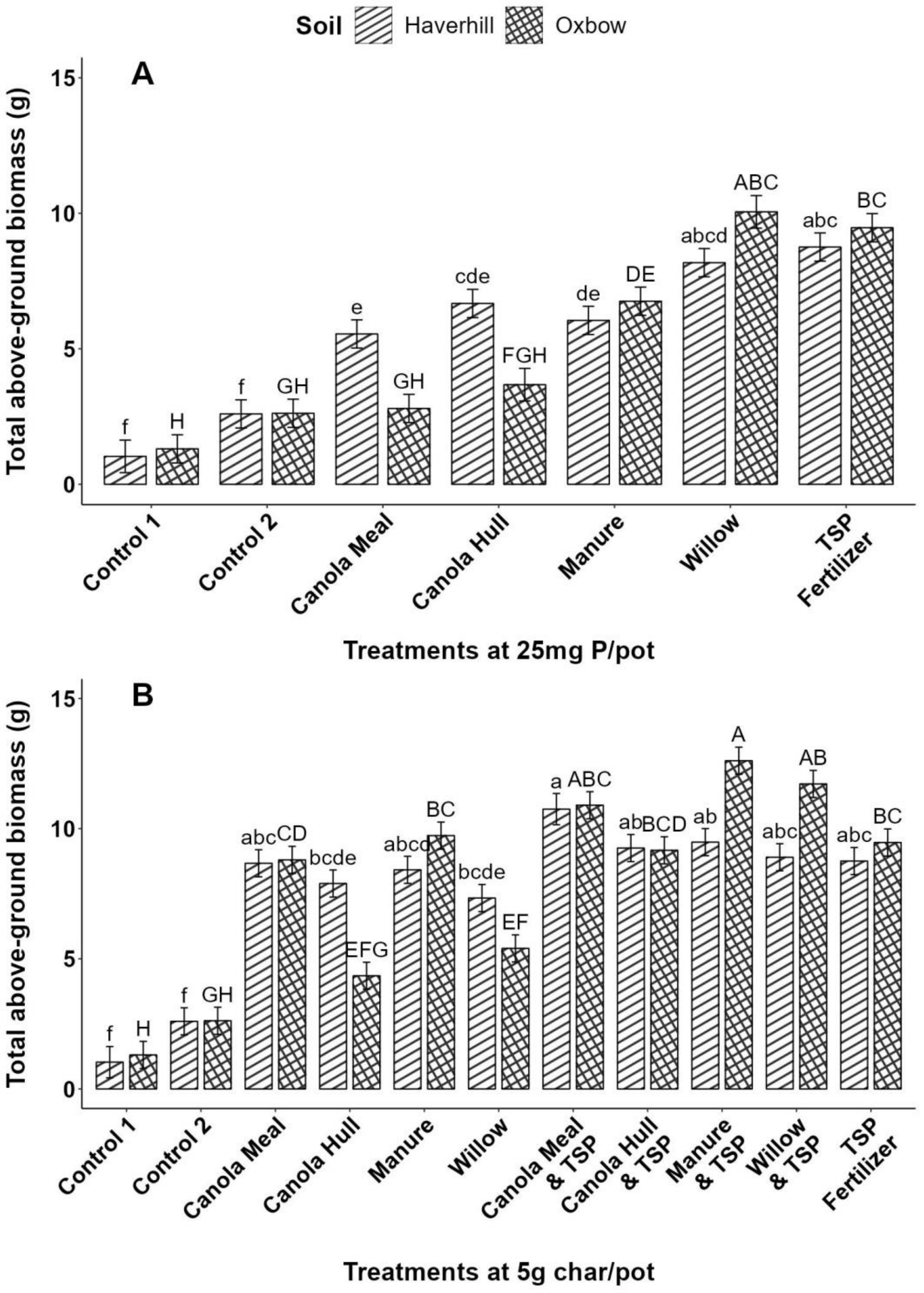

***Fig. 3.8.** Canola study total biomass for the char treatments made (A) at a constant P rate of 50kg P/ha equivalent to 25mg added P as char per pot and Triple Superphosphate (TSP) fertilizer at 50kg P/ha, and (B) for the char treatments at a rate of 10t/ha of char equivalent to 5g of added char per pot (variable P rate) and TSP. Treatments included include two controls (control 1 – no basal fertilizer; control 2 – basal N, K and S fertilizer only), canola hull char, canola meal char, manure char (2021), willow char and TSP. Error bars indicate standard error and Tukey HSD significant differences are indicated by letters. Treatments are compared within and not between soil types.*

3.5.1.2 Effect of char application on canola phosphorus uptake

In comparing treatments which received the same amount of P added as amendment (25mg P/pot) (Fig. 3.9A), overall, the amendments increased P uptake. The P uptake was highest in the willow char and TSP fertilizer treatments. The canola P uptake in the willow char treatment was not significantly different than the TSP fertilizer and had just slightly less mean P uptake than the TSP fertilizer treatment. Significantly less P uptake was observed in the canola meal and hull char amended soil, with the manure char treatment intermediate in P uptake. Phosphorus uptake by canola for chars all added at the same rate of product (5g per pot) (Fig. 3.9B) was significantly higher in the char and TSP treatments compared to the controls, with many of these treatments performing better than the commercial fertilizer without char. The manure char treatment without TSP performed on par with most treatments that had added TSP. The highest P uptake could be seen in the Oxbow soil with manure char plus TSP fertilizer. The canola hull char and willow char amended biomass in the Oxbow soil were not significantly different in P uptake from the controls. Overall, the Oxbow soil responded less to amendment treatment in crop nutrient uptake than the Haverhill soil, with only about half the P uptake in the canola meal char and canola hull char treatments compared to Haverhill soil. It is likely that the willow char performed as well as it did because of the quantity of char used, as this was the only treatment where the total char applied at the 25kg P/pot level was higher than in the 5g of char product/pot level.

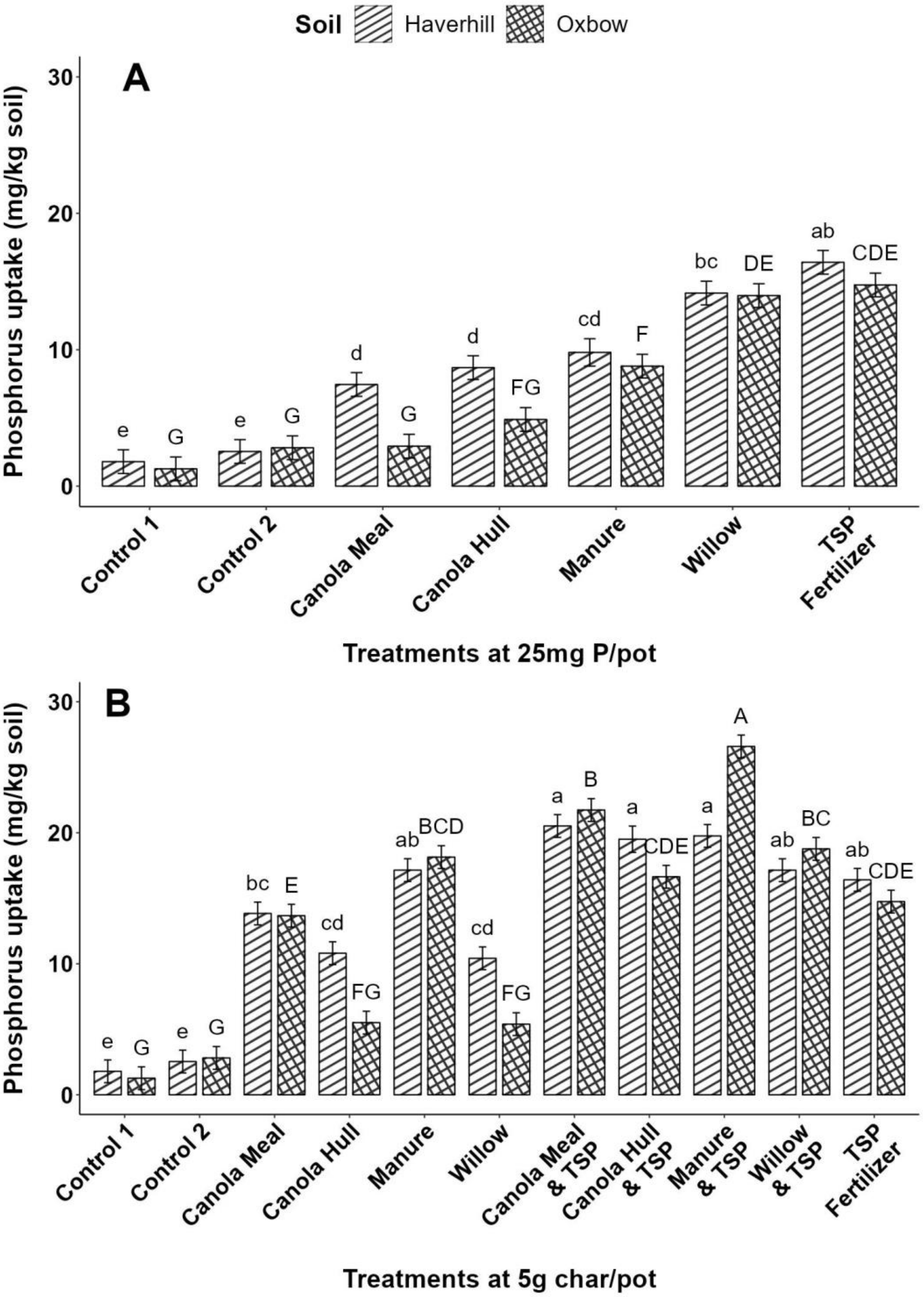

***Fig. 3.9.** Canola study phosphorus uptake indicated in mg P per pot (1kg of soil) for (A) the 50kg P/ha (25mg P per pot) treatments and (B) in the 10t/ha (5g of char per pot) treatments. Error bars are standard error and Tukey HSD compact letter display is used to indicate significant differences. Treatments are compared within and not between soil types.*

3.5.1.3 Effect of char application on canola phosphorus recovery

Apparent recovery in the crop of the phosphorus added in in the 25mg P/pot (50kg P/ha) treatments (Fig. 3.10A) revealed that the P added as willow char was recovered to a similar extent as the P added as TSP fertilizer at around 50% of added P. Recovery of manure char was about half of the TSP fertilizer and willow char recovery rate. The canola meal char and canola hull char treatments were only slightly less than the manure char in the Haverhill soil but showed almost no recovery in the Oxbow soil (0.5% and 2% respectively). Residual soil P levels for these treatments (see following section) were only marginally higher than the control and were significantly less than for the other treatments, suggesting that more of added P in the canola-based chars remained in an occluded form in the soil that was not available for plant uptake or measurable in any of the soil labile pool measurements. The residual soil pH, EC and organic carbon (OC) concentrations for these two treatments were also not significantly different from the controls, although they were significantly lower than the other treatments applied at this rate. The P recovery in the same product rate 10t/ha (5g char per pot) treatments (Fig. 3.10B) was highest in the willow char treatment without TSP (93% P recovery), followed by the willow char with TSP and the TSP fertilizer at around 50%. The other treatments all showed significantly lower P recovery with the canola meal and hull chars being the lowest. The canola meal char and manure char responded slightly to the addition of TSP compared to other treatments, and the canola hull char without TSP performed better in the Haverhill soil than with added TSP. The high percentage recovery of P from the willow char source suggests it is an efficient source of P for the canola crop.

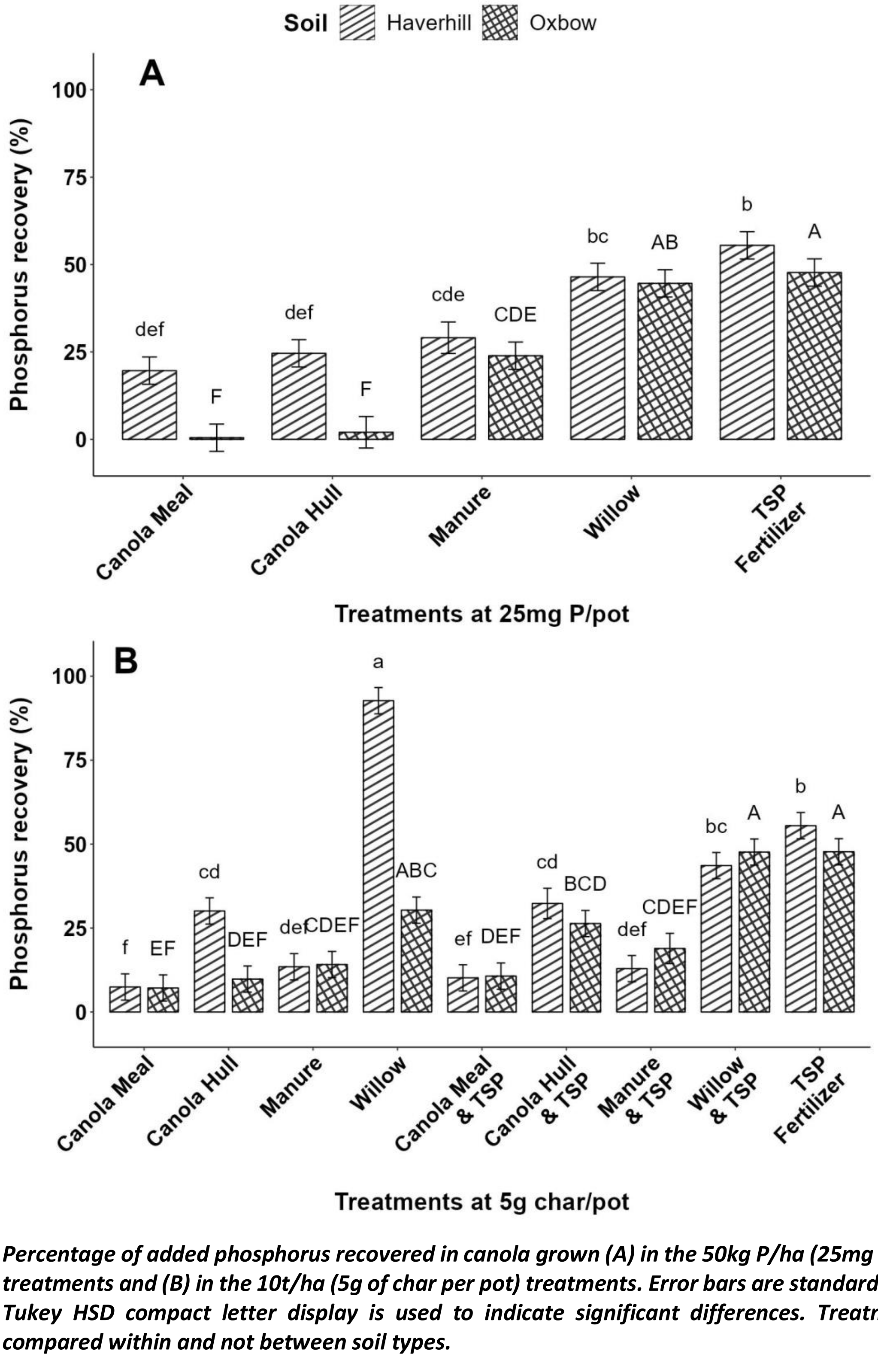

Fig. 3.10. Percentage of added phosphorus recovered in canola grown (A) in the 50kg P/ha (25mg P per pot) treatments and (B) in the 10t/ha (5g of char per pot) treatments. Error bars are standard error and Tukey HSD compact letter display is used to indicate significant differences. Treatments are compared within and not between soil types.

3.5.1.4 Effect of char application on canola phosphorus use efficiency

Phosphorus use efficiency was calculated in grams of biomass produced over the unfertilized control 2 per gram of added nutrient as per equation C1 in Appendix C. Phosphorus use efficiency (PUE) was highest in the willow 10t/ha treatment, corresponding to the highest levels of phosphorus recovery (Table C3).

3.5.1.5 Effect of char on residual soil nutrients and chemical properties

All treatments except manure char added at 10t/ha had lower residual soil test MK extractable P (Table 3.7) at the end of the study compared to the initial pre-study levels. Manure char and TSP produced higher residual MK-P than other treatments, a trend that was particularly evident in the Haverhill soil. The manure 10t/ha and the TSP was also the highest for both the resin exchangeable P and water soluble P fractions (Tables 3.8 and 3.9), consistent with high P content of the manure derived char. Interestingly, combining TSP fertilizer with char tended to reduce the labile residual P compared to char alone, despite the additional contribution to the soil P load from the TSP along with the char. When TSP was combined with char, the canola P uptake was increased (Fig. 3.9B) which would contribute to lower residual levels, but combination of TSP with char may also tie up a proportion of the TSP.

Table 3.7. Canola study post-harvest Modified Kelowna (MK) extractable phosphorus (mg P/kg).

Treatment	**Haverhill soil rate of application**			**Oxbow soil rate of application**		
	50kg P/ha	***10t/ha***	***10t/ha & TSP***	***50kg P/ha***	***10t/ha***	***10t/ha & TSP***
Control 1		5.7 g[†]			2.1 f	
Control 2		6.4 fg			2.7 def	
Canola meal char	9.4 cde	12.2 bcd	8.6 def	2.7 def	3.0 de	2.5 def
Canola hull char	9.4 cde	11.7 bcd	9.1 cde	3.4 cd	4.8 b	2.9 def
Manure (2021) char	13.9 b	20.0 a	10.2 bcde	4.7 bc	10.3 a	2.5 def
Willow char	7.7 efg	12.3 bcd	9.7 cde	2.4 ef	2.6 def	2.8 def
TSP fertilizer	12.6 bc	-	-	3.1 de	-	-
ANOVA (Type III) p-value[‡]	***Treatment***		***Soil***		***Treatment x Soil***	
	*6.4e-52****		*4.7e-27****		*8.5e-12****	

[†] Means with the same letter are not significantly different at p<0.05 for a Tukey HSD multi-treatment comparison.

[‡] *** shows significance at α = 0.001.

Table 3.8. Canola study post-harvest anion exchange resin membrane phosphorus (μg P/cm^2/24h).

Treatment	Haverhill soil rate of application			Oxbow soil rate of application		
	50kg P/ha	***10t/ha***	***10t/ha & TSP***	***50kg P/ha***	***10t/ha***	***10t/ha & TSP***
Control 1		0.03 fg[†]			0.08 cd	
Control 2		0.01 g			0.07 d	
Canola meal char	0.08 de	0.17 bc	0.05 ef	0.11 bcd	0.17 abc	0.10 bcd
Canola hull char	0.06 e	0.09 cde	0.06 e	0.10 bcd	0.17 abc	0.08 bcd
Manure (2021) char	0.20 b	0.44 a	0.09 bcde	0.17 ab	0.34 a	0.12 bcd
Willow char	0.06 e	0.15 bcd	0.10 bcde	0.08 bcd	0.14 bcd	0.10 bcd
TSP fertilizer	0.09 cde	-	-	0.17 ab	-	-
ANOVA (Type III) p-value[‡]		***Treatment***		***Soil***		***Treatment x Soil***
		*3.3e-69****		*0.06*		*2.2e-09****

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

[‡] *** shows significance at $\alpha = 0.001$.

Table 3.9. Canola study post-harvest residual soil water soluble phosphorus (mg P/kg).

Treatment	Haverhill soil rate of application			Oxbow soil rate of application		
	50kg P/ha	***10t/ha***	***10t/ha & TSP***	***50kg P/ha***	***10t/ha***	***10t/ha & TSP***
Control 1		2.4 de			2.2 e	
Control 2		2.2 e			2.5 de	
Canola meal char	2.5 cde	3.5 bc	2.5 cde	3.5 bc	2.5 cde	3.5 bc
Canola hull char	2.1 e	3.5 bc	2.1 e	3.5 bc	2.1 e	3.5 bc
Manure (2021) char	4.0 b	6.4 a	4.0 b	6.4 a	4.0 b	6.4 a
Willow char	2.1 e	4.0 b	2.1 e	4.0 b	2.1 e	4.0 b
TSP fertilizer	3.3 bcd	-	3.3 bcd	-	3.3 bcd	-
ANOVA (Type III) p-value[‡]		***Treatment***		***Soil***		***Treatment x Soil***
		*3.3E-47****		*0.00088****		*0.047**

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

[‡] * and *** shows significance at $\alpha = 0.05$ and 0.001.

The post-harvest soil pH values are shown in Table 3.10. In the Haverhill soil, the pre-study pH levels were matched only by the manure 10t/ha plus TSP treatment as well as the TSP fertilizer alone, with all other treatments having a small decrease in pH from beginning to end of study. This is not necessarily as a result of the char addition as the controls had the lowest pH levels in this soil. About half the treatments in the Oxbow soil were at or exceeded the pre-study pH levels while the lowest residual pH level was only 0.27 pH points lower than the pre-study level as observed for the willow 10t/ha treatment. The highest pH level in the Oxbow soil was observed in control 1.

Table 3.10. Canola study post-harvest soil pH.

Treatment	**Haverhill soil rate of application**			**Oxbow soil rate of application**		
	50kg P/ha	***10t/ha***	***10t/ha & TSP***	***50kg P/ha***	***10t/ha***	***10t/ha & TSP***
Control 1	7.8 f[†]			8.0 a		
Control 2	7.8 f			8.0 abc		
Canola meal char	7.9 c	8.0 a	7.9 ef	7.9 bc	7.7 e	8.0 ab
Canola hull char	7.9 c	8.0 bc	7.9 def	8.0 abc	7.7 ef	7.9 c
Manure (2021) char	8.0 ab	8.1 a	7.9 cde	8.0 ab	7.8 d	8.0 ab
Willow char	8.0 a	8.0 a	7.9 cd	7.7 f	7.8 d	8.0 abc
TSP fertilizer	8.1 a	-	-	7.8 d	-	-
ANOVA (Type III) p-value[‡]	***Treatment***		***Soil***		***Treatment x Soil***	
	*2.2e-16****		*2.2e-16****		*2.2e-16****	

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

[‡] *** shows significance at $\alpha = 0.001$.

The salinity decreased slightly in all treatments for both soils (Table 3.11), with the Haverhill soil maintaining lower EC levels than the Oxbow soil, as was the case in the pre-study measurement. This is attributable to removal of salts by leaching during watering of the pots. Comparing treatments, the amendments had minimal effect on EC and therefore soil content of soluble salts. The EC was slightly reduced in the willow char treatment compared to the control with basal fertilizer, suggesting this char may absorb salt cations and anions while the canola char with slightly elevated EC, may release them.

Table 3.11. Canola study post-harvest soil electrical conductivity (mS/cm).

Treatment	**Haverhill soil rate of application**			**Oxbow soil rate of application**		
	50kg P/ha	***10t/ha***	***10t/ha & TSP***	***50kg P/ha***	***10t/ha***	***10t/ha & TSP***
Control 1	0.22 de[†]			0.22 d		
Control 2	0.28 ab			0.23 bcd		
Canola meal char	0.21 de	0.22 de	0.22 de	0.22 bcd	0.22 bcd	0.23 bcd
Canola hull char	0.29 a	0.30 a	0.28 abc	0.33 a	0.33 a	0.33 a
Manure (2021) char	0.24 bcd	0.24 cde	0.22 de	0.26 bc	0.24 bcd	0.22 cd
Willow char	0.20 e	0.20 e	0.21 de	0.26 b	0.21 d	0.23 bcd
TSP fertilizer	0.21 de	-	-	0.22 cd	-	-

ANOVA (Type III) p-value[‡]	**Treatment**	**Soil**	**Treatment x Soil**
	1.3e-36***	0.034*	2.1e-7***

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

[‡] * and *** shows significance at $\alpha = 0.05$ and 0.001.

The residual organic carbon (OC) concentration in the Haverhill soil (Table 3.12) was increased by biochar amendment compared to the pre-study OC concentrations, suggesting that added biochar C remained in the soil for the duration of the study and contributed to C storage. However, it should be noted that the controls also had higher levels of OC than before the study, even though the control OC levels were lower than most of the treatments. This likely reflects addition of carbon from root biomass produced in all treatments. In the Oxbow soil, only the canola hull 50kg P/ha and the willow 50kg P/ha treatments had higher OC levels than the pre-study levels. In the Haverhill soil the 10t/ha treatments had slightly higher %OC when compared to the 50kg P/ha treatments.

Table 3.12. Canola study post-harvest soil organic carbon concentrations (%).

Treatment	**Haverhill soil rate of application**			**Oxbow soil rate of application**		
	50kg P/ha	***10t/ha***	***10t/ha & TSP***	***50kg P/ha***	***10t/ha***	***10t/ha & TSP***
Control 1		1.7 def[†]			2.8 bcd	
Control 2		1.4 f			2.8 bcd	
Canola meal char	2.0 bc	2.1 b	1.5 ef	2.8 bcd	2.6 cd	2.8 bcd
Canola hull char	1.8 bcd	2.0 bc	1.9 bcd	2.8 cd	2.6 cd	3.3 ab
Manure (2021) char	1.8 bcd	2.0 bc	1.8 cde	2.6 d	2.6 d	3.0 bc
Willow char	1.8 bcd	2.1 b	2.6 a	2.7 cd	2.8 bcd	3.6 a
TSP fertilizer	1.9 bcd	-	-	2.5 d	-	-

ANOVA (Type III) p-value[‡]	***Treatment***	***Soil***	***Treatment x Soil***
	*1.3e-36****	*1.2e-18****	*1.3e-17****

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

[‡] *** shows significance at $\alpha = 0.001$.

3.5.1.6 Water holding capacity

The water holding capacity experiment was completed to determine if there is an effect on water holding capacity from the addition of biochar to these prairie soils. As no replications were done due to the time-consuming nature of the measurements, the data was not statistically analyzed. Treatments used included control 2 with basal fertilizer and each of the four chars from the canola study at a rate of 10t char/ha. The results from the pressure plate measurements showed differences between the two soils with an overall volumetric water content mean of 21.71% for the Haverhill soil and 23.47% for the Oxbow soil, in line with the slightly higher clay content of the Oxbow soil. Refer to Table C1 for the textural class (sand, silt and clay fractions) of each soil. The volumetric water content at field capacity of the char amended soils were all higher than the control, indicating a positive effect of the chars on water holding capacity (Fig. 3.11).

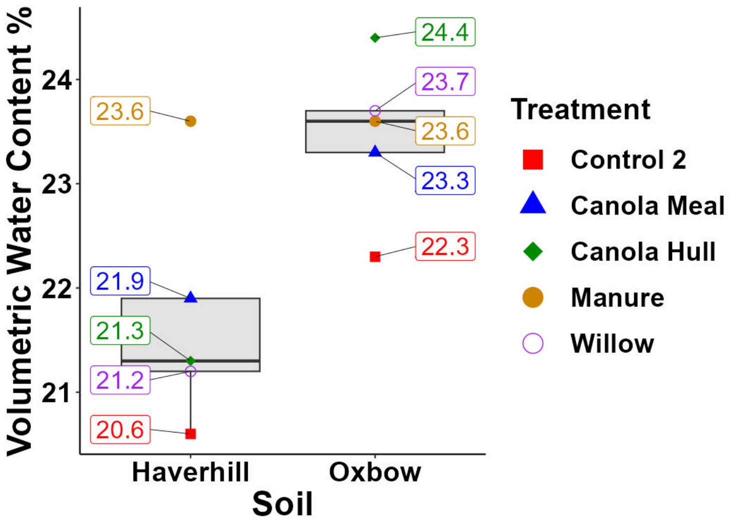

Fig. 3.11. Volumetric water content for each treatment in the canola study water holding capacity experiment. Boxplots indicates differences between soils. Boxplots and points are not to scale in terms of quartile ranges.

3.5.2 Wheat study

3.5.2.1 Small plot component

Due to the grasshopper infestation and feeding in the field in the summer of 2022, the observed effect of the treatments on canola biomass and nutrient uptake is not considered a reliable indicator of treatment effect, as the feeding removed dry matter and nutrients to a large and similar extent across all treatments. Unsurprisingly then, there were no significant differences among any of the treatments for the biomass, P and N uptake and recovery, with recoveries of P and N added in the treatments very low as expected (Appendices A and B). Nutrient use efficiency was not calculated due to the loss of biomass.

The only residual soil properties (Appendices A and B) that had statistically significant differences were NO_3-N and EC ($p<0.05$). For NO_3, refer to Appendix A. For EC levels, control 2 and both MBMA fractions were the highest, followed by control 1, manure char, canola meal char and the TSP fertilizer. The latter four treatments were not statistically different from the first three or willow char, however, willow char with EC levels almost half that of control 2 is statistically different. All treatments except for willow char showed increased levels of EC compared to the pre-study levels, indicating possible release of inherent soluble salts from these chars, or an increase in the solubility of native salts in the soil. As these compounds were not identified as part of this study, the specific effect of the char on EC cannot be verified.

3.5.2.2 Effect of char application on wheat yield

In the study with wheat grown on soil cores collected from the grasshopper damaged single row canola field treatments, the wheat was grown to maturity and biomass was split into grain and straw yields (Fig. 3.12). Significant differences were noted for both the grain and the straw yield. In the grain component, the MBMA coarse fraction performed the best of all the treatments, followed by the TSP fertilizer and manure char, canola meal char, willow char and the MBMA fine fraction. All treatments performed better than the two controls. In the straw yield component, the MBMA coarse fraction again outperformed the other treatments. The TSP fertilizer performed marginally better than the willow and manure treatments, while the canola meal and MBMA fine fraction were similar to control 2. All amendment treatments produced higher mean yield than control 1.

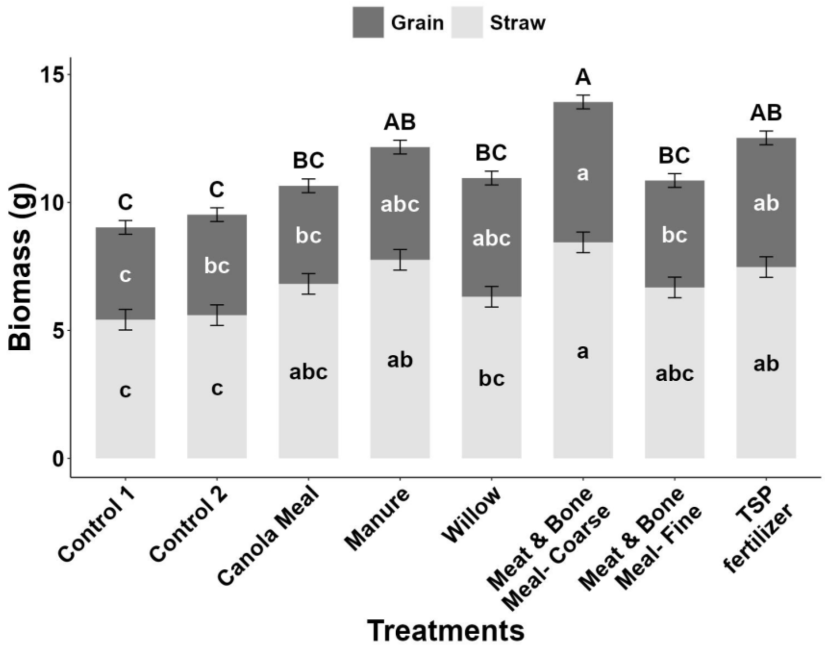

Fig. 3.12. Wheat yields (grain, straw) measured in grams for treatments added at a rate of 25kg P/ha. Error bars indicate standard error and significant differences are indicated using compact letter display with a Tukey HSD multi-treatment comparison. Treatments are compared within and not between categories (grain, straw and total biomass).

3.5.2.3 *Effect of char application on wheat phosphorus uptake*

The nitrogen and phosphorus uptake were combined for the grain and straw yield (i.e. total biomass). It should be noted that nitrogen was added to all cores at the start and during the experiment, including control 1 (no basal fertilizer). This was done to supplement any nitrogen losses that would have occurred in the field, and the second application was to compensate for N deficiency noticed during the tillering and heading stage. Nutrient recovery and nutrient use efficiency were not calculated for this component of the study due to the loss of nutrients from the field component rendering the nutrient uptake/recovery data from the field component as suspect, and specifically for N recovery, due to the addition of nitrogen to the cores. The TSP fertilizer and MBMA coarse fraction had the highest P uptake for the wheat (Fig. 3.13), followed by the manure char. Of the char treatments, canola meal char had the lowest P uptake, however, all the chars had higher levels of P uptake than control 2, even if just marginally so as in the case of canola meal char.

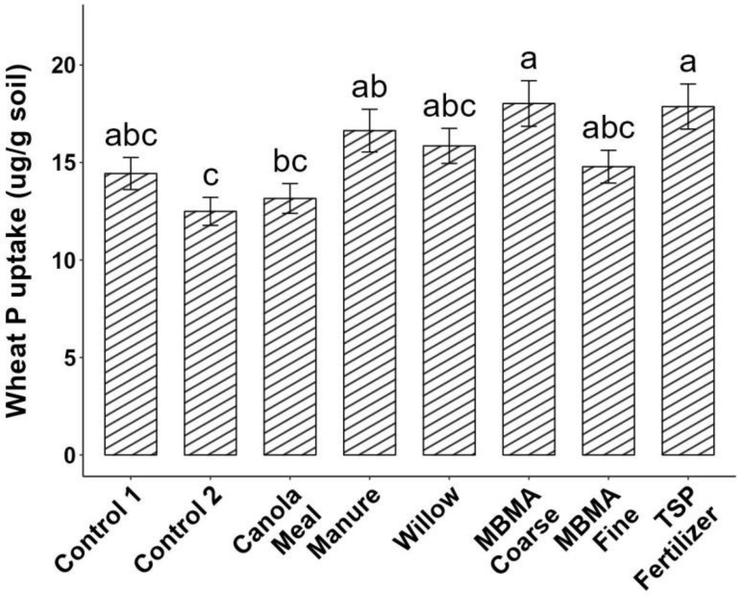

Fig. 3.13. Wheat study phosphorus uptake (µg of P per g of soil) in the wheat crop for treatments added at a rate of 25kg P/ha. Error bars indicate standard error and significant differences are indicated using compact letter display with a Tukey HSD multi-treatment comparison.

3.5.2.4 Effect of char application on residual soil nutrients and chemical properties

There were significantly higher post-harvest, post-leaching concentrations of modified Kelowna extractable available P and water soluble P (Table 3.13) in the treatment with TSP fertilizer compared to the controls; and the char treatments on average had higher concentrations of residual MK extractable P and water soluble P than the controls, except for canola meal char. Resin P levels were the highest in willow char and the lowest in canola meal char and MBMA coarse fraction, with all other treatments not significantly different from the willow or canola meal char treatments. Overall, there was a slight increase in organic carbon except in the control 2. Willow char had the highest OC levels, up from 1.5% in the field to 2.3% in the cores. Differences in measurements between the field and the cores may be due to sampling in the field, which may not have captured all the variability resulting from banding the treatments.

Table 3.13. Wheat study controlled environment component phosphorus uptake (mg nutrient per core) and residual soil phosphorus and percentage organic carbon (OC). P fractions shown include Modified Kelowna P (µg nutrient per gram of soil), water soluble P (µg nutrient per gram of soil) and resin P (µg/cm^2 of membrane surface per 24 hours).

Treatment	***MK-P***	***Soluble P***	***Resin P***	***OC (%)***
Control 1	6.7 abc[†]	8.0 bc	0.0150 ab	1.6 b
Control 2	5.3 c	7.4 c	0.0142 ab	1.5 b
Canola meal char	6.0 bc	8.2 bc	0.0123 b	1.7 b
Manure (2022) char	7.7 abc	9.8 abc	0.0139 ab	1.7 b
Willow char	11.7 abc	8.5 abc	0.0183 a	2.3 a
MBMA coarse	12.9 ab	10.5 ab	0.0123 b	1.8 b
MBMA fine	8.2 abc	9.2 abc	0.0134 ab	1.6 b
TSP fertilizer	13.5 a	11.4 a	0.0141 ab	1.7 b
ANOVA (Type III) *p*-value[‡]	*2.02E-05****	*1.32E-06****	*0.737*	*8.2e-09****

[†] Means with the same letter are not significantly different at $p<0.05$. Letters represent the multi-treatment comparison using the Tukey HSD method.

[‡] *** shows significance at $\alpha = 0.001$.

3.5.2.5 Nutrients in leachate

The concentration of the nutrients leached from the cores is reported on a µg nutrient per gram of soil in the core basis (Table 3.14). Compared to the controls, all treatments showed greater mean amounts of PO_4-P removed from the soil in the leachate from the cores applied after wheat harvest.

The TSP fertilizer and MBMA coarse fraction resulted in largest amounts of P leached from the cores, consistent with higher residual levels of water soluble P in the soil in these treatments following leaching as shown in Table 3.13 and in Fig. E1 in Appendix E. Willow char and MBMA fine fraction resulted in amounts of phosphate leached that were just slightly higher that the unamended controls. P fertilizer and MBMA coarse fraction are linked to higher levels of residual soil P (modified Kelowna and water soluble), however, the leachate pattern did not hold for the other treatments. A correlation of the leachate PO_4-P and the soil residual P fractions (Appendix E) showed a similar pattern.

Table 3.14. Phosphate P leached (ug P removed in leaching water per g of soil in core) in the controlled environment wheat study post-harvest leaching experiment. Values are in µg nutrient leached per gram of soil in the core and include the treatment mean, standard error and Tukey HSD significant differences as letters.

Treatment	Leachate PO_4-P[†]
Control 1	0.004+-0.002 ab
Control 2	0.002+-0.001 b
Canola meal char	0.015+-0.007 ab
Manure (2022) char	0.018+-0.009 ab
Willow char	0.005+-0.003 ab
MBMA coarse	0.030+-0.017 a
MBMA fine	0.007+-0.003 ab
TSP fertilizer	0.023+-0.011 ab
ANOVA (Type III) p-value	*0.0026***

[†] Means with the same letter are not significantly different at p<0.05 for a Tukey HSD multi-treatment comparison.

[‡] ** shows significance at α = 0.01.

3.6 Discussion

3.6.1 Canola study

3.6.1.1 Biomass, nutrient recovery and nutrient use efficiency

Biochars applied at 50kg P/ha are directly comparable to the commercial P fertilizer applied at the same rate in the evaluation of the fertilization value of the chars. Except for willow char, the char treatments all had less biomass than the TSP fertilizer, as expected. The willow char, which had the lowest P content at 0.17%P, performed best compared to the Triple Superphosphate (TSP) fertilizer. This is likely due to the willow char having been applied at a much higher product rate (almost 30t/ha) than any other char to achieve the target of 50kg P/ha. This is a higher rate than applied in a previous study using this biochar, with a much greater response than previously seen, even at 20t/ha (Stefankiw, 2012) It is expected that the other beneficial properties of the char, including the increased specific surface area (SSA) and cation exchange capacity (CEC) as well as any other nutrients contained in the willow char could be contributors to higher biomass (Glaser & Lehr, 2019). In the Haverhill soil, there was no significant difference between the willow char applied at 50kg P/ha and the willow char applied at 10t/ha & TSP, with only a very slight increase in the 10t/ha only treatment. In the Oxbow soil there was a significant difference, but again, the willow char at 10t/ha performed best. This indicates that any added P outside of what was contained in the char did not increase the char's ability to increase biomass. The Stefankiw (2012) study found that the willow char when added with P fertilizer gave a much bigger response in both a brown and a black chernozem. This indicates that char-soil reactions for the willow char is variable, potentially due to ageing of the char.

The higher performance seen in the willow char treatment was not as strongly evident in the P uptake, but the P recovery showed the same trend. A striking difference is the P recovery in the willow char 10t/ha in the Haverhill soil, which at 93% was much higher compared to other treatments and higher than that normally observed for P fertilizers in Western Canada of ~30 to 50% (Grant and Flaten, 2019). This was accompanied by an exceptionally high phosphorus use efficiency (PUE) for this treatment at 57% higher than the other chars added at 10t/ha. Although the Canola Council of Canada states that canola typically responds well to P fertilizer additions and that the crop is efficient at recovering P from the soil (Canola Council, 2023), P recovery rates in the first season after application are typically much lower (Selles *et al.,* 2011, Savaliya *et al.,* 2018). Crops typically recover a higher percentage of added nutrients at lower rates of nutrient addition – this may thus partly explain the greater recovery (Grant and Flaten, 2019). However, it would be expected that the residual soil phosphorus would be much lower in this treatment than in others, which is not the case. As this is also not the result of an excessive outlier, it is likely that the level of char added, as well as the conditions in the Haverhill soil were optimal for short term fertility, while at the same time resulting in moderate residual P levels, indicative of simultaneous benefits to long-term fertility. Although higher P uptake was seen in the Stefankiw (2012) study at the 10t/ha rate compared to other char application rates (recovery was not calculated), this phenomenon was not noted. Hangs *et al*. (2021)

also did not see such an excessive increase from the willow biochar. It is thus likely that the results from this study is due to a unique combination of variables in the canola study.

Although the canola meal and canola hull chars had higher biomass at the 50kg P/ha rate in the Haverhill soil, the manure had overall better performance in both soils and at all rates. This is to be expected based on the higher P content as well as additional nutrients (not measured for this study) expected from an animal-based biochar (Rose *et al*., 2019) P uptake followed a similar trend to the willow char in most treatments, showing a good response of canola to the P additions. The Triple Superphosphate P fertilizer showed around 50% recovery, similar to or better than that observed for P fertilizer recoveries in the year of application in many field studies in western Canada (Grant and Flaten, 2019). This may be explained by ideal growth conditions in the chamber and a limited volume of soil in the pots that was thoroughly explored by roots. With the exception of willow char, other 50kg P/ha treatments had around 25% recovery of the added char P, except the canola meal char and canola hull char in the Oxbow soil – these P recovery rates were just above 0% indicating very low plant utilization. Also, the soil residual labile P was not elevated in these treatments, suggesting the char P was in, and/or formed and remained in an occluded or non-labile form in this soil. Although the severity of these results did not repeat at higher char application rates, the canola meal char had low P recovery at all rates, while the canola hull showed some improvement with added TSP fertilizer. As both the canola meal char and canola hull char showed this trend, it is likely that there was an unexplored interaction between the canola feedstock chars and the Oxbow soil, that could potentially be tempered for canola hull chars by adding additional P fertilizer. It is unclear whether this could be extrapolated to other black chernozem soils, or if it was just this specific soil.

Overall, canola meal char did not perform well compared to the other chars. Canola hull char performed somewhat better, but manure char and willow char had the best performance. Higher application rates of product char showed increased performance as shown in other studies (Tenic *et al*., 2020). This is likely due to the biochars' beneficial effect on properties other than P content and availability, as well as higher application rates having a larger effect on the soil in terms of chemical and physical alterations (Glaser & Lehr, 2019). These findings are in line with the hypothesis and provides some additional insights into the beneficial effects of the co-application of char and P fertilizer.

3.6.1.2 Residual soil characteristics and nutrients

The soil pH in the Haverhill soil was lowered by at least 0.1 pH points in all treatments post-harvest, except for TSP fertilizer. As the two controls showed the largest pH decreases it is very likely that the chars were not responsible for the decrease in pH and may have slightly buffered the pH decrease associated with protons derived from nitrification of native N and added basal N fertilizer (de Luca *et al.*, 2006). The pH changes in the Oxbow soil varied much more – the chars show both increases and decreases in pH, with no discernible patterns linked to the application rate. In acidic tropical soils, chars have been shown to have a liming effect: increasing pH substantially and preventing reacidification (Tenic *et al.,* 2020). However, the soils used in this study were not acidic and the effect of chars in soils with neutral to alkaline pH has not been studied as extensively. It is anticipated that the chars used in this study, in the amounts added to the pots, would have little to no effect on soil pH as observed, and that it was rather the inherent properties and constituents of the soils like carbonates and organic matter that affected the pH (Tenic *et al.,* 2020).

Electrical conductivity decreased below pre-study levels in all treatments and controls for both soils. Canola hull char treatments consistently had the lowest salinity across both soils. The other chars did not present a clear pattern, and the rate of application did not appear to have any effect on salinity. Chars themselves are not significant sources of soluble salts and the majority of chars have been reported to reduce salt stress in crops (Tenic *et al.,* 2020). However, as the salt content of the soils used in the canola study were low and the soils considered not saline to start with, it is likely that any effect the chars may have had would be muted. Further studies with chars in soils with salinity problems would be useful.

In interpreting the P fractions measured for each of the treatments applied it can be stated that treatments showing higher labile soluble P levels remaining in the soil indicates an enhancement of P availability for successive crops grown on the soil and therefore a lasting effect related to long term fertility (Grant & Flaten, 2019). This is opposed to P taken up by the plants in the season of application, which is indicative of short-term fertility effects, and which was measured through analysis of crop biomass. The discussion focusses on these aspects of the biochar treatments applied.

For residual soil P left after harvest and that would potentially be available for utilization by subsequent crops, the 50kg P/ha and the 10t/ha treatments rates of manure char were consistently higher than other treatments, including P fertilizer, for all P fractions in both soils. This is explained by Jin *et al*. (2016) as resulting from higher levels of pyrophosphates and orthophosphates present in the manure char that increases the inorganic P content in soil. Although the manure char was not characterized for P species, one or both of those were likely present in the manure char used in this study, based on the findings of Huang *et al.* (2017). As manure char had moderately high biomass and P recovery and PUE, this char appears to have performed well in providing both short- and long-term P fertility enhancement. In addition to the environmental benefits linked to the charring of manure, such as reducing transport costs by reducing volume and mass and getting rid of pathogens and weed seeds (Cantrell *et al.,* 2012; Glaser & Lehr, 2019), the performance of manure char in this study showed promise as an agricultural additive in the place of raw or composted manure. The other chars resulted in lower amounts of residual P across all P fractions investigated, and although these treatments were lower than the TSP fertilizer, they were all higher than or similar to the controls. This is in line with the findings of Rose *et al*. (2019) in which increased plant available P was found with the application of various biochars to a neutral sandy soil. Overall, the chars with added TSP had slightly lower residual soluble, labile and available P than the treatments without added P. As the treatments with added TSP resulted in higher biomass and P recovery, this indicates that chars may enhance the availability and crop utilization of fertilizer P in the short-term and there may be benefit from adding the two sources together. Few studies are available comparing the effects of combined P fertilizer and biochar to biochar-only applications, however, a similar observation was made in an acidic tropical soil (Phares *et al.,* 2020). On the other hand, in a clayey soil in Brazil, dos Santos *et al*. (2019) found that although the combination of P fertilizer with biochar did not increase the P uptake in a single growing season, it increased available P in soil. Although char with added P fertilizer treatment may result in short-term fertility increases, it could also have a net-zero or negative effect on long-term fertility (Kalu *et al.,* 2021; Tesfaye *et al.,* 2021). The current study showed lower residual labile P when TSP was added along with char compared to adding just char alone, that may be attributed to immobilization of added fertilizer P by the char. A long-term study in the Canadian prairies showed that for P applied during a single season, crops are highly efficient at recovering P in subsequent seasons (Selles *et al.,* 2011). As adding P fertilizer with chars may have a negative long-term effect, longer-term study on P supply from chars added with and without added P fertilizer may be worthwhile. These findings are in line with the hypothesis and research questions postulated for this study.

The organic carbon content of the post-harvest soil was increased in the low organic carbon Haverhill soil compared to the pre-study soil levels for all treatments. In the Oxbow soil, all treatments except the canola hull and willow chars at $10^{t/ha}$ and TSP resulted in a reduction of OC levels. Apart from the manure char, for which no carbon data is available, all chars used in this component of the study had very high carbon content (63% - 71%), while the soil SOC was 1.3% and 3.1% respectively in the Haverhill and Oxbow soils (Table C5 in Appendix C). As noted by El Naggar *et al*. (2019), a char C:SOC ratio of more than 2 will result in significant increases in CO_2 emissions due to an increase in microbial activity, thereby negating the effect of carbon sequestration. The chars in the canola study had a ratio well above 2 (ranging from 48 to 54), indicating that although the overall SOC levels increased, this may rather be due to increased microbial activity as well as measured root carbon. To obtain a clearer indication of a char's ability to increasing carbon storage as has been shown in other studies (Lehman *et al.,* 2006; Alotaibi *et al.,* 2013; Alotaibi, 2014; House & Bever, 2019; Tenic *et al.,* 2020) a more detailed measurement of the carbon pools would need to be analyzed. Based on these findings, the assumption that the chars would lead to carbon sequestration was not supported.

3.6.1.3 Water holding capacity

All char amendment treatments performed better than the controls in terms of water holding capacity, indicating that the chars can increase a soil's water holding capacity, even if just marginally so as was the case with willow char and canola hull char in the Haverhill soil. The willow char had slightly increased the water holding capacity compared to a control in a controlled environment study using both a brown and a black chernozem (Hangs et al., 2016). Manure char is the only treatment that performed equally well in both soils. However, as the manure char was outperformed by willow char and canola hull char in the Oxbow soil, it suggests that the effect that a biochar has on water holding capacity is not only linked to the feedstock and production conditions (Shareef & Zhao, 2016; Hussain *et al*., 2020), but also strongly linked to the char's interaction with soil (Mukherjee & Lal, 2013). As most studies with biochar have been undertaken on tropical or more acidic soils, this interaction should be further studied in prairie soils to determine the extent to which different chars can improve water holding capacity of the soil, which is especially important in a semi-arid environment like Saskatchewan. These findings are in line with the hypothesis that chars would increase water holding capacity.

3.6.2 Wheat study

The canola crop, seeded in the spring of 2022 in the field on biochar treated soils, was lost to a grasshopper infestation. As a result, intact cores were collected from the field plots in September 2022 and seeded to wheat which was grown to maturity in the growth chamber. The damage to canola in the field was severe and the plots were uniformly afflicted, resulting in very little difference in biomass. As was anticipated from the uniform destruction, the nutrient uptake and recovery also did not show any significant differences. With about two to three months worth of growth, the crop had sufficient time to remove nutrients from the soil and affect the soil in different ways, however, the residual nutrients among the treatments also did not show significant differences. This is largely ascribed to the size of the rows, which potentially resulted in some nutrient drift or other bleeding effects between treatments, except for P which is not very mobile.

While the effects of biochar and ash on emergence rates and soil temperature were not investigated as part of this study, it may have provided some insights which were not available after the grasshopper infestation. Although these may prove difficult to monitor in the field, adding these aspects to future studies could provide a more comprehensive account of the biochars' impact.

The field component provided an opportunity to examine the effect of different char sources after they had aged for a period ~3.5 months under field conditions. Biochar ageing occurs naturally through exposure to oxygen, water, changes in temperature and microbial biodegradation (Liu and Chen, 2022). These authors noted that most studies showed the following as an effect of ageing – a decrease in pH, an increase in SSA and CEC, an increase in oxygen levels with a simultaneous dissolution of carbon and an increase in N. Other elements were affected more variably depending on the soil's properties as well as that of the biochar, but overall, there is a decrease in ash content. The effects of ageing will vary based on the duration and conditions of ageing (Liu and Chen, 2022), and it is with this in mind that the following discussion takes into account these changes.

3.6.2.1 Wheat yield and nutrient uptake

Wheat yield in the core chamber study was divided into grain and straw yield components. The MBMA coarse fraction and TSP fertilizer performed best in terms of both the grain and the straw yields followed by the manure char. This is in line with previous studies undertaken with bone char and manure char, which showed increased effectiveness of these chars when compared to wood or other plant-feedstock chars (Zwetsloot *et al.,* 2015; Tsai *et al*., 2019; Amante, 2021). All treatments gave better yields than the two controls, however, canola meal char, willow char and MBMA fine fraction only marginally so. P uptake followed a similar pattern to yield, with MBMA coarse fraction and TSP fertilizer having the highest mean P uptake followed manure char. The patterns differed from that observed in the field, which is likely due to ageing of the char which affected the soil's ability to provide plant available P (Kalu, 2021). The poorer yield of MBMA fine fraction when compared to the MBMA coarse fraction suggests that the remaining ash may have strongly desorbed P to the soil to become plant available. This is corroborated by the lower levels of post-harvest residual P compared to willow char, MBMA coarse fraction and P fertilizer. In a previous study (Alotaibi, 2014), the MBMA fine fraction at the same rate of application (25kg P/ha) only slightly improved crop responses when compared to a control. Alotaibi (2014) also found that compared to other amendments such as dried distillers' grains ash, the MBMA fine fraction was less effective at providing plant available P, which may be related to the high Ca content in this ash, resulting in P being bound more than in other chars. Canola meal char had the lowest P uptake both in the field and under controlled environment conditions. This coupled with the canola meal char having low residual P levels compared to the other treatments, shows canola meal char to be a poor overall performer.

3.6.2.2 Residual soil characteristics and nutrients

Residual soil nutrients in the wheat study were measured after leaching of the cores took place. This may be more representative of field conditions where leaching from late season rainfall events can lead to loss of nutrients. The residual soil test modified Kelowna P levels are substantially lower when compared to the field component level, as is to be expected from the wheat P uptake. However, the water soluble P was higher (average 9.1µg per gram of soil in the cores vs 3.6µg per gram of soil in the field). As P fertilizer reaction products age in the soil, their solubility and availability generally decline (El-Naggar *et al.,* 2019, Mia *et al.,* 2019). This increase in water soluble P is thus surprising but could reflect the effect of the leaching experiment. Lack of a large significant effect of treatment on P uptake by the wheat in this study compared to uptake by canola in the small plot component of this study may reflect reduced availability of the amendments following aging in soil.

There was an overall increase in organic carbon between the wheat study field component and the controlled environment component – the SOC increased from 1.5% pre-study levels to between 1.5% and 1.7% at the end of the field season, with a further increase to between 1.5% and 2.3% after the study. However, as noted for the canola study, this increase may not solely be due to the addition of biochar. Willow char, with the highest char addition, had the lowest OC content at the end of the field season, and the highest OC content at the end of the controlled environment study. The MBMA fine and coarse fractions had 0.1% and 0.9% C respectively, resulting in char C:SOC ratios of 0.6 and 0.1 (Table C5 in Appendix C), but the OC content at the end of the study was not the lowest. The other chars had char C:SOC ratios between 17% and 46%. Root biomass affecting the OC measurements, as well as higher carbon chars which may have resulted in higher levels of microbial activity with associated increased emissions, may explain why the overall SOC levels post-study were very similar (Sarfaraz *et al*., 2020). However, there was likely an unmeasured interaction that had a larger effect on the soil OC, especially with ageing of the char.

The differences seen between the field and controlled environment components of the wheat study, as well as between the two controlled environment studies suggest an effect of char ageing on nutrient availability that depends on char feedstock and production conditions.

3.6.2.3 Nutrients in leachate

All chars except MBMA coarse fraction had lower amounts of phosphate leached per gram of soil compared to the P fertilizer, which is in line with previous findings (Bradley *et al*., 2015, Huang *et al*., 2021), showing that chars have the potential to retain and/or immobilize P to some extent. Of note is the canola meal char which had comparatively high levels of leachate P (65% of the TSP leachate P levels), combined with low residual P and low P uptake. This char had very poor performance in this study with potentially deleterious effects. Based on the findings, the overall conclusion is that the chars influenced the mobility of P in the soil in diverse ways, as has been shown in other studies

(Madiba *et al.,* 2016; Shabaan *et al.,* 2018; Huang *et al.,* 2021). There was no strong relationship between the leachate and residual soil P fraction concentrations. Further study is required to determine the levels of char required alone or in combination with P fertilizer to reduce P in leachate.

Overall, the wheat study supported the hypothesis, with some exceptions such as the canola meal treatment's generally poor performance, and the higher P losses during leaching in the MBMA coarse fraction.

3.7 Conclusions

Overall, the results of the work described in this chapter indicate that chars and ash can benefit canola and wheat yield, P nutrition and recovery as per the hypothesis and research questions. Biochars and ash produced from willow-, manure- and meat and bonemeal derived feedstocks were generally more effective than canola meal and canola hull chars. The canola meal char performed poorly compared to the other chars, however, this feedstock also has much higher value in uses such as animal feed than the other feedstocks. Both composted and fresh manure char showed moderately good potential as a soil amendment.

Amendment of two prairie agricultural soils with chars produced from various feedstocks under different conditions shows overall positive yield responses in canola under controlled conditions that can be attributed at least partially to enhanced P availability from P originating within the char. In the canola study, recoveries of added P were highest in willow char, followed by manure char, canola hull char and canola meal char. Char treatments with added TSP typically resulted in higher yields and P recovery that suggest a benefit of chars in enhancing the availability and crop utilization of P in the short-term. In addition to the assumptions made at the start of this study, yield and P utilization can be increased above that of commercial fertilizer when the fertilizer is co-applied with a biochar. Overall high uptake and removal of P by canola resulted in limited differences in residual soil P after harvest. Soil organic C was higher in char amended soils, however, due to the underlying processes, this is not necessarily indicative of carbon sequestration.

In the wheat controlled-environment study, the P recovery was higher in the manure char treatment followed by willow char. As seen in the canola study, canola meal char performed overall poorly in terms of both wheat yield and P recovery. The field study allowed ageing of the char, the effects of which were visible in the wheat grown in cores taken in fall from the field experiment to which char was added in spring and canola was grown. The wheat crop and soil analysis revealed the greatest yield in MBMA coarse fraction amended soil, followed by TSP fertilizer, willow char, manure char and canola meal char. Similar to the growth chamber pot study with canola, canola meal char was least effective in producing wheat yield increase. Aging of the amendments in the field appeared to reduce plant availability of the P, however, the MBMA coarse fraction and manure were most effective at taking up P. P sources of greater plant availability and solubility like MBMA and P fertilizer appear to result in greater potential for loss by leaching. However, the overall P losses in a 5cm leaching event were very small (<0.02 µg P per g of soil). As with many other properties of chars, the leachate data collected in this study shows that the potential of a char to increase nutrient retention in soil is highly dependent on the char feedstock material and production conditions.

In general chars have the potential to improve nutrient retention in prairie soils, but further study is required to reveal the specific benefits of different chars and reasons for differences in efficacy. The following specific recommendations are made in this regard:

- Chars should be tested at different rates of nutrient application to determine relative efficacy of nutrient contained in chars versus commercial fertilizer sources, and synergies or antagonisms when combined together.
- Additional studies looking at all carbon pools are necessary to determine the nature of carbon sequestration in low carbon soils when adding chars with high levels of carbon.
- Further studies should be conducted with manure char from different sources and at different rates.
- Future studies should focus on chars derived from agricultural wastes, rather than agricultural co-products with commercial value to optimize the use and value thereof.
- Longer term field trials should be undertaken with chars produced under different conditions to determine the effect of ageing the chars in prairie soils on nutrient use and retention, and on water holding capacity.

- Blending of chars may provide a greater benefit to both agronomic and environmental performance.

4. EFFECT OF WILLOW BIOCHAR AMENDMENT ON CANOLA YIELD, PHOSPHORUS UPTAKE, RETENTION AND LOSSES IN WATER IN THE FIELD

4.1 Preface

This chapter (Chapter 4) describes field research undertaken to compares the impact of willow biochar added at varying rates to commercial P fertilizer by assessing crop yield and phosphorus levels in the soil and in snowmelt runoff. The field study, conducted in a farm field in the brown soil zone in south-central Saskatchewan, evaluated the performance of willow biochar under field conditions to complement the previous work (Chapter 3) conducted with several biochars under controlled conditions. Straw and seed yield of canola were evaluated along with the uptake and apparent recovery of phosphorus by the canola crop, residual soil phosphorus, and concentrations of phosphorus in simulated snowmelt run-off from intact soil slabs collected from the field plots in fall. The effects of biochar on water infiltration were also measured in the field.

4.2 Abstract

Biochars have been shown to be effective in enhancing soil properties and plant growth in various settings when applied alone or co-applied with fertilizers. Very few studies have compared the effects of biochar added at different rates alone and in conjunction with a commercial fertilizer (Triple Superphosphate (TSP)) to that of applying TSP alone. Specifically, such studies have not been undertaken in the Canadian prairies where the effects of such different applications could be investigated as it pertains to crop yield, soil fertility and soil-water relations. To test the effects of these different applications on prairie soils, a wood feedstock (willow) biochar was added in the field at rates of 25kg P/ha to match the rate of added TSP, as well as at a rate of 10t/ha char, and 10t/ha char co-applied with TSP and the effect thereof tested on a canola crop. The field experiment was undertaken in 2022 in an agricultural field with low phosphorus soil near Central Butte, Saskatchewan. The effect of treatment on canola yield, P uptake and recovery, retention of P in the soil after harvest, and P losses in simulated snowmelt runoff were assessed. Infiltration impacts were determined in the field using a double ring infiltrometer falling head technique. Amendment with willow char revealed very limited effects on yield, and overall positive effects on nutrient retention and preventing nutrient loss in runoff as well as improving infiltration. The willow char added at a rate of 10t/ha provided the best performance overall. It was found that co-applying biochar with TSP has the potential to increase

P recovery above that of char or TSP when applied alone, increase residual P in the soil and reduce P losses in snowmelt runoff compared to adding TSP alone due to ability of the char to bind P. In general, the research indicated that a balance may be obtained between biochar supplying P or allowing P to be more available during the growing season while preventing P from entering the snowmelt runoff the following spring. Biochar was also effective in improving infiltration; however, the results of this study also indicate a possible link between added levels of the TSP and infiltration, rather than just an effect resulting from biochar. Willow char applied at a rate of 10t/ha, especially when co-applied with TSP fertilizer would be a suitable soil amendment in a brown chernozem soil to improve soil and water conditions for phosphorus efficiency and crop growth.

4.3 Introduction

Biochar is a carbon dense by-product from pyrolysis processes. Wood feedstock biochars, such as char made from willow wood has a high lignin content and associated higher C content, resulting in a high C:N ratio compared to chars produced from straw and other agricultural wastes (Shabaan *et al.,* 2018). This in turn is linked to reduced nitrogen mineralization rates, which makes chars from wood feedstock material useful for retaining nutrients in soil over the longer term, while reducing nitrogen losses in runoff and through leachate (Mukherjee & Lal 2013, 2014; Jin *et al.,* 2016; Li *et al.,* 2020). Even so, high lignin chars have nutrients which can potentially be made plant available during the growing season. However, the effect of amendment with this type of char on soil phosphorus has received relatively little attention to date.

Phosphorus is an essential macronutrient required for plant growth and often added as a fertilizer for crop production. In 2015, 81% of soil samples in Saskatchewan tested below the critical P level (25mg/kg Bray P1 equivalent), with a median P level of 14mg/kg (IPNI, 2015). In addressing P deficiencies through addition of fertilizer or manure, excess addition can result in environmental damage such as downstream eutrophication (Grant and Flaten, 2019). To combat these negative effects, various improvements to agricultural practices have been made over the last few decades, including the 4R Nutrient Stewardship framework which promotes the use of '*the Right fertilizer sources, applied at the Right rate, at the Right time and with the Right placement'* (The Nutrient Stewardship, 2017).

Another mechanism to improve agricultural practices and improve P usage is the application of co-amendments with the fertilizer, including biochars. Numerous studies (incl. Mukherjee & Lal 2013, 2014; Shabaan *et al.,* 2018; Tenic *et al.,* 2020) have investigated the potential agronomic benefits associated with biochar addition to agricultural soils, including a few studies with Saskatchewan soils at the University of Saskatchewan (Stefankiw, 2012; Ahmed, 2014; Alotaibi, 2014; Hangs *et al.,* 2016; Hangs *et al*., 2021). While many studies have incorporated the co-application of biochar with P fertilizer (commercial or otherwise) or examined the effects of char compared to other fertilizers, few have looked at the effects of biochar alone compared to fertilizer alone as well as co-applied char and fertilizer. Adding biochar may reduce the bioavailable, mobile phosphate in soil through sorption of soil and fertilizer phosphate, but also may increase availability through mobilization and desorption of the phosphorus contained within the char, depending on conditions and timeframe examined.

As rock P is a finite resource and P movement into surface water in run-off from agricultural fields is a concern, methods to reduce P losses have been investigated. In the Canadian prairies, snowmelt water is the major source of runoff, transporting P in dissolved and particulate forms, with resulting losses from croplands to surface water (King, 2015; Schneider *et al*., 2019; Wiens *et al.,* 2019). Schneider *et al*. (2019) reported on a long-term study to determine the effects of various management practices in reducing nutrient loss in runoff. Their findings at Swift Current, SK, indicated elevated concentrations of P in run-off above previously established environmental thresholds for all sites under various management practices. A study by Wiens *et al*. (2019) focussed on the P fertilizer placement strategies to minimize P in runoff in the Canadian prairies and found that broadcasting P fertilizer without incorporation resulted in increased P runoff compared to in-soil placement. Literature on snowmelt runoff in the Canadian prairies indicated that fertilizer and land management should be complemented by alternative methods to reduce nutrient runoff in snowmelt. Biochar has been shown to be effective in reducing P in rainfall runoff in tropical soils (Van Zwieten *et al*., 2010; Mukherjee & Lal, 2014; Tenic *et al.,* 2020), however, no research has been conducted to determine the effectiveness of biochar in reducing nutrient losses in snowmelt runoff in the prairies.

Soil hydrological properties including water holding capacity and infiltration rate are linked to soil physical properties such as bulk density and porosity, surface area and aggregate stability (Mukherjee & Lal, 2013, 2014). Although these authors reported improvements in water retention due to biochar amendments, as was also found in this thesis work (see Chapter 3), other studies have indicated that the highest overall benefits may be seen in clayey soils, with diminishing returns in silt-loam and sandy soils (Tenic *et al.,* 2020). Water infiltration is desirable to reduce water volume moving across the soil surface in the form of runoff that carries dissolved and particulate nutrients. However, to date, there is no information available on the impact of biochar amendment to Canadian prairie soils on infiltration under field conditions.

A willow feedstock biochar which has been used in previous studies at the University of Saskatchewan was chosen for this component of the thesis research as it was effective in enhancing yield in the chamber studies (see chapter 3) and was available in the large quantities needed for field testing. The field site used for this study was chosen because it had relatively low available phosphorus levels (11mg/kg soil test extractable P) and had been farmed using management practices typical of the Canadian prairies: cereal-pulse-oilseed rotation under no-till. As the willow biochar was also low in phosphorus at 0.17% P, it was deemed suitable to observe effects on both retention and supply.

It is postulated that due to its low P content and ability of chars to retain as well as release P, that the willow biochar would not be as effective at providing available P to crops and increasing yield compared to a commercial fertilizer such as Triple Superphosphate (TSP). At the same time, it was hypothesized that the char would increase residual P fertility compared to TSP, increase infiltration rates and reduce the potential loss of P in snowmelt runoff after harvest. This chapter responds to the questions on the efficacy of a low P containing char in improving agronomic and environmental performance through the provision of P to the crop; the retention of P post-harvest for longer term soil fertility and in improving infiltration to prevent P losses through runoff.

4.4 Materials and methods

4.4.1 Site description and experimental design

Experimental plots[6] were located in a wheat stubble field ~2km north of Central Butte, SK (50°44'35.04"N 106°26'14.64"W) (Fig. 4.1) in a low-lying, but well drained area of the field with no salinity or flooding concerns. The site was chosen due to the low existing P levels in the soil that enabled evaluation of the degree to which the biochar could act as a P source, and the effect of the biochar on P retention and water infiltration post-harvest. Soils at this site are a loamy textured mixture of brown solonetzic soils and brown chernozemic soils of the Echo-Haverhill Association (SKSIS, 2023). The topography is very gently sloping (almost flat) with the experimental plots located near the bottom of a catena. SKSIS indicates salinity class 2 for the broader area (slight effect on crops) and as found at the site described in Chapter 3, although the average surface electrical conductivity (EC) observed for these soils (0.15mS/cm) is considered non-saline, other factors influence the overall salinity class determination. Weather data for the large plot site is the same as described in Chapter 3 for the small plot site (Fig. 3.4).

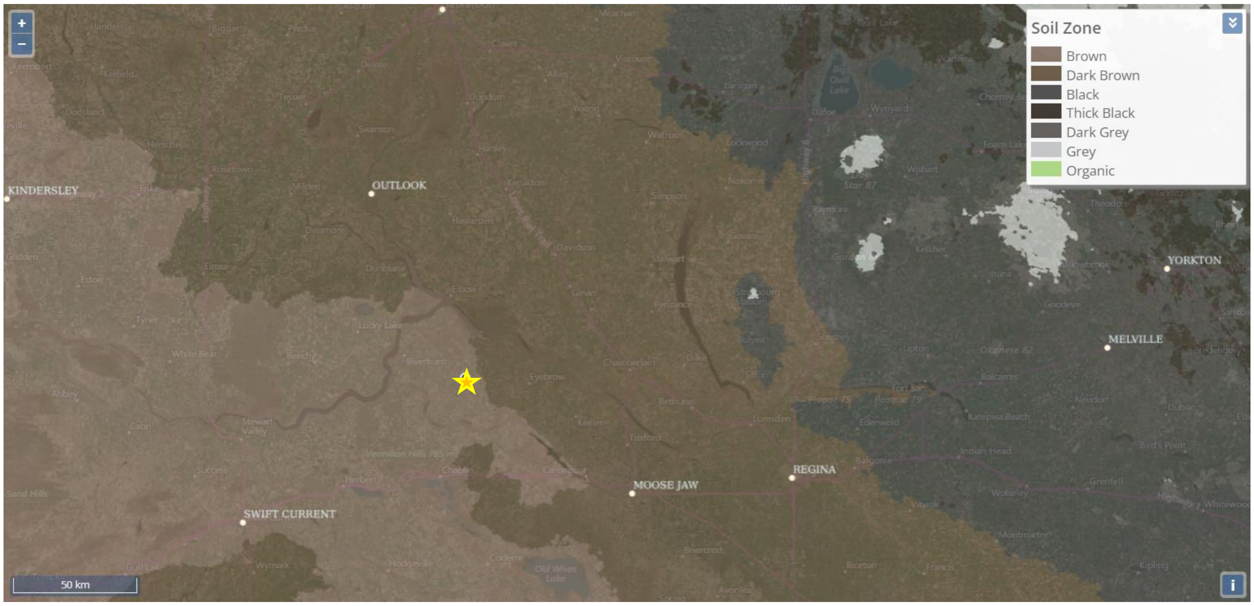

Fig. 4.1. Large plot field study site location (yellow star) in relation to the soil zones of Saskatchewan (map extracted from the Saskatchewan Soil Information System, sksis.ca/map, January 2023)

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[6] Sometimes referred to as 'large plots' or the 'large plot site' to distinguish it from the smaller plots described in Chapter 3, which are referred to as 'small plots' or 'single rows'.

Soil sampling was undertaken in spring of 2022 prior to seeding. Five random soil core samples across the study area were taken at depths of 0-15cm, 15-30cm and 30-60cm to characterise the soils. Spring soil samples were air dried prior to being ground, then sieved and analyzed for baseline physico-chemical properties (pH, EC and organic C content), nutrient content and P & N supply rate (Table 4.1 and Table C2 in Appendix C).

Table 4.1. Selected nutrients, pH, electrical conductivity (EC), % organic carbon and texture of the soil (0-15cm) from the 2022 field study measured on soils collected in spring 2022.

Properties	pH	EC (mS/cm)	N as NO_3 (mg/kg)	S as SO_4 (mg/kg)	MK† P (mg/kg)	MK K (mg/kg)	Organic carbon (%)	Textural class
Analysis	6.8	0.15	13.5	3.7	11.2	382	1.49	Loam – sandy loam

† Denotes Modified Kelowna extractable available (soil test) P and K

The field experiment was designed as a Randomized Complete Block Design (RCBD) consisting of six (6) treatments in 1m x 4m plots. There were four (4) blocks of replicate treatments with 2m alleys in between (Fig. 4.2). Treatments included a control 1 with no added basal fertilizer; control 2 with added basal N,K, S fertilizer; willow biochar added at a rate to provide 25kg P/ha from the char itself for comparison to Triple Superphosphate (TSP, a commercial fertilizer source) added at same rate; willow biochar added at a rate of 10t char per hectare (typical field-scale product based application of biochar and other organic amendments) which added 17kg P/ha as P in the char itself ; willow biochar added at 10t/ha along with 25kg P/ha TSP to provide a total of 32kg P/ha; and TSP at 25kg P/ha. All treatments except control 1 received a basal fertilizer application consisting of 100kg K_2SO_4/ha (0-0-47-17) and 217kg urea/ha (46-0-0; the urea rate was calculated based on adding 100kg actual nitrogen per hectare, at 46% N content in the urea).

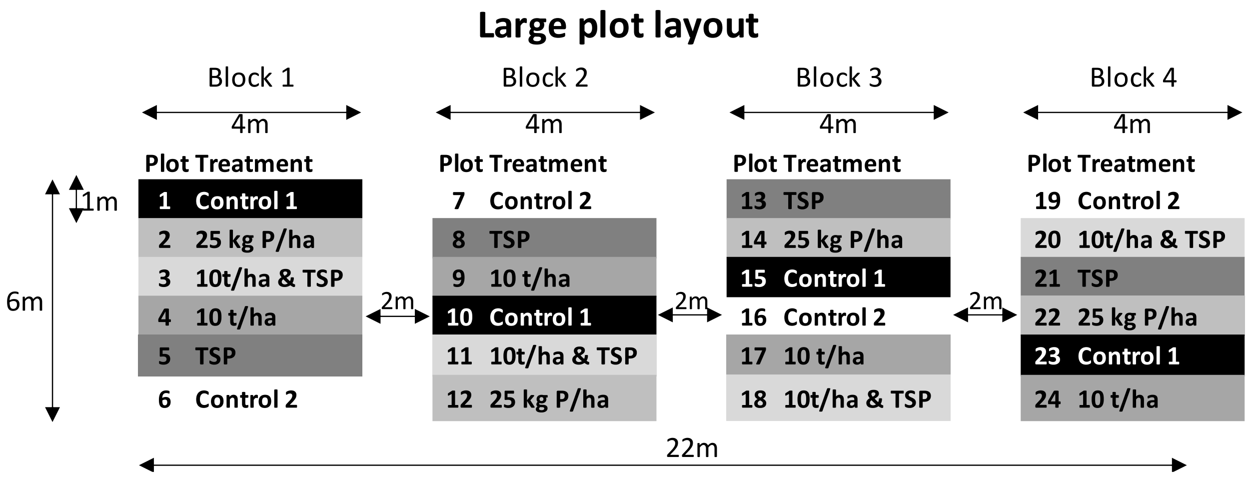

Fig. 4.2. Large plot 4-row study layout. control 1 - no treatments; control 2 – basal N, K, S treatment; willow biochar at 25kg P/ha & basal application; willow biochar at 10t/ha & basal application; willow biochar at 10t/ha & Triple Superphosphate (TSP) fertilizer & basal application; TSP fertilizer at 25kg P/ha & basal application.

Characteristics of the willow biochar is detailed in Table 3.1. Quantities of nutrients added and the nutrient content in each treatment which were used in the apparent nutrient recovery and nutrient use efficiency calculations are shown in Table 4.2.

Table 4.2. Quantities of char, N and P applied per treatment for the field study.

Treatment	**Char added (kg/ha)**	**%N in treatment**	**N applied (kg/ha)**	**%P in treatment**	**P applied (kg/ha)**
Control 2	-	-	100.00	-	-
Biochar 25 kgP/ha	14705.88	1.40%	305.88	0.17%	25
Biochar 10t/ha	10000.00	1.40%	240.00	0.17%	17
Biochar 10t/ha & TSP	10000.00	1.40%	240.00	0.17% + TSP	42
TSP fertilizer	-	0.00%	100.00	19.40%	
Mean nutrient uptake in the control used of the calculation					**kg/ha**
Control 1 – used for N uptake as no N was added to this control					43.69
Control 2 – used for P uptake as basal fertilizer was added to this and all treatments					7.12

All plots were prepared by harrowing the chaff and straw from the previous growing season. Amendments were applied using a broadcast and incorporate application method to maximize interaction of char with the soil and the potential benefit of the char on reducing P run-off losses. The treatment application involved spreading the char and TSP fertilizer uniformly across the plot surface, followed immediately by a shallow (5cm depth) incorporation with a rotary tiller to mix the char or P fertilizer with the top 5cm of soil and prevent loss of biochar to wind. The controls also received the same tillage operation. Canola (*Brassica napus*, var. Liberty Link 233P) was used as the crop (Fig. 4.3), seeded at a rate of 6kg per ha. The basal fertilizer N, K and S was applied beside the seed-row in a sideband at the time of seeding.

Fig. 4.3. Large plot setup for canola growing in plots (taken on July 8, 2022), looking south. The surrounding field was cropped with peas.

In the last week of August 2022, canola was harvested from the plots by cutting, drying and threshing to separate grain and straw for yield measurements. After harvesting, in the last week of September 2022, soil cores were taken at depths of 0-10cm, 10-20cm and 20-30cm from each plot using a punch truck. The measured parameters for the crop included grain and straw yields, total N and P, and for soil it included extractable NO_3, PO_4, resin exchangeable P, water soluble P, pH, EC and %OC using the analytical laboratory methods described in section 3.4.3.

4.4.2 Water infiltration

Various methods have been developed over the years to determine infiltration in the field. The method used in this thesis work is the double ring infiltrometer method, first described by Bouwer in 1963. It involves the use of two metal rings of differing diameters which are installed concentrically.

Water in the outer ring saturates the soil beneath the space between the rings which allows water in the inner ring to move downwards without lateral movement (Bouwer, 1986, Jabro & Mikha, 2021). Measurements of changes in water levels in the inner ring at related time intervals are recorded (referred to as the falling head technique) and used to calculate infiltration. Although this is not necessarily the most accurate method, as explained by Bouwer in 1986, it remains a popular infiltration measuring method. Bouwer also added that infiltration measurements are often subject to high variability due to inconsistent field conditions.

Infiltration rates were determined in August 2022 after harvest using a modified double ring infiltrometer falling head technique (Bouwer, 1986; Jabro & Mikha, 2021). Two metal rings (15cm and 30cm diameter rings) were placed in each plot with the smaller ring centred in the outer ring, inserted into the ground approximately 5cm deep (Fig. 4.4). A ruler was affixed to the inner ring and both rings were simultaneously filled to the 10cm mark. Time measurements were taken at every 1cm drop in the water level until all the water was drained (depth=0cm), or where very little change was observed after 90-100 minutes, the water level was recorded every 20 minutes until about three hours passed. The outer ring was kept at the same water level as the inner ring throughout. After the infiltration

Fig. 4.4. Infiltration measurements in the field set up for each plot (left). A close-up of the setup (right) shows the water levels in both rings.

measurements were taken, bulk density samples in- and outside of the infiltration zone were taken for each plot to identify the moisture response in soil resulting from different treatment combinations.

Infiltration analysis was undertaken in three steps:

1. Initial and final infiltration rates were calculated as cumulative infiltration over time at the first and final measurements. As infiltration rate is not a linear function, both the sorptivity and the K_{fs} values are required to accurately reflect the effect of a treatment on infiltration. These were calculated from the measured data as slope and intercept values for each field plot using equation 4.1 (Philip, 1957[2]).

$$v_0 = \frac{1}{2} S t^{-\frac{1}{2}} + A$$

Eq. 4.1

Where v_0 signifies the infiltration rate in cm/h, $S/2$ is the slope, t is time in hours, and A approaches hydraulic conductivity. For the purposes of this study, A is approximated as field saturated hydraulic conductivity (K_{fs}). Slope and intercept values were calculated for each set of infiltration data by plotting v_0 against $t^{-0.5}$. The intercept represents K_{fs} while slope x 2 represents sorptivity (S).

2. Using the calculated S and A values in the Philip two term model (equation 4.2) (Philip, 1957[2]), the predicted cumulative infiltration values were calculated for each measured time. The infiltration was plotted against the cumulative infiltration and the predicted cumulative infiltration. As the final time measurements differed for each field plot, the data was only graphically plotted to a maximum of two hours.

$$i = St^{1/2} + At$$

Eq. 4.2

i is the cumulative infiltration in cm (referred to as CI in this thesis), S indicates sorptivity, as calculated with Eq. 4.1, which together with $t^{0.5}$ (time), represents the first term of the model, namely that of the initial infiltration filling the large pore spaces, before field saturation is achieved.

At is the second term of the two-term model, namely the K_{fs} or saturation at a given time. The latter represents a gravity factor whereby infiltration occurs much more slowly as it is driven by gravity. The two terms gradually shift from one end to the other with both terms occurring simultaneously. *At* is negligible during initial infiltration but becomes increasingly more important as the infiltration process progresses until it is the only active component.

3. The percentage moisture was calculated from the bulk density samples. Final CI rates for analysis were recalculated at a predicted rate of 2 hours to standardize the output.

4.4.3 Snowmelt runoff

Although in-situ snowmelt measurements can be done (Liu *et al.,* 2014), these are time consuming and expensive, and is difficult to implement on a small plot scale. Simulated snowmelt runoff experiments can be used to approximate the P losses of in-situ snowmelt events. The larger field plots (when compared to the rows described in Chapter 3) allowed for the removal of intact slabs of soil for the simulated snowmelt runoff study to best represent soil conditions (structure, residue and root distribution) as they exist in the field. An experimental method for simulating snowmelt events was developed by King & Schoenau (2009) involving the removal of intact soil slabs from the field and adding snow under controlled conditions. The resulting runoff is captured, the volume measured, and the nutrient concentrations analyzed. Since 2009, this method has been improved and expanded (Weiseth, 2015; King, 2015; Wiens 2017; Wiens *et al.,* 2019).

Samples were collected from each plot in August 2022, using a shovel and placing the soil in aluminium trays of approximately 25cm x 20cm x 10cm (as per Wiens *et al.*, 2019). Water was added to field capacity before storing the samples in a freezer until January 2023 at which time they were measured and weighed, prior to being set up for the snowmelt-runoff study. Snow was collected in early January from the Goodale Research Farm, southeast of Saskatoon, SK (52°03'32.2"N 106°30'12.3"W). The soil in each tray was measured to obtain the soil weight and volume, and the trays were measured before and after the snowmelt simulation.

Each tray was placed on a thin piece of wood to imitate a 3% slope (Fig. 4.5). Note that while the field study did not have a slope, this was necessary to allow runoff to be collected. Then 600g of snow was added to each tray, representing 7.5cm of snow in the field. The snow was left to melt for 20 hours at approximately 13ºC. Filtered runoff was collected from 20 trays after 20 hours to minimize evaporation and subsequent concentration of nutrients. Three trays had no water and one had very little water collected, none from the same treatment. This was because three of the four trays 'leaked' water – it was observed that in these three trays water flowed back along the plastic runoff sheet and pooled under the trays. As the nutrients were removed from these trays, it was not deemed appropriate to add more snow to obtain a larger liquid sample. All four trays were thus tilted to a 30-degree angle and left for a further 3-4 hours to collect remaining water for analysis. All trays were weighed again after the snowmelt simulation. Runoff water was vacuum filtered through a 0.45um membrane in a Millipore vacuum system and analyzed for soluble reactive inorganic P (PO_4-P), ammonium (NH_4-N) and nitrate (NO_3-N) in the AA3 auto-analyzer. Fresh snow melt was analyzed for baseline P and N concentrations which was subtracted from the runoff concentrations. The P in runoff was calculated using the sample volume and P concentration, as well as the slab volume as follows:

Fig. 4.5. Snowmelt-runoff study setup – initial setup shown on the left, with PRS® probes and added snow on the right. Aluminium containers and plastic sheets were used to funnel the runoff water into the containers using cheesecloth as a filter.

$$Nutrient\ load\ (kg/ha) = \frac{P\ concentration * runoff\ volume}{Slab\ area} \qquad Eq.\ 4.3$$

Prior to adding the snow, Plant Root Simulator (PRS®) probes were inserted horizontally into the soil approximately 1cm from the surface to determine available P and N dynamics during the actual melt process. These dynamics were determined through measurement of labile inorganic PO_4-P and NO_3-N that is directly exchangeable and bioavailable during the run-off. This assisted in determining treatment effect on and whether/how much the biochar affected nutrient retention during run-off. The probes were left in the trays for 24 hours. Then they were washed in distilled water and kept in a fridge until they could be analyzed as per Qian & Schoenau (2002). The probes were placed in 0.5M HCl for an hour, after which the eluent was analyzed for phosphate and nitrate in the AA3.

4.4.4 Statistical analysis

Refer to Section 3.4.4 for the analytical statistics undertaken for the biomass and soil analyses. For snowmelt and infiltration, the following statistical methods were used in RStudio (version 2022.12.0).

Snowmelt run-off variables were tested for normality using a Shapiro-Wilk test, plotting a histogram and checking skewness and kurtosis. Equality of variance was tested by means of a Levene test. The data was analyzed using linear mixed effects models (lmer, lme, glmm and glmer) – for the model applicable to each parameter, refer to Table C6 in Appendix C. The models were compared using r squared, AIC and BIC values to determine the best fit for the data. An ANOVA Type III test determined overall significance, followed by a post hoc Tukey HSD test at alpha=0.05. It was noted that some of the ANOVA tests indicated significant differences while this was not reflected in the Tukey HSD test, even when tested at alpha=0.1. This is due to, in part, the high variance among replicate and large standard errors for the snowmelt values, inherent to non-homogenized intact field samples being used in the run-off assessments. It should be noted that the ANOVA, as a global test indicates whether at least one pair of means is likely to show a significant difference while the post-hoc test does a pair-wise comparison of the means to find the differences between them. Because of the different approaches, there can be different outcomes, and thus one can show significant differences while the other may not. As the differences between treatments determined in the post-hoc test is the focus of this study, the discussion will revolve around the post-hoc results, however, the ANOVA results have been included for reference.

For infiltration data, a non-linear model was required and as per Eq. 4.2, the Philip two term model was used as a simple, data specific approach to determining sorptivity and hydraulic conductivity. Outliers for initial and final infiltration rates, moisture content, slope, sorptivity and intercept were analyzed and removed based on the interquartile ranges. These parameters were modelled using a linear mixed effects model (lme) to determine if there were significant differences at alpha=0.05. The outliers from these analyzed parameters were used along with a visual inspection of the plotted infiltration curves (Fig. E4 in Appendix E) to remove outlying sets of data for specific treatment/block combinations. The cleaned data was used with the Philip model to calculate predicted cumulative infiltration values. In a reiterative process, the predicted CI values were used to determine the final infiltration rates at time=2 hours to standardize the output. However, measured data to the maximum times for each treatment/block combination have been included in Appendix E for reference.

Interaction effects between measured variables were determined using covariance, correlation, and principal component analysis. The output of these interactions is available in Appendix D. The data and analytical code for this thesis work is available at: https://github.com/AnelD13/BiocharAshAmendments_ImproveSoil_P_Fertility_WaterRelationsRetention (Dannhauser, 2023).

4.5 Results

4.5.1 Effect of char application on canola crop yield

An analysis of the grain and straw yields, as well as the combined total biomass (Fig. 4.6) showed no statistically significant differences ($p \leq 0.05$) among treatments. Looking at the overall mean yields, control 2 had a higher mean than the other treatments at 3297kg/ha, while the Triple Superphosphate (TSP) fertilizer had the lowest mean yield at 2606kg/ha.

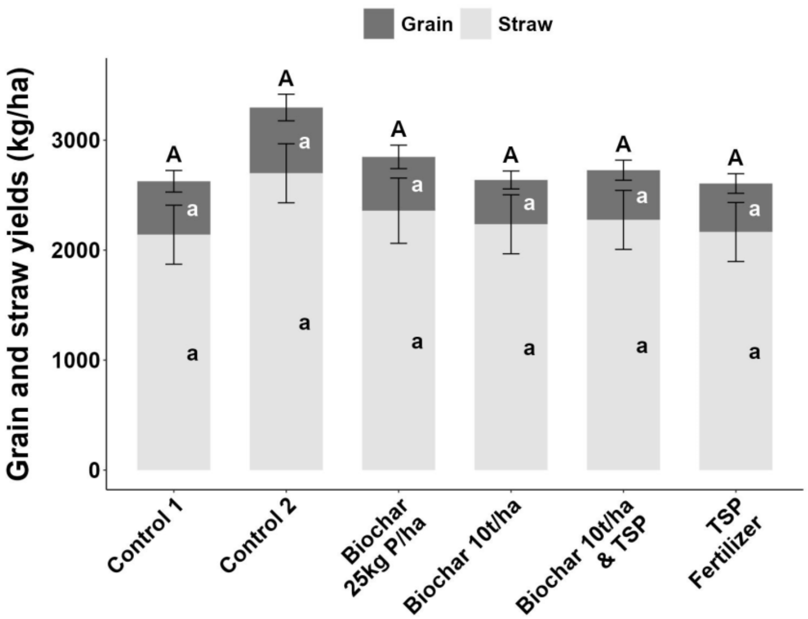

Fig. 4.6. Canola yields (grain, straw and total biomass) measured in kg/ha in the 2022 field study. Error bars indicate standard error and the multi-treatment comparison compact letter display using Tukey HSD indicates significant differences. Treatments are compared within and not between categories (grain, straw and total biomass).

4.5.2 Effect of char application on phosphorus uptake and recovery

Combined phosphorus uptake (kg P/ha) was determined for the grain and straw (i.e. total biomass) yield. Consistent with similar and non-significant effects of treatments on yield, the treatments were not significantly different ($p \leq 0.05$) in a multi-treatment comparison of either P uptake, P recovery or P use efficiency, most likely due to the extremely large standard error linked to high variability in the data (Table 4.3 and Fig. 4.7). Although not significantly different, the highest mean P uptake could be seen in the 10t/ha & TSP treatment, consistent with a greater amount of total P added in this treatment with P coming from both char and TSP. The remaining treatments except for control 1 were almost identical.

Overall, the recovery of added P was very low (Fig. 4.7) and is explained by sufficient P provided by the soil for the limited growth requirement of the canola under drought, such that little or no plant uptake of the added P occurred. Also, it is possible that the shallow surface placement of the amendments in dry surface soil in the spring limited the ability of the roots of the canola to access the

P that was applied to the soil. The 25kg P/ha and TSP fertilizer treatments showed negative recovery rates, which is most likely due to a combination of the above-mentioned factors along with the P being fixed in the soil or having leached out during the summer, making it less available to the crop.

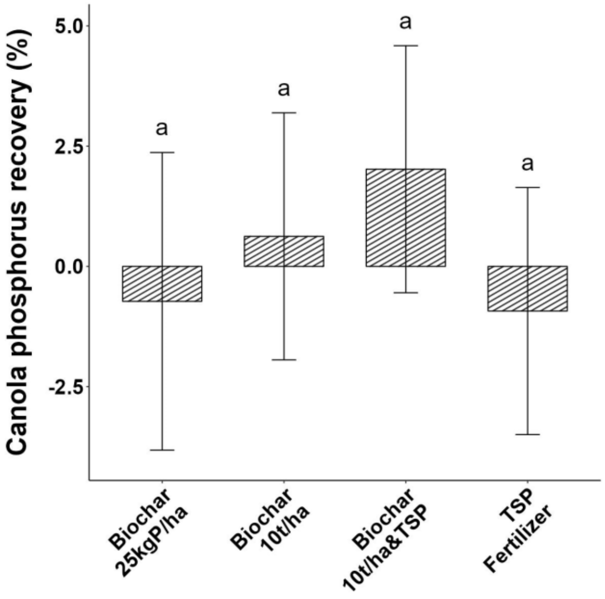

Fig. 4.7. Recovery of phosphorus added in char and or fertilizer by the canola in the 2022 field trial. Means with the same letter indicates that there is no statistically significant difference between the means based on a Tukey HSD test at alpha=0.05. Error bars indicate standard error.

Phosphorus use efficiency (PUE), calculated in kg of total biomass produced over the unfertilized control (control 2) per kg of added nutrient as per equation C1 in Appendix C showed no statistically significant differences (Table 4.2) (PUE SE for the model was 11.7). The two char treatments with no TSP added showed the highest levels of PUE, followed by TSP and char with TSP at less than half the PUE of the other two char treatments.

Table 4.3. Phosphorus uptake (kg phosphorus in total biomass per hectare) and phosphorus use efficiency (kg total biomass per kg phosphorus added).

Treatment	P uptake	P use efficiency
Control 1	6.3 a†	-
Control 2	7.1 a	-
Biochar 25kg P/ha	7.3 a	58.2 a
Biochar 10t/ha	7.2 a	54.5 a
Biochar 10t/ha & TSP‡	8.0 a	24.8 a
TSP fertilizer	6.9 a	36.7 a

ANOVA (Type III) p-value[‡]	*0.389*	*0.022**

† Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

‡ * shows significance at $\alpha=0.05$.

An analysis of nitrogen uptake, recovery and use efficiency is available in Appendix A.

4.5.3 Effect of char application on residual soil nutrients and properties

Residual available soil phosphorus fractions, organic carbon (OC), pH and electrical conductivity (EC) were measured at three depths (0-10cm, 10-20cm and 20-30cm) (Fig. 4.8). Residual available phosphorus and OC followed the expected pattern where the highest levels were found in the 0-10cm layer, decreasing with depth. No significant differences were observed for the P fractions among treatments throughout the profile. Despite more total P added to the soil in the 10t/ha biochar plus TSP treatment compared to other treatments, the levels of residual labile P in the soil after harvest were not significantly higher than other treatments. Phosphorus added to soil may be transformed into less soluble, non-labile forms over time by reaction with calcium, iron and aluminium, such that it may take several years of repeated P applications to produce large increases in soil test P values in highly buffered soils (Grant and Flaten, 2019). The lack of elevation in labile P observed in this study may reflect some interaction between the char and TSP fertilizer products that reduces solubility and bioavailability of the added P in soil. The means did not differ greatly in the 10-30cm layers, consistent with placement of the P containing amendments on the soil surface followed by shallow incorporation.

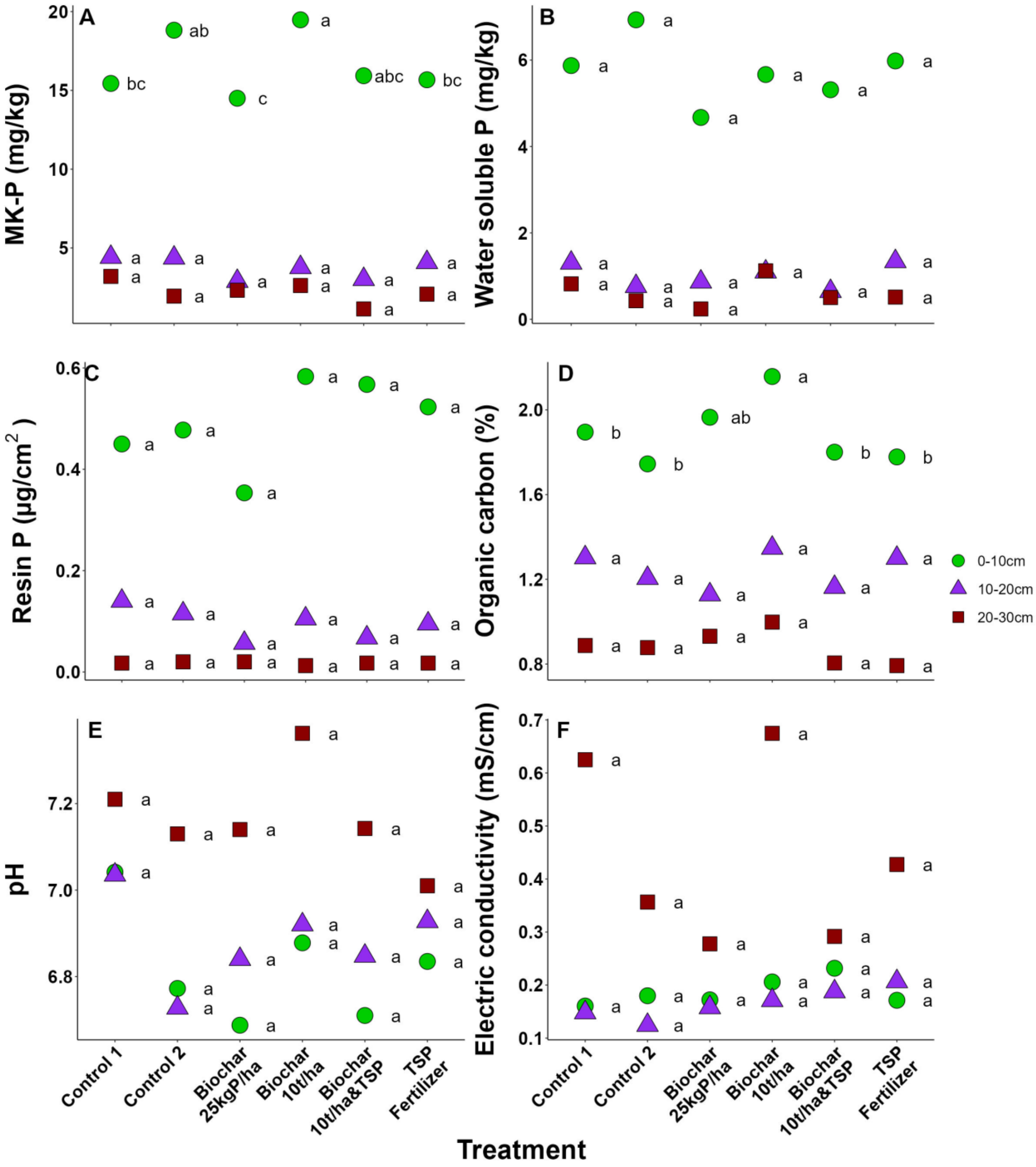

Fig. 4.8. Residual after-harvest soil characteristics in the 2022 field study: (A) modified Kelowna (MK) extractable PO_4, (B) water soluble phosphorus, (C) resin exchangeable phosphorus, (D) organic carbon, (E) pH and (F) electrical conductivity. Residual nutrients and characteristics are shown at depths of 0-10cm, 10-20cm and 20-30cm increments. For a given characteristic, means with the same letter at the same depth are not significantly different at alpha=0.05 using the Tukey HSD multi-treatment comparison method. Significant differences were measured within and not between depths.

The three char treatments resulted in the highest soil OC content (Fig. 4.8D) while TSP fertilizer had the lowest. There were no significant differences among treatments in OC in the 10-30cm layers. Both pH (Fig. 4.8E) and EC (Fig. 4.8F) were highest in the 20-30cm layer, explained by calcium carbonate and calcium sulfate salts that have accumulated in the C horizon from weathering and leaching during pedogenesis, with neither showing statistically significant differences among treatments at any depth. Overall, the 10t/ha treatment had the highest levels of pH throughout the profile, followed by the other two char treatments and control 2. The TSP fertilizer had the least variation across the profile and was slightly more acidic than the other treatments. Soil salinity (EC) was low (less than 0.25mS/cm) in the surface soil and therefore considered non-saline with slight elevation in the 20-30cm depth. There were no significant differences for EC between any treatments throughout the profile.

4.5.4 Effect of char application on infiltration rates

Initial and final cumulative infiltration (CI) rates, sorptivity, hydraulic conductivity and moisture content for the infiltration experiment is shown in Table 4.4. Only the final CI rate showed any statistically significant differences between the treatments. The10t/ha char treatment had the highest

Table 4.4. Initial and final infiltration rates, sorptivity, hydraulic conductivity and moisture content of the treatments in the large plot study. Final infiltration rates are given as predicted at 2 hours by the Philip two term model.

Treatment	Cumulative Infiltration rate (cm/h)		Sorptivity ($cm/h^{1/2}$)	Hydraulic conductivity (cm/h)	Moisture content (%)
	Initial	Final			
Control 1	69.4 a †	3.0 b	13.9 a	-4.04 a	48.5 a
Control 2	43.6 a	2.9 b	12.1 a	-2.14 a	43.7 a
Biochar 25kg P/ha	87.3 a	4.4 ab	15.5 a	-4.95 a	43.3 a
Biochar 10t/ha	47.2 a	5.7 a	13.5 a	-2.97 a	43.5 a
Biochar 10t/ha & TSP‡	58.5 a	4.3 ab	16.7 a	-6.40 a	44.7 a
TSP fertilizer	80.3 a	4.2 ab	14.5 a	-5.42 a	46.3 a
ANOVA (Type III) p-value ‡	*0.422*	*0.0013***	*0.709*	*0.419*	*0.866*

† Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

‡ ** shows significance at $\alpha = 0.01$.

final CI rate, followed by the other char treatments and TSP fertilizer treatment. The two controls were significantly lower. Although the initial CI rate was not shown to be significantly different, both the 25kg P/ha char and TSP fertilizer treatments had much higher rates while the two controls and the 10t/ha char treatments had much lower CI rates. The differences between the treatments in terms of initial and final infiltration rates can be seen in Fig. 4.9, where it was plotted with the observed and predicted CI rates.

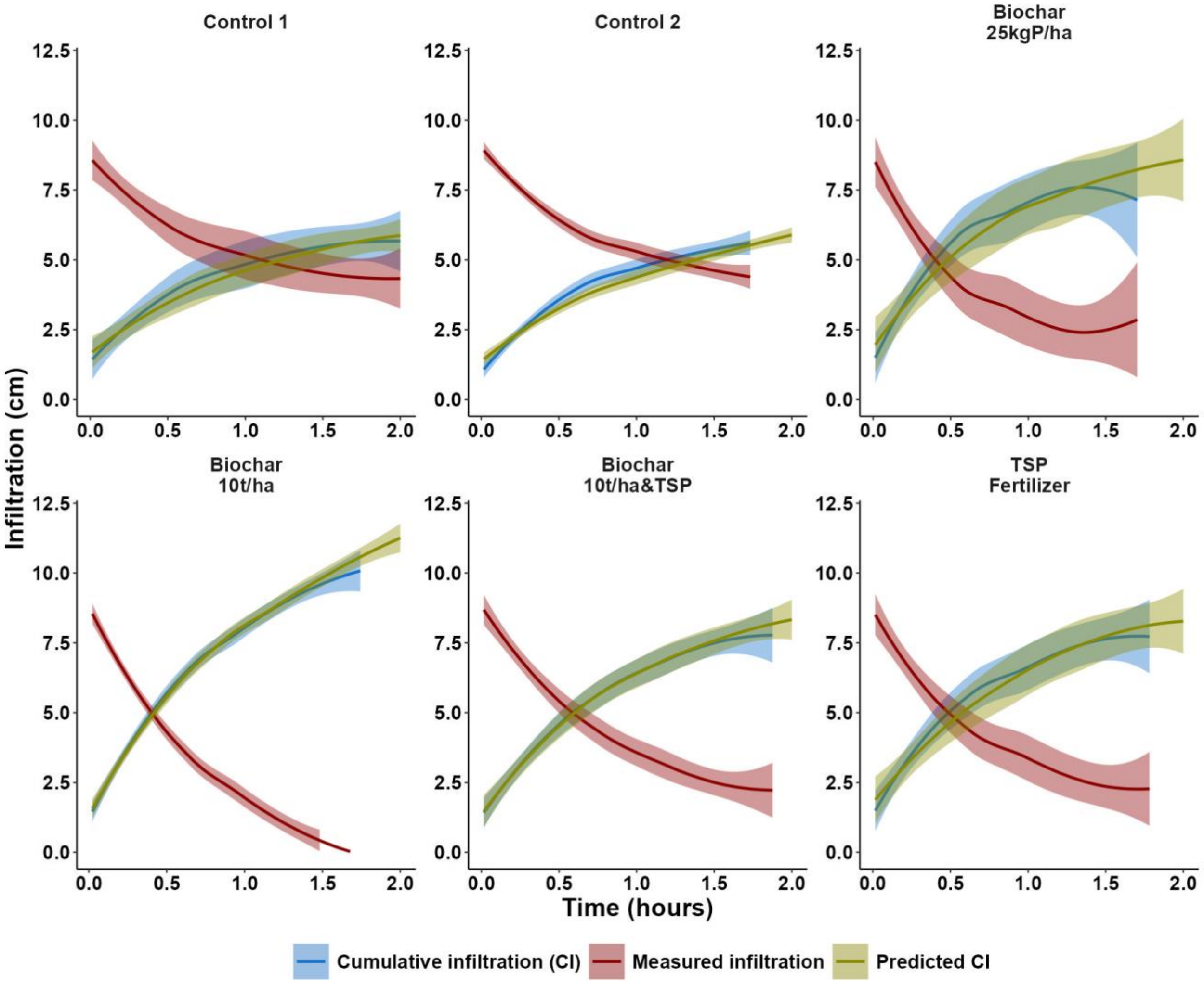

Fig. 4.9. Infiltration rates in 2022 canola field study plotted with observed and predicted cumulative infiltration (CI). Shaded areas indicate standard error. Infiltration (I) and observed CI lines are shown up to the closest recorded time to 2 hours whereas the predicted CI was cut off at 2 hours.

The slope of the curve in Fig. 4.9 shows the sorptivity (S) and field saturated hydraulic conductivity (K_{fs}) parameters. Steeper slopes with curves that take longer to plateau indicates higher sorptivity. Flatter slopes that plateau more quickly indicate that K_{fs} is reached more quickly, which will result in runoff occurring more quickly than where sorptivity is higher. Slopes of unamended control treatments are visibly flatter later on in the infiltration period compared to treatments amended with biochar (Fig. 4.9). Although there are no statistically significant differences between the treatments in terms of sorptivity, the char and TSP fertilizer treatments all had much higher mean sorptivity than the two controls, with the 25kg P/ha char and 10t/ha char & TSP treatments showing the highest mean levels of sorptivity. Note that K_{fs} was not fully achieved in this experiment as is evident in the negative values. Lower K_{fs} values (25kg P/ha, 10t/ha & TSP and TSP fertilizer treatments) are linked to higher levels of sorptivity. The moisture content, measured as the difference between the wet and the dry soil (inside and outside of the rings) was very similar between all treatments and the char did not appear to have influenced lateral water movement below the surface. Overall, amendment with willow char appears to have a positive effect on enhancing water entry into the soil that may contribute to reduce loss of water and its constituents in run-off in the field.

4.5.5 Effect of char application on snowmelt runoff

The nutrient load as measured in the simulated snowmelt water collected in the run-off study is reported on a kg/ha basis to a depth of approximately 5cm (average depth of the slabs taken from the field). In addition, Plant Root Simulator™ (PRS) probes were used to determine the exchangeable PO_4-P and NO_3-N variations within the soil during the runoff simulation, reported in µg nutrient sorbed per cm^2 of the probe exchange membrane surface area during a 24 hour period. The four samples where very little water was available for measurement were excluded from the analysis as outliers. Soluble reactive inorganic phosphate results are covered in this section. Nitrogen results are reported in Appendix A.

The phosphate load in the snowmelt runoff (Fig. 4.10A) showed no statistically significant differences between the treatments, however, the standard error is extremely large due to variations in factors such as soil structure, residue amount and position, old fertilizer bands, root channels that exist in the intact slabs that create variability in nutrient content and water flow. This could have been removed by taking samples of soil that are mixed and homogenized before applying the snow, but this would not represent the field conditions that exist in terms of soil structure, residual nutrient distribution and surface residue positioning that affect transport under actual field conditions. All three chars resulted in lower mean soluble reactive P export in the snowmelt water compared to the TSP fertilizer; and the 25kg P/ha and 10t/ha char treatments were similar to the control 2 treatment which had basal N, K and S fertilizer, the same as the char and TSP treatments. The 10t/ha char treatment had the lowest mean P export in simulated snowmelt run-off which suggests an ability of willow biochar to sorb soluble P and protect from run-off.

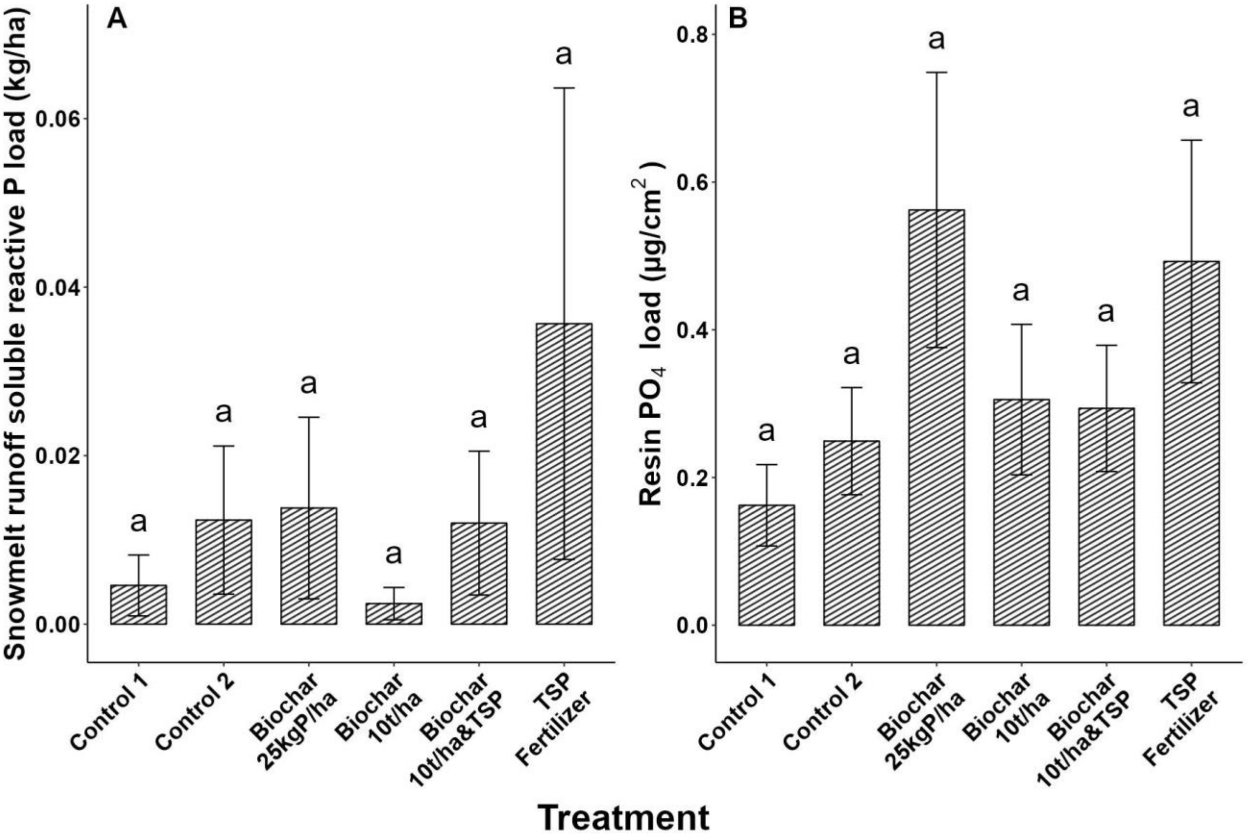

Fig. 4.10. 2022 field study (A) soluble reactive P load as kg P removed in simulated snowmelt per ha and (B) PRS resin exchangeable P in soil slabs taken after harvest. Means with different letters indicate significant differences between means (α=0.05) as per a Tukey HSD multi-treatment comparison. Error bars show standard error.

The resin P data (Fig. 4.10B) similarly had very large variability and significant differences at $p \leq 0.05$ were not evident. However, the two treatments adding char at the 10t/ha rate showed substantially lower resin exchangeable PO_4 levels compared to the lower 25kg P/ha char rate and the TSP fertilizer treatments. The 25kg P/ha char treatment had the highest resin PO_4 levels even though it did not have the highest added P level. Both controls had lower levels of resin exchangeable PO_4 than any of the other treatments, reflecting a supply of phosphate from the amendments in all treatments.

4.6 Discussion

As noted in Chapter 3, treatments with higher P levels remaining in the soil after a season of crop growth indicates a potential lasting effect of the amendment on soil P fertility while plant P uptake that is higher in the season of application is indicative of short-term benefits to soil P fertility (Grant & Flaten, 2019). The P levels and load removed in snowmelt water are indicative of the solubility and mobility of the nutrient under conditions of surface moving water such as during spring snowmelt. The discussion focusses on these aspects of the biochar treatments applied in the field in the 2022 field study.

4.6.1 Effect of char application on canola crop yield, nutrient uptake and recovery

It was postulated that the treatments would result in yields following the pattern TSP fertilizer>biochar>control as seen in a previous study under controlled conditions (Stefankiw, 2012). However, no significant differences were observed in yield among treatments. This is explained by the effects of the ongoing drought in 2022 and the grasshopper infestation that reduced the crop demand for P to such an extent that the increased soil available P content associated with amendment in the spring was not needed or taken up by the crop (Grant & Flaten, 2019). It should be noted that not only was there drought conditions, but the rainfall in 2022 was also very sporadic, with only a few small rainfall events between mid-June 2022 and the end of July 2022 when crop demand for water is high, and with only one large rain event (25mm) in early July 2022. This, tied to rapidly alternating cold and hot days ranging from 15°C to 40°C between June and August 2022, may have negatively affected the canola’s growth pattern. The higher levels of willow char resulting in higher yields which was observed in the canola controlled-environment study described in Chapter 3, was not observed in the 2022 field study. It could thus be said that biochar most likely does not have the ability to counter environmental/climatic (drought, heat) stress factors encountered in the field.

The possibility also exists that insufficient basal nutrients were supplied in the form of urea and K_2SO_4 thereby limiting the growth potential of the canola (Jones & Olson-Rutz, 2016; Dobrohotov *et al*., 2023). However, the rates applied were for normal, typical growing conditions in the region which recommend more total N, K and S for the crop than under dry conditions. As the control 2 treatment with basal N, K and S nutrients had approximately 20% higher mean yield than control 1 without basal fertilizer, it can be said that the added basal nutrients may have had some effect, albeit limited. There is a greater possibility that the phosphorus added either in the form of char or TSP had a negative effect under drought conditions. An explanation for this effect was given by Shukla *et al.* (2017), whereby in a study with thale cress (*Arabidopsis thaliana*) under growth chamber conditions, the addition of excess P resulted in a shallower root system, and fewer lateral roots, resulting in less opportunity for the plant to access available nutrients. Field studies with more replication under environmental conditions that are more optimal for crop growth and nutrient uptake and over a longer period are needed to confirm the suitability of biochar amendment under a variety of conditions. These findings contradict the hypothesis, where under the conditions of this study with plants that were moisture stressed and affected by pests, biochar amendment had limited benefit on yield and P uptake.

The 10t/ha biochar treatments added less char and thus less associated P contained within the char (17kg P/ha) than the biochar treatment set up to add 25kg P/ha (~14.7t/ha char), the same rate that the TSP fertilizer alone was added. The 10t/ha rate of willow biochar plus TSP treatment added a total of 42kg P/ha. The level of added P is not reflected in the P uptake or recovery. Similar to the findings in this study, Stefankiw (2012) found that the 10t/ha willow biochar rate had the highest crop P concentration in both a brown and a black soil, and higher than that observed for the biochar and TSP co-applied in that study. The shallow root system explanation by Shukla *et al.* (2017) could explain the lack of treatment effect on P uptake to some extent. However, other factors not analyzed as part of this study are likely playing a larger role in the variability and lack of recovery. Nitrogen uptake and recovery were also analyzed for the crops (Appendix A). While not discussed here in detail, the nitrogen uptake was significantly lower in control 1 (no fertilizer N addition), while the rest of the treatments showed no significant difference, and there were no significant differences in terms of N recovery either.

4.6.2 Effect of char application on residual soil nutrients and properties

The distribution of labile P among the three depths 0-10cm, 10-20cm and 20-30cm gives an insight into the vertical stratification of nutrients and physical characteristics, and how this may influence root formation and nutrient usage. Labile, plant available phosphorus was measured as Modified Kelowna (MK) P, water soluble extractable P and resin membrane exchangeable P. The 10t/ha rate retained the most soil labile P, in contrast to previous findings using the willow biochar (Stefankiw, 2102) where the TSP fertilizer had a much bigger effect on P retention. The pre-planting soil samples involved measurement of MK-P in the 0-15cm layer as is done in a normal soil test by growers, with an aggregated average of 11.2 mg/kg, considered deficient to marginally deficient for crop growth under normal conditions (Grant and Flaten, 2019). This is compared to the post-harvest MK-P levels in the 0-10cm layer ranging from 14.5 mg/kg (biochar 25kg P/ha) to 17.8 mg/kg (biochar 10t/ha). Root depth was not measured as part of this study, however, as P is not very mobile, the focus of this discussion is on P retention in the upper soil layer. Uptake of P ranged from 6.3kg/ha (control 1) to 8.0kg/ha (10t/ha char & TSP). Therefore, uptake of P by the canola, which was reduced because of the drought conditions, had little influence on the soil test P levels. The labile available pools of P in the soil are buffered by other more stable pools and it is likely that other P fractions such as organic P or mineral P from the char/TSP or native P in the soil were transformed between non-labile and labile and soluble forms (Shabaan *et al.*, 2018; Spohn, 2020; Ghodszad *et al.,* 2021). This appears to have taken place even in the control treatments, showing that the chars had no discernible effect (Mukherjee & Lal, 2013).

The lower levels of P in the 10-30cm depth compared to the surface is typical of P stratification as seen in other systems such as those described by *Zhu et al*. (2021) and Nunes *et al*. (2020). P is immobile in soil to a large extent (Prasad & Chakraborty, 2019). As such, P in agricultural systems tends to accumulate in the upper layers, especially in no-till soils such as at the study site (Nunes *et al.,* 2020). Therefore, char and fertilizer P added to the surface in the treatments would remain close to the soil surface where it was dry and root growth and activity was low. This would restrict the ability of P to move to the roots and be utilized by the crop. The residual P was relatively static in the lower layers, with very little variability. In the water soluble P analysis, char treatments had overall lower P levels than the other treatments in the 10-30cm layers, corresponding to comparatively lower levels in the 0-10cm layer. This suggests that perhaps the P associated with char is more mobile than fertilizer P, explaining its greater apparent utilization by the crop. The addition of TSP may have also resulted in some immobilization by the microbial populations reflecting that there may be different processes affecting P at different depths as indicated by Zhu *et al*. (2021) who found that extreme and limiting temperature and precipitation had the greatest effects on the distribution and gradient of P along the soil profile. Less well-developed root systems due to excessive P will also influence the degree to which root uptake and removal occurs in the soil profile (Shukla *et al.,*2017), influencing the distribution with depth.

Although the 10t/ha char had significantly higher mean OC levels than the controls and TSP fertilizer, it was not significantly different from the other chars at $p \leq 0.05$. Control 1 was only marginally lower than the 25kg P/ha and 10t/ha char& TSP. All chars increased the OC levels from the pre-planting levels (1.49% OC) in the surface layer, similar to the findings of Hangs *et al*. (2016). These authors found that the willow char acted as a net carbon sink by increasing methane consumption under laboratory conditions, and while not specifically stated, this could lead to increases in soil organic matter. Ahmed *et al*. (2014) found only small and non-significant increases in surface soil organic carbon concentrations with the addition of biochar at a rate of 2t/ha, as the amount of carbon added in the char is small relative to the total amount of humus carbon in the soil. Stefankiw (2012) found that under controlled environment conditions, higher rates of application of the willow biochar resulted in significant increases in soil OC. The 25kg P/ha char treatment added the most char carbon (10.4 tonnes of total carbon per hectare compared to 7.1 tonnes C per hectare in the 10t/ha char treatments). It would thus be expected that the 25kg P/ha char treatment would have higher mean OC concentrations compared to the 10t/ha treatments, which was not the case, suggesting that the addition of chars may enhance organic carbon decomposition, linked to the higher specific surface area and cation exchange capacity. This contrasts with the findings of Tenic *et al.* (2020) who found that most biochars resulted in a delay or reduction of soil organic matter decomposition, however, most of these findings were reported on acidic soils. As the OC data did not display a direct significant link between the carbon added by the chars and the remaining OC in the soil, it is possible that some mineralization of the char to carbon dioxide took place. Sarfaraz *et al*. (2020) found that CO_2 mineralization is increased through the alteration of carbon pools due to biochar-induced changes in microbial activity. Linked to this, as discussed in the canola and wheat studies in Chapter 3, the char

C:SOC ratio for the willow char in the large plot soil was 47, well above the recommended ratio of 2 to prevent CO_2 emissions (El Naggar *et al*., 2019). Although repeated applications of biochar in large volumes may be required to produce significant measurable increases in soil organic carbon (El-Naggar *et al.,* 2019), it is recommended that large scale and long-term studies be undertaken to determine the effect that biochar of differing carbon levels have on carbon emissions versus sequestration in low carbon soils such as the prairies.

The TSP fertilizer adds phosphorus as monocalcium phosphate (15% Ca) which has limited effect on soil pH (Havlin *et al*., 2014) while the willow biochar had a 22% Ca. Chars have been shown to increase pH in acidic soils by addition of base cations like calcium and may also influence pH by means of functional groups on the char that could contribute some acidity through release of protons. However, chars have been reported to have little to no effect on pH in alkaline soils, (Tenic *et al.,* 2020). This was evident in the upper layers, where the char treatments had similar pH compared to control 2, with the TSP fertilizer at a slightly higher pH than seen in the pre-planting soil samples in the 0-15cm depth (pH 6.8). Only control 1 had overall increased pH levels, indicating that the basal addition of nutrients and the associated microbial activity may have buffered the soil pH. In the lower layers, all but the biochar 10t/ha (increase) and TSP fertilizer (decrease) were in line with the pre-study pH levels in the 15-30cm layer (pH 7.1).

The electrical conductivity of surface soil in all treatments was low and therefore considered non-saline (Havlin *et al.,* 2014). The pre-planting EC level was 0.15-0.22mS/cm in the top 0-30cm of soil. The post-harvest EC levels in the 0-20cm layers ranged from 0.15 to 0.23mS/cm, indicating that the treatments did not affect the salt content in the upper layers. However, an increase was noted in the 20-30cm layer (0.44-0.88mS/cm) which may indicate that salts moved out of the surface horizon during the growing season. Overall, it appears that that the char amendments did not affect salinity throughout the profile.

4.6.3 Effect of char application on infiltration rates

Initial infiltration rates were measured at the time it took 1cm of water to infiltrate. Initial infiltration rates and sorptivity are linked to a soil's ability to allow rainfall or snowmelt water to infiltrate without running off. Chars are typically hydrophobic and as such cause the soil to become more hydrophobic (Mao *et al.,* 2019). These authors noted that in highly hydrophilic soils, biochars can increase not just the hydrophobicity, but also the water holding capacity as also reported in Chapter 3 of this thesis. However, this is dependent on the soil's OC content and hydrophobicity as well as the char's characteristics. Although the soil and char were not analyzed for hydrophobicity, the initial infiltration would be affected by this property of biochar – higher hydrophobicity would lead to decreased initial infiltration, higher runoff volumes and potentially more erosion (Mao *et al.,* 2019). While some hydrophobicity was noted on the willow char treated plots during the infiltration experiment (visual observation), it did not appear to have been as great as that observed for some of the other chars discussed in Chapter 3. This, however, did not appear to have directly affected the initial infiltration rate. There also does not appear to be a consistent link between the initial infiltration rates and the measured soil physical or chemical characteristics. The three treatments with the highest levels of added P had the highest initial infiltration rates, but the 10t/ha treatment which still had higher P than either control had only about two thirds of the rate of control 1. In terms of sorptivity, defined loosely as the soil's capacity for continued infiltration into the large pore spaces (Buckingham, 1907), the 25kg P/ha char and 10t/ha char & TSP showed the highest levels of sorptivity, followed by TSP fertilizer. The calcium added in the TSP and char may promote infiltration as calcium is known to be a flocculating agent that promotes good structure (Havlin *et al.,* 2014). Only control 2 had lower sorptivity that the 10t/ha treatment. As with initial infiltration, it is inconclusive whether biochar had a strong effect on sorptivity. Some potential effect was noted which may be elucidated with further study.

It is with the final infiltration rate where the effects of the char were most evident. It should be noted that the final infiltration, capped at two hours, is not in fact the measured final infiltration rate or the point where field saturated hydraulic conductivity (K_{fs}) was reached, it is merely a consistent endpoint partway through the infiltration process. The 10t/ha treatment performed very well with a final infiltration rate almost double that of control 2. The 25kg P/ha char & 10t/ha char & TSP treatments were on par with the TSP fertilizer, but all performed better than either control. Overall, amendment with chars may be anticipated to have a positive effect on infiltration characteristics of soils similar to the one used in this thesis research.

Higher levels of K_{fs} are linked to lower levels of sorptivity. As K_{fs} was not fully achieved in this study, the pattern observed is very close to that of sorptivity. Although the soils were able to continue allowing water to infiltrate without becoming fully saturated within the time of the experiment (ranging from 1.25 – 3 hours), this does not indicate that there will not be runoff. The point at which runoff will commence is related to the strength of the rainfall event, the existing saturation/moisture content of the soil at the time of the event, the soil's physical characteristics and the level of vegetation coverage. While this study shows that biochar can possibly improve infiltration in a brown chernozem, further study in this regard is required.

The percentage moisture was measured as the difference between the soil moisture content within and outside of the infiltration rings. There was not much variability between the treatments. This is also true of the moisture content in the dry samples, the means of which ranged from 3.1% to 3.3%. It should be noted that it was the second year in a drought cycle and the infiltration measurements were done towards the end of September 2022 under very dry soil conditions. Nonetheless, the biochar had no discernable effect on moisture retention in the field based on bulk density samples. It may be worthwhile following up the bulk density related moisture retention with a water holding capacity experiment on the field soils in future studies.

4.6.4 Effect of char application on snowmelt runoff

The variability of the P load in snowmelt runoff measured on intact soils is high, as has been observed in other studies (Wiens *et al.*, 2019). The 10t/ha char treatment did appear to have a trend towards reducing soluble reactive PO_4 exported from surface soil in snowmelt runoff water, in contrast to the findings of Saarnio *et al*. (2018), where the addition of biochar resulted in increased dissolved PO_4-P losses. These authors concluded that not all chars are suitable for reducing P export in snowmelt runoff and that chars need to be carefully chosen with verified effects prior to field application. The 10t/ha char treatment had a P load in simulated snowmelt run-off that was almost half that of the control 1 which is notable as the 10t/ha treatment also had the highest mean level of residual labile P in the soil. This suggests that biochar can help retain some P in the soil in a potentially plant available but also non-mobile form. The 25kg P/ha char and 10t/ha char & TSP treatments have the same dissolved reactive P load in snowmelt runoff as control 2. Control 2 had no added P but had basal N, K and S fertilizer and showed higher levels of residual PO_4 post-harvest. There may be an underlying process controlling the conversion of organic or mineral P to plant available P in this treatment, possibly linked to the availability of basal nutrients enhancing microbial activity (Zwetsloot *et al.,* 2015). The TSP fertilizer had levels of soluble reactive P more than double that of any of the other treatment, indicating that this fertilizer is highly soluble and can easily be exported in runoff. This seems to have been tempered by the added char in the 10t/ha & TSP treatment. Wang *et al*. (2021) explains the mechanism by which a char reduces P losses in snowmelt runoff as an effect of the strong sorption capacity of the char. The 10t/ha char treatment showed the highest capacity for retaining available P over the winter period and during thawing while being moderately effective at reducing P losses in snowmelt.

The PRS probe exchangeable PO_4 measured during the snowmelt showed the 25kg P/ha char treatment to have the highest levels of exchangeable, available P, approximately 14% higher than for TSP fertilizer. The 10t/ha char treatments had equal levels of available P, even though the 10t/ha & TSP treatment had 25kg P/ha more than the treatment without added TSP. These two comparisons suggest that TSP may be reducing phosphate exchange with the membrane surface, possibly an effect of the added calcium in the TSP fertilizer. All treatments had higher P supply during snowmelt than the two controls, with the two 10t/ha treatments about 20% higher than control 2. As the soil slabs for the snowmelt experiment were collected at the same time as the soil cores for the chemical analysis, the levels of resin membrane sorbed phosphate P reflect what might happen to bioavailable P during a snowmelt event. It should be noted here that the slabs were brought to field capacity prior to being frozen ahead of the simulated snowmelt event, which could result in additional differences in P availability between these samples. Available P in the post-harvest soil cores presented a different pattern in the 0-10cm profile, with the 10t/ha and 10t/ha & TSP treatments having the highest availability (respectively 66% and 93% higher than measured in the snowmelt experiment), followed by the TSP fertilizer (3.5% lower) and the 25/kg P/ha treatment (26% lower). Control 1 and control 2 were 177% and 91% higher respectively. The differences in exchangeable, available P show the complex nature of phosphorus dynamics during winter freeze-thaw cycle and the actual spring snowmelt events, as has been found in other studies (Su *et al.,* 2011; Özgül *et al.,* 2012).

4.7 Conclusions

Amendment with willow biochar at different rates showed potentially positive effects on nutrient retention and preventing phosphorus losses in runoff as well as improving infiltration. However, canola yield and P uptake were not significantly affected by treatment in the field at this site, in contrast to the significant positive responses observed in the growth chamber study with a similar soil. It should be noted that this study was conducted in the field in a year that the crop was under severe plant stress from drought and insects, which would reduce the potential for response to fertilization treatment. Although many studies have been undertaken using different rates of biochar, or co-applying char with fertilizers, very few of the previous studies compared the fertilizer with chars applied alone and chars co-applied with fertilizer. This study showed that co-applying char with TSP appears to be an effective way to increase P recovery and retention, increase residual P in the soil for future crops and also reduce P losses in snowmelt runoff compared to adding TSP alone.

There was a trend for char amendment to increase soil organic carbon concentration and reduce pH of this low organic matter, neutral pH soil. As with the findings of Chapter 3, increased OC at the end of one season does not necessarily indicate long term carbon sequestration. The amendment with char had no discernible effect or trend on soil salinity in this non-saline surface soil.

Biochar was also effective in improving initial infiltration rates, sorptivity and field saturated hydraulic conductivity in a brown chernozem soil. However, the results of this study also indicate a possible link between added levels of P and infiltration perhaps related to calcium. Although a leachate experiment was not a part of the field experiment in this section of the thesis, in retrospect it would have been interesting to measure the P levels in the dry and wet bulk density samples to determine if and how much P was removed during the infiltration experiment.

Overall, a trend was observed towards the chars being able to reduce P export in snowmelt runoff, however, the mechanism remains unclear based on the outcome of this study. Variability may be reduced by using homogenized soil in simulated snowmelt run-off assessments, but this would also mask the effect of many factors affecting run-off as it actually exists in the field.

A few knowledge gaps have been identified in this study and the following is recommended to address these gaps:

- Biochar field studies in the prairies should investigate and compare more and different char types and fertilizer combinations in future.
- Most biochar studies do not report the effect of char on pH or OC at depth. It would be useful to continue measuring biochar effects on pH and OC at different depths in future studies to determine its long-term effects on acidification or alkalization as well as on carbon sequestration in prairie soils at depth.
- The positive effects on infiltration related variables as noted here may be further elucidated with expanded study in a range of soil types in the field. It would also be useful to examine whether there is a link between different types of added phosphorus and calcium on infiltration rates.
- It may be worth considering incorporating a leachate component into future infiltration studies linked to nutrient management projects.
- Further field assessments with more replicates and using different levels of char in combination with P fertilizer are necessary to determine the effectiveness of char at reducing P in snowmelt export. Larger and/or more slabs may be more effective in addressing variability issues encountered in the snowmelt component of the study.

5. OVERALL SYNTHESIS AND CONCLUSIONS

5.1 Summary of findings

This study aimed to determine the separate and combined effects of biochar, ash and P fertilizer amendments on soils and crops in the Canadian prairies as related to crop yield, phosphorus uptake and recovery, soil phosphorus retention, water dynamics and phosphorus loss in leachate and runoff. Based on previous studies in the prairie region as well as elsewhere, it was anticipated that biochar with lower P content would have a limited effect on crop yield while biochar higher in P and when co-applied with commercial P fertilizer would improve crop production and P utilization on soils of low fertility. Under optimal conditions of the growth chamber, biochars were shown to contribute some available P for plant uptake and in both the growth chamber and the field, the chars increased residual P in soil to varying extents depending on feedstock and soil. The effects of biochar amendments on crop yield were variable and differed among char types leading to the conclusion that the effects are influenced by biochar feedstock and production conditions as it influences char properties and interaction with soil as has been shown in many other studies with biochar. The largest benefit observed in this study relates to increased nutrient retention, both after the growing season as well as during leaching and snowmelt runoff events. To a smaller extent the chars proved to be effective at improving water holding capacity and water infiltration. Measurable increases in organic carbon concentration as reported in other studies was not seen with all char treatments, and only under controlled conditions, but only a single application was made in this study. Repeated applications of biochar at higher rates (≥10t/ha) are likely required to produce measurable increases in organic C, however, this should be carefully investigated as the addition of high C biochars in low C soils may rather result in C emissions than sequestration.

The results of the application of various biochars and ashes (Chapter 3) showed that the chars produced from animal by-products, namely the meat and bonemeal ash and the manure chars had the best overall performance in terms of increasing crop yield and supplying P to the crop and increasing residual available P in the soil. Willow char (woody feedstock) was sometimes a good performer and canola hull char (agricultural by-product) performance was variable and impacted by soil type, while canola meal char (agricultural co-product) was rather consistently a poor performer and may result in harmful effects. Overall, added P recovery in the crops for the char amendments was about half that observed for commercial P fertilizer, with higher rates of char showing increased performance.

The field research (Chapter 4) revealed limited positive effects of willow char on canola yield and short-term soil P availability, but with a trend towards positive effects on improving infiltration and reducing nutrient loss in snowmelt runoff. Co-application of willow char with TSP has the potential to maintain or increase P recovery by the crop above that of char or TSP when applied alone, contribute to greater replenishment of P fertility in the soil and reduce P losses in snowmelt runoff compared to adding TSP alone, which is attributed to ability of the char to bind P. A link was shown between added levels of P and infiltration, possibly related to calcium in the char and TSP which has a flocculating effect, promoting improved soil structure and thereby increasing infiltration.

5.2 Conclusions

Research with biochar in prairie soils has increased over the past decade, but it is still very limited. Specifically, very few past studies anywhere have included a comparison between the chars and fertilizer both applied alone, and chars co-applied with fertilizer. This study showed some of the differences between the co-application and individual application of biochar and a commercial fertilizer and some important interactions. Overall, biochar showed some positive effects on various agronomic factors, including yield increases, phosphorus uptake and recovery, increasing retention of phosphorus in the soil, reducing phosphorus losses in snowmelt and in leachate; and improving infiltration and water holding capacity. There exists a trade-off between optimizing crop production and reducing environmental impacts, which needs to be balanced, and in this regard, biochar may at least in part provide a solution when combined with commercial fertilizers. The field work conducted in this thesis was under moisture, heat and pest stress conditions where plant and microbial growth were restricted. Evaluation under better conditions in the field would be desirable.

The type and associated properties of biochar, as has been noted in other studies, is the largest contributor to its effect in agricultural settings. Canola meal biochar resulted in low yield, crop P uptake and retention of P in soil in this study, while having moderately high P levels in leachate under controlled conditions, indicating potentially neutral to deleterious effects. As canola meal has value as a feedstock, it is not recommended that it be used to produce chars for agricultural soil enhancement. This study has also shown that there are agronomic benefits from charring both fresh and composted manure. Charring manure would eliminate environmental concerns related to the use of manure such as pathogens, weed seeds and hormones, as well as reduce the economic burden related to managing and transporting raw or composted manure. Willow char showed potential benefits at higher levels of application than seen in previous studies, although repeated applications may be required. As willow is a common and easily obtainable feedstock for bioenergy production, using the char as an agricultural additive would consume the by-product as well as provide agronomic benefits. Both canola hull char and meat and bonemeal ash can be used in agricultural settings with beneficial effects, although to temper any neutral to potentially negative effects, it may be beneficial to co-apply these chars with other chars. Based on the overall improvements noted in this study, and as shown in other studies, char applied at 10t/ha appears to work well as an application rate for biochar in prairie soils. However, chars may prove to be more efficient when applied at rates supplying specific nutrient concentrations.

Overall, the results of this study indicate that chars and ash products produced from agricultural feedstocks can potentially benefit canola and wheat production in prairie soils, by enhancing P nutrition and recovery, and that a balance may be obtained between biochar supplying P or allowing P to be more available during the growing season while at the end of the season reducing P loss in the spring snowmelt runoff or during leaching events.

5.3 Recommendations

- Chars should be tested at different rates of nutrient application to determine the relative efficacy of nutrients contained in chars versus commercial fertilizer sources.
- The adsorption-desorption processes and P species formation as linked to biochar should be further investigated.
- Patterns regarding soil organic carbon (SOC) and pH noted in this study should be investigated in future to determine long-term effects on carbon capture and acidity at depth.

- Further studies in low carbon prairie soils with chars of differing carbon content and potentially with repeated applications of char is required to determine the effect that biochar of differing carbon levels have on carbon emissions vs sequestration in these settings.
- Potential positive effects of biochar on infiltration that were observed in this thesis work should be expanded on by using a range of soil types in the field.
- The link between different types of added phosphorus and calcium on infiltration rates noted in this study should be further investigated.
- A leachate component should be introduced to future infiltration studies, especially where the same experiment is subjected to snowmelt studies.
- The effect of different biochars on emergence rates should be incorporated into future studies.
- Biochars and ash with larger particles are more likely to provide agronomic and environmental enhancements. Studies with larger grain sizes could be beneficial.
- Further research work, especially with aged char is required to determine the levels of char required alone or in combination with P fertilizer to reduce P in leachate. Soil residual properties and nutrient levels should be compared both before and after ageing the char.
- The mechanism by which the chars reduced P export in snowmelt runoff should be further investigated. Larger slabs and/or more replicates, e.g. two to four slabs per experimental plot, may prove more effective in reducing variability noted in this study.
- Changes in field moisture levels should be measured throughout the season using bulk density samples collected and by undertaking a water holding capacity experiment.
- Manure char from different feedstocks and at different rates should be further investigated.
- Mixing of char types and/or loading of char prior to application should be studied in the prairies.
- Longer term field trials, extending over several years, should be undertaken with different chars applied as well as co-applied with fertilizer at different rates to determine the longer-term effects from repeated applications and ageing of the chars in the field.

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APPENDIX A: NITROGEN DATA

Canola study

There was only a slight significant difference between the treatments in terms of N uptake (Table A1), and no difference compared to the control that received basal N fertilizer. However, all treatments performed better than the control with no basal fertilizer. There were significant differences between treatments in terms of N recovery and nitrogen use efficiency. In the 50kg P/ha treatments, the chars performed the same or slightly poorer than control 2 in the Haverhill soil. In the Oxbow soil, only manure char performed better. The same held true for the manure char 10t/ha and 10t/ha & TSP treatments, however, the other willow char and canola hull char performed better compared to the 50kg P/ha rates. As with P recovery, the canola meal char performed poorly, showing the lowest N recovery of all the treatments in either soil at all application rates.

Residual soil nitrogen did not reflect the same pattern as residual soil phosphorus. The residual N levels were higher in the Oxbow soil than in the Haverhill soil, even for the controls. In contrast, the pre-study soil NO_3-N levels were much higher in the Haverhill soil at 17.5mg/kg *vs*. 7mg/kg in the Oxbow soil. It thus appears that the N was more plant available in the Haverhill soil, or potentially that this soil resulted in increased N emissions compared to the Oxbow soil. However, this is not linked to the treatment with chars based on the available data. The 50kg P/ha treatments all had the lowest residual N concentrations across both soils. While this may indicate that lower quantities of biochar results in lower residual N, it should be noted that willow char, which was added at a higher weight in the 50kg P/ha treatment than in either of the 10t/ha treatments did not reflect this pattern. It is unclear how effective the chars were at providing N to the crop and in retaining N for future growing seasons based on this study, which is in line with the variable findings of Tenic *et al*. (2020).

Table A1. Canola study – N uptake and recovery in canola and the soil residual N as NO_3 and NH_4.

Treatment	**Haverhill soil**				**Oxbow soil**			
	N uptake	***N recovery***	***NO_3-N***	***NH_4-N***	***N uptake***	***N recovery***	***NO_3-N***	***NH_4-N***
Control 1	13.3 c[†]	-	4.8 c	11.1 a	7.7 c	-	5.1 cde	12.8 bc
Control 2	40.3 b	13.5 abcd	3.1 c	8.4 ab	64.8 ab	28.6 ab	4.9 de	4.0 d
Canola meal 50kg P/ha	56.6 ab	16.3 abcd	4.6 c	10.0 ab	55.6 b	18.0 cde	6.3 bcde	14.8 b
Canola hull 50kg P/ha	54.6 ab	11.7 bcd	6.5 c	9.1 ab	61.2 ab	15.2 de	3.1 e	11.4 bc
Manure (2021) 50kg P/ha	56.3 ab	20.4 ab	5.9 c	8.9 ab	84.0 a	36.1 a	4.7 de	2.8 d
Willow 50kg P/ha	58.8 ab	11.2 bcd	3.1 c	8.1 ab	71.1 ab	15.6 cde	10.7 abcd	11.9 bc
Canola meal 10t/ha	59.3 ab	7.6 d	15.0 b	8.9 ab	80.0 ab	12.0 e	14.9 a	10.0 c
Canola hull 10t/ha	57.1 ab	11.9 bcd	23.7 a	7.6 ab	71.8 ab	17.5 cde	11.7 ab	12.7 bc
Manure (2021) 10t/ha	56.1 ab	17.2 abc	2.6 c	10.7 a	65.3 ab	23.1 bcd	3.3 e	10.9 bc
Willow 10t/ha	50.6 ab	13.8 abcd	5.5 c	8.4 ab	55.4 b	17.7 cde	4.1 e	3.8 d
Canola meal 10t/ha & TSP	64.7 a	8.5 cd	3.5 c	6.6 b	78.6 ab	11.7 e	4.8 cde	21.3 a
Canola hull 10t/ha & TSP	61.0 ab	13.0 abcd	3.7 c	8.1 ab	62.4 ab	14.9 de	6.4 bcde	4.6 d
Manure (2021)10t/ha & TSP	55.5 ab	17.0 abcd	6.6 c	11.0 a	77.4 ab	28.0 ab	11.7 abc	12.6 bc
Willow 10t/ha & TSP	66.6 a	19.8 ab	3.2 c	9.2 ab	75.3 ab	25.0 bc	3.8 e	3.6 d
TSP fertilizer	58.0 ab	22.4 a	3.8 c	7.5 ab	70.9 ab	31.6 ab	3.7 e	14.9 b

ANOVA (Type III) p-value for treatment effects[‡]	***N uptake***	***N recovery***	***NO_3-N***	***NH_4-N***
	2e-16***	1.3e-08***	6.8e-43***	0.00087***

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

[‡] *** shows significance at $\alpha = 0.001$.

Wheat study

Small plot component

There were no significant differences between the treatments for N uptake and recovery, however, there was quite a bit of variability in N recovery. The standard error was larger than some of the means, which is likely the cause of the lack of significance in this variable. All chars except canola meal char had N uptake values within 6% of control 2 – canola meal had almost 17% less N uptake than the control. MBMA fine was the only other treatment that also had lower N uptake than the control. In terms of recovery, all treatments except canola meal char had increased levels of N recovery compared to the control, with MBMA coarse fraction showing the highest N recovery. An analysis of the residual soil NO_3 showed that there were significant differences between treatments to some extent, but there were more similarities than differences. The manure char had the highest levels of residual NO_3, the char appearing to have had a nitrogen fixing effect while willow char had the lowest levels of residual NO_3, possibly indicating an increased availability of N to the crop or increased nitrogen emissions.

***Table A2.** Wheat study small plot component nitrogen uptake and recovery in the crops and residual soil NO_3-N.* ¶

Treatment	N uptake (kg N/ha)	% N recovery	NO_3-N (µg/g of soil)
Control1	14.9 a†	-	17.9 bc
Control 2	19.1 a	1.2 a	30.5 abc
Canola meal char	15.8 a	0.6 a	22.0 abc
Manure char (2022)	20.2 a	3.2 a	39.7 a
Willow char	19.3 a	1.5 a	13.8 c
MBMA‡ Coarse	19.6 a	4.7 a	34.2 ab
MBMA Fine	18.4 a	3.5 a	30.3 abc
TSP fertilizer	20.6 a	5.7 a	22.3 bc
ANOVA (Type III) p-value§	*0.62*	*0.18*	*6.4e-07****

¶ The nitrogen uptake and recovery values were affected by the grasshoppers and are thus likely not representative of what would have been seen in the field otherwise

† Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

‡ MBMA = Meat and bonemeal ash

§ *** shows significance at $\alpha = 0.001$.

Controlled environment component

N uptake was the highest in willow char, while canola meal char and MBMA coarse fraction had the lowest N uptake. There were no significant differences between the other treatments or the controls. Soil residual NO_3 levels were approximately 30% of that seen after harvest in the field component. Much higher levels of N fertilizer were applied to the pots than in the field, and this was reflected in the high N uptake levels in this component of the study compared to the canola study. As N typically increases in char after ageing, it is likely that the added N along with the increased N from ageing combined to allow greater levels of N uptake, with a subsequent reduction in residual soil N. There were no significant differences between treatments in residual NO_3, however, manure char and MBMA coarse fraction showed about half the residual NO_3 levels of willow char, with canola meal char and MBMA fine fraction just slightly higher. All treatments except willow char had lower NO_3 levels than control 2.

Table A3. ***Wheat study controlled environment component nitrogen uptake in the crops (mg N per pot) and residual soil N (µg/g).***

Treatment	**Crop N uptake**	**Soil nutrients**	
		NO_3	***NH_4***
Control 1	150.4 ab†	5.4 a	2.51 a
Control 2	142.1 ab	9.1 a	2.85 a
Canola meal char	123.9 b	7 a	3.61 a
Manure char (2022)	139.7 ab	5.3 a	2.69 a
Willow char	183.1 a	12.4 a	3.39 a
MBMA coarse	123.6 b	6.2 a	2.84 a
MBMA fine	134.9 ab	7.4 a	3.08 a
TSP fertilizer	142.0 ab	6.4 a	2.48 a
ANOVA Type III p-value‡	*0.0065***	*0.075*	*0.184*

† Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

‡ ** shows significance at α = 0.01.

2022 Field study

Both N uptake and N recovery had very little variation, except in control 1 which was much lower as it received no basal N fertilizer. There were no significant differences between the treatment for N recovery. As with soil residual phosphorus, the residual NO_3 also followed the pattern of highest levels of NO_3 in the upper 0-10cm layer, and for the most part decreasing in concentration with depth. The 25kg P/ha treatment had slightly higher levels of NO_3 in the 10-20cm layer than in the 20-30cm layer, while control 1 had similar levels in both lower layers. In the 0-10cm layer TSP fertilizer had the highest levels of NO_3 and control 1 the lowest, while the biochar and control 2 were not significantly different from either control 1 or TSP fertilizer.

Table A4. 2022 field study nitrogen uptake (kg/ha) and percentage recovery in the crops, and residual soil NO_3-N (mg/kg). ¶

Treatment	**Crop**		**Soil NO_3**		
	N uptake	***N Recovery***	***0-10cm***	***10-20cm***	***20-30cm***
Control 1	42.9 b	-	8.5 b	3.0 b	3.1 a
Control 2	72.5 a	12.6 a	10.4 ab	8.7 ab	6.2 a
Biochar 25kg P/ha	73.0 a	6.9 a	9.1 ab	4.2 b	5.0 a
Biochar 10t/ha	63.9 a	0.5 a	11.0 ab	6.7 ab	4.3 a
Biochar 10t/ha & TSP‡	64.5 a	1.1 a	12.3 ab	6.3 ab	5.9 a
TSP fertilizer	62.7 a	-0.3 a	14.0 a	10.3 a	4.4 a
ANOVA (Type III) p-value‡	*4.6e-06****	*0.55*	*Treatment: 0.02*; Depth: 0.004***		

¶ The nitrogen uptake and recovery values may not be meaningful as the crop was affected by the grasshoppers.

† Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

‡ *, ** and *** shows significance at $\alpha = 0.05$, 0.01, and 0.001 levels.

APPENDIX B: DATA SHOWING NO STATISTICALLY SIGNIFICANT TREATMENT EFFECTS

Canola study

There were no variables that had no significant differences between treatments.

Wheat study

Small plot component

The crops were uniformly afflicted by grasshoppers resulting in very few differences between the treatments. The nutrient uptake and recovery are thus more reflective of the nutrient concentrations in the crops than real uptake and recovery (Table B1). The treatments didn't show statistically significant differences between the N and P uptake and recovery ($p<0.05$ and $p>0.1$ respectively), however, as the standard error was very high compared to the means, this discussion focusses on the differences between the means.

Table B1. Wheat study small plot component yield, phosphorus uptake and phosphorus recovery.

Treatment	Yield (kg/ha)	P uptake (kg/ha)	P recovery (%)†
Control 1	503.7 a†	0.96 a	-
Control 2	590.5 a	1.23 a	-
Canola meal char	493.0 a	1.03 a	-0.78 a
Manure char (2022)	552.7 a	1.42 a	0.69 a
Willow char	588.6 a	1.33 a	0.41 a
MBMA – Coarse‡	583.8 a	1.26 a	0.10 a
MBMA – Fine‡	581.9 a	1.16 a	-0.28 a
TSP fertilizer	616.9 a	1.34 a	0.44 a
ANOVA (Type III) p-value	*0.93*	*0.65*	*0.65*

† The standard errors of the treatment means were larger than the means for all except canola meal char, possibly skewing the multi-treatment comparison. A multi-treatment comparison indicated no statistically significant difference between the treatments using Tukey HSD largely linked to the effect of the grasshoppers on the above-ground crop biomass (see Section 3.4.2.1 of this thesis).

Canola meal char had very low P uptake (23% lower) and recovery than P fertilizer (-0.78% compared to 0.44%). The only treatment that had higher P uptake and recovery levels than the TSP fertilizer is manure char with an almost 6% increase in uptake. The canola meal performance is similar to that seen in the canola study discussed in Section 3.6.1 as is manure and willow char in terms of P recovery. Both MBMA fractions have very high P content, however, compared to the TSP fertilizer both MBMA fractions compared poorly. Interestingly, the coarse fraction performed better than the fine fraction even though the fine fraction had more P content (19.4% P in the fine fraction compared to 17.7% P in the coarse fraction). It is possible that the fine fraction had other components that were deleterious to yield, or negatively impacted soil structure compared to the larger grain structure of the coarse MBMA. The coarser fragments may also have been more persistent in the field, being less susceptible to movement away from the zone of placement in wind and water over the season before the cores were collected and thus was retained better than the fine fraction.

P recovery was the highest in the manure char followed by the TSP fertilizer treatment, while canola meal char and the MBMA fine fraction had negative P recovery. Except for canola meal char, this is different from what was observed in the canola study, where manure char recovered approximately three quarters of the amount that the TSP fertilizer recovered, while the willow char was almost on par with the TSP fertilizer. The differences in how manure char led to recovery of P can be ascribed to the 2021 manure being composted while the 2022 manure was fresh. Canola meal char performed poorly in both studies. The poor performance in the field component of the wheat study is likely as a result of the loss of the crop to grasshoppers. However, the weather also very likely contributed to the reduced uptake and recovery. Not only were the crops planted later in the season than is typical for the region, but the area also experienced moderate drought conditions, with the 2022 regional rainfall about 30% lower than the average accompanied by lower-than-average daytime temperatures over the growing season.

Residual soil characteristics and nutrients

There was an overall decrease in the soil pH from pH 7.8 in the pre-study soil to a range of pH 7.3 to 7.5 at the end of the field season. It’s noted that the controls also showed reduced pH. It is likely that due to the narrow width of the rows (0.25m wide), there could have been a bleeding effect between the treatments, affecting not just the soil pH, but potentially other factors as well. In terms of salinity, only willow char showed reduced salinity (0.21mS/cm compared to pre-study levels of 0.26mS/cm), control 2 and both MBMA fractions had the highest salinity. It should be noted that both controls increased substantially from the pre-study levels. The chars may have contained ions that could sorb in the soil to increase salinity, or itself have an effect on the native soil constituents, potentially solubilizing salt forming cations such as sodium, potassium and calcium. The organic carbon (OC) increased by 0.1 to 0.2% in some of the treatments, including the controls. There is no statistically significant difference between the treatments, and as half the treatments have the same OC content as the pre-study soil, there appears to have been no effect on carbon sequestration.

Table B2 Wheat study small plot component residual soil data including Modified Kelowna (MK) PO_4-P, resin P, water soluble P (WSP), pH, electrical conductivity (EC) and organic carbon (OC).

Treatment	**MK P (µg P/g)** [§]	**Resin P (µg P/cm^2)**	**WSP (µg P/g)**	**pH**	**EC (mS/cm)**	**% OC**
Control1	12.4 a[†]	14.9 a	2.9 a	7.5 a	0.36 ab	1.5 a
Control 2	15.4 a	19.1 a	4.9 a	7.5 a	0.40 a	1.7 a
Canola meal char	15.0 a	15.8 a	4.0 a	7.3 a	0.32 ab	1.7 a
Manure char (2022)	15.8 a	20.2 a	3.7 a	7.5 a	0.35 ab	1.6 a
Willow char	12.2 a	19.3 a	3.0 a	7.3 a	0.21 b	1.5 a
MBMA coarse	16.1 a	19.6 a	3.7 a	7.4 a	0.38 a	1.6 a
MBMA fine	13.6 a	18.4 a	3.3 a	7.5 a	0.39 a	1.5 a
TSP fertilizer	14.7 a	20.6 a	2.9 a	7.4 a	0.27 ab	1.5 a
ANOVA (Type III) p-value[‡]	*0.80*	*0.367*	*0.137*	*0.199*	*0.00034****	*0.104*

† Means with the same letter are not significantly different at p<0.05 for a Tukey HSD multi-treatment comparison. Lack of differences may in part be attributed to the effect of the grasshoppers on the crop biomass (see Section 3.4.2.1 of this thesis).

‡ *** show significance at α = 0.001 level.

There was no significant difference between the treatments for any of the residual soil P fractions. P concentrations are unlikely to have been affected by diffusion between plots as P mobility is limited in soil. This is strikingly different from the canola study results, which showed highly significant differences between the treatments. It is thus anticipated that some other factors may have affected the P distribution in the soil. This conformity could also explain some of the similarities between treatments in terms of P uptake. Overall, the residual soil characteristics does not provide a clear picture of the effects of the treatments on changes in the soil.

Controlled environment component

There were no significant differences in pH between the treatments. Electrical conductivity (EC) also showed no significant differences, however, the standard error on EC was 28.85 for the model, which likely affected the outcome of the multi-treatment comparison. Manure char appears to be the most effective at lowering salinity.

Table B3. Wheat study controlled environment component pH and electrical conductivity (EC) in post-harvest soil.

Treatment	**pH**	**EC (mS/cm)**
Control 1	7.24 a[†]	0.13 a
Control 2	7.22 a	0.16 a
Canola meal char	7.17 a	0.13 a
Manure (2022) char	7.23 a	0.11 a
Willow char	7.24 a	0.18 a
MBMA coarse	7.18 a	0.16 a
MBMA fine	7.18 a	0.13 a
TSP fertilizer	7.16 a	0.14 a
ANOVA (Type III) p-value	*0.98*	*0.46*

[†] Means with the same letter are not significantly different at $p<0.05$ for a Tukey HSD multi-treatment comparison.

APPENDIX C: SOIL DATA, NUTRIENT DATA AND CALCULATIONS

Pre-study soil characteristics for field studies

Table C1.: ***Wheat study small plot component pre-study soil characteristics from spring 2022.***

Properties	**Depth**	**Transect point**					**Average**
		1	***2***	***3***	***4***	***5***	
NO_3 (µg/g)	0-15cm	16.2	11.6	40.1	20.8	19.3	21.6
	15-30cm	32.7	20.5	29.7	18.8	32.5	26.8
	30-60cm	13.9	18.8	8.2	4.6	21.3	13.4
pH	0-15cm	7.7	8.0	7.4	7.9	8.0	7.8
	15-30cm	7.8	8.0	7.8	8.0	8.0	7.9
	30-60cm	8.0	8.1	8.1	8.1	8.1	8.1
EC (mS/cm)	0-15cm	0.20	0.26	0.27	0.32	0.26	0.26
	15-30cm	0.33	0.28	0.33	0.27	0.31	0.30
	30-60cm	0.24	0.26	0.25	0.20	0.27	0.24
P (µg/g)	0-15cm	15.2	5.3	16.2	11.5	3.1	10.2
K (µg/g)	0-15cm	291.9	246.3	421.9	332.4	233.6	305.2
% OC	0-15cm	1.3	1.2	1.4	1.3	1.1	1.3
% Sand	0-15cm	51.9	50.6	45.6	44.4	38.1	46.1
% Clay	0-15cm	18.1	16.3	15.0	19.4	19.4	17.6
% Silt	0-15cm	30.0	33.1	39.4	36.3	42.5	36.3
Textural Class	0-15cm	Loam	Loam	Loam	Loam	Loam	-

Table C2. ***2022 field study pre-study soil characteristics from spring 2022.***

Properties	**Depth**	**Transect point**					**Average**
		1	***2***	***3***	***4***	***5***	
	0-15cm	7.5	14.7	10.9	18.5	15.8	13.5
NO_3 (µg/g)	15-30cm	8.0	19.9	21.4	16.9	26.9	18.6
	30-60cm	8.7	8.5	6.9	4.4	10.7	7.8
	0-15cm	7.0	6.9	6.9	6.9	6.6	6.8
pH	15-30cm	6.9	6.8	7.4	7.0	7.5	7.1
	30-60cm	7.4	7.4	7.4	7.5	7.9	7.5
	0-15cm	0.13	0.17	0.17	0.16	0.13	0.15
EC (mS/cm)	15-30cm	0.14	0.17	0.38	0.16	0.25	0.22
	30-60cm	0.23	4.22	8.37	1.00	0.31	2.82
P (µg/g)	0-15cm	8.5	11.4	13.7	14.3	8.2	11.2
K (µg/g)	0-15cm	424.0	420.7	379.6	367.5	320.8	382.5
% OC	0-15cm	1.6	1.7	1.4	1.4	1.4	1.5
% Sand	0-15cm	48.8	48.8	48.1	43.1	59.4	49.6
% Clay	0-15cm	12.5	13.1	14.4	13.8	11.9	13.1
% Silt	0-15cm	38.8	38.1	37.5	43.1	28.8	37.3
Textural Class	0-15cm	Loam	Loam	Loam	Loam	Sandy Loam	-

<u>Nutrient use efficiency</u>

Nutrient use efficiency is determined as the changes in unit mass of yield produced over the unfertilized control per mass of nutrient added (g or kg of yield per g or kg of nutrient). The N and P applied data in Table C1 was used to calculate N and P use efficiency (NUE and PUE) for the canola study and the 2022 field study using equation C1. Due to the devastation caused by the grasshoppers and the subsequent unknown uptake of N and P in the field, the NUE and PUE was not calculated for the wheat study.

$$Nutrient\ use\ efficiency = \frac{Treatment\ yield - Control\ yield}{P\ application\ rate}$$

Eq. C1

Canola study

Table C3. Canola study nutrient use efficiency (g of yield per g of added nutrient).

Treatment	**Nitrogen use efficiency**		**Phosphorus use efficiency**	
	Haverhill	Oxbow	Haverhill	Oxbow
Control 2 - basal only	18.7 bcd†	8.3 e	-	-
Canola meal 50kg P/ha	7.8 d	6.6 e	105.2 b	31.7 c
Canola hull 50kg P/ha	12.6 d	12.4 de	167.2 b	85.0 bc
Manure (2021) 50kg P/	23.7 abcd	25.8 bcd	141.4 b	163.5 abc
Willow 50kg P/ha	17.6 cd	15.4 de	227.3 b	194.5 abc
Canola meal 10t/ha	11.6 d	15.9 de	43.1 b	39.0 c
Canola hull 10t/ha	22.4 bcd	21.4 cde	197.2 b	60.2 bc
Manure (2021) 10t/ha	29.7 abc	33.8 abc	56.8 b	63.9 bc
Willow 10t/ha	23.4 abcd	15.2 de	564.3 a	322.9 a
Canola meal 10t/ha & TSP	17.0 cd	5.6 e	33.9 b	45.2 c
Canola hull 10t/ha & TSP	16.0 cd	9.9 de	130.3 b	122.8 abc
Manure (2021) 10t/ha & TSP	33.9 ab	45.4 a	54.6 b	73.2 bc
Willow 10t/ha & TSP	29.2 abc	38.6 ab	191.4 b	269.8 ab
TSP fertilizer	38.6 a	40.8 ab	250.1 b	271.7 ab
ANOVA (Type III) p-value[‡] for treatment effects	***NUE efficiency***		***PUE efficiency***	
	*1.36e-29****		*1.75e-38****	

† Means with the same letter are not significantly different at p<0.1 for a Tukey HSD multi-treatment comparison.

‡ *** shows significance at α = 0.001.

Canola large plot study

Table C4. Large plot study nitrogen and phosphorus use efficiency.

Treatment	**Nitrogen use efficiency**	**Phosphorus use efficiency**
Control2	12.6 a[†]	-
Biochar25kgPha	6.9 a	58.2 a
Biochar10tha	1.4 a	54.5 a
Biochar10thaTSP	1.1 a	24.8 a
TSP fertilizer	-4.6 a	36.7 a
ANOVA (Type III) p-value[‡]	*0.25*	*0.02**

† Means with the same letter are not significantly different at p<0.1 for a Tukey HSD multi-treatment comparison.

‡ * shows significance at α = 0.05.

Organic carbon ratios

Table C5. ***Ratios of char carbon to soil organic carbon (SOC) for all study components. Ratios greater than 2 [†]are bolded for reference.***

Biochar feedstock		Canola meal	Canola hull	Manure 2021[‡]	Manure 2022	MBMA coarse	MBMA fine	Willow biochar
%C in biochar		66.4	63.0	N/A		0.9	0.1	70.7
Haverhill soil	*SOC*				1.3			
	C:SOC	66.4:1.3	63:1.3	N/A				70.7:1.3
	Ratio	**50.3**	**47.7**	N/A				**53.6**
Oxbow soil					3.1			
		66.4:3:1	63:1.3	N/A				70.7:3.1
		21.1	**20.1**	N/A				**22.5**
Small rows	*SOC*				1.3			
	C:SOC	66.4:1.3			26.4:1.3	0.9:1.3	0.1:1.3	70.7:1.3
	Ratio	**51.9**			**20.6**	**0.7**	**0.1**	**55.2**
Cores	*SOC*	1.7			1.6	1.6	1.5	1.5
	C:SOC	66.4:1.7			26.4:1.6	0.9:1.6	0.1:1.5	70.7:1.5
	Ratio	**38.6**			**16.9**	**0.6**	**0.1**	**46.3**
Large plots	*SOC*							1.5
	C:SOC							70.7:1.5
	Ratio							**47.4**

[†] As per El-Naggar *et al*. (2019), a ratio of >2 will result in increased CO2 emissions.

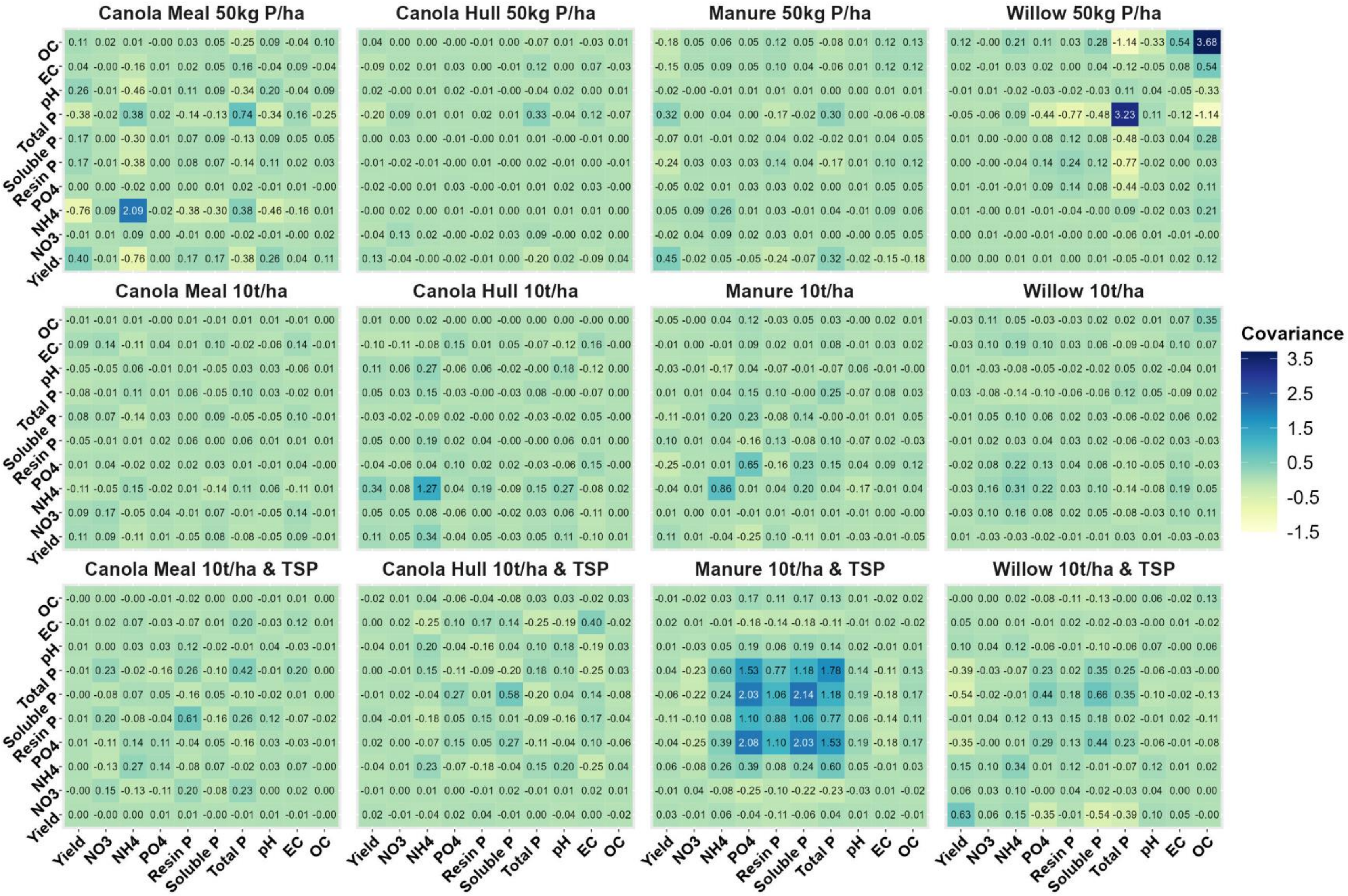
[‡] The 2021 manure used in the canola study was not tested for carbon content and no char remains to be tested.

Table C6. R model used for each parameter of the study components

Parameter	**R linear mixed effects models**			
	Canola study	***Wheat study (field)***	***Wheat study (cores)***	***Field study***
Biomass / Yield	glmmTMB	lme	glmmTMB	glmmTMB
N uptake	lmer	glmmTMB	glmmTMB	glmmTMB
N recovery	glmmTMB	glmmTMB	-	lmer
P uptake	glmmTMB	glmmTMB	lmer	glmmTMB
P recovery	glmmTMB	glmmTMB	-	lmer
Soil NO_3	glmmTMB	glmmTMB	glmmTMB	glmmTMB
Soil NH_4	glmmTMB	-	glmmTMB	-
Soil PO_4	glmmTMB	glmmTMB	glmmTMB	lme
Soil water soluble P	glmmTMB	glmmTMB	glmmTMB	glmmTMB
Soil Resin P	glmmTMB	glmmTMB	glmmTMB	lmer
Soil pH	glmer	glmmTMB	glmmTMB	glmmTMB
Soil electric conductivity	glmmTMB	glmmTMB	lme	glmmTMB
Soil organic carbon	glmmTMB	lme	glmer	lmer
Leachate / Snowmelt NO_3	-	-	glmmTMB	lme
Leachate / Snowmelt NH_4	-	-	glmmTMB	glmmTMB
Leachate / Snowmelt PO_4	-	-	glmmTMB	lmer
Snowmelt resin NO_3	-	-	-	lmer
Snowmelt resin PO_4	-	-	-	glmmTMB
Infiltration – initial rate	-	-	-	lme
Infiltration – final rate	-	-	-	lme
Infiltration – sorptivity	-	-	-	lme
Infiltration – hydraulic conductivity	-	-	-	lme
Infiltration – moisture	-	-	-	lme

APPENDIX D: INTERACTION PLOTS

Canola study



Canola Meal 50kg P/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.11	0.02	0.01	-0.00	0.03	0.05	-0.25	0.09	-0.04	0.10
EC	0.04	-0.00	-0.16	0.01	0.02	0.05	0.16	-0.04	0.09	-0.04
pH	0.26	-0.01	-0.46	-0.01	0.11	0.09	-0.34	0.20	-0.04	0.09
Total P	-0.38	-0.02	0.38	0.02	-0.14	-0.13	0.74	-0.34	0.16	-0.25
Soluble P	0.17	0.00	-0.30	0.01	0.07	0.09	-0.13	0.09	0.05	0.05
Resin P	0.17	-0.01	-0.38	0.00	0.08	0.07	-0.14	0.11	0.02	0.03
PO4	0.00	0.00	-0.02	0.00	0.00	0.01	0.02	-0.01	0.01	-0.00
NH4	-0.76	0.09	2.09	-0.02	-0.38	-0.30	0.38	-0.46	-0.16	0.01
NO3	-0.01	0.01	0.09	0.00	-0.01	0.00	-0.02	-0.01	-0.00	0.02
Yield	0.40	-0.01	-0.76	0.00	0.17	0.17	-0.38	0.26	0.04	0.11

Canola Hull 50kg P/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.04	0.00	0.00	-0.00	-0.01	0.00	-0.07	0.01	-0.03	0.01
EC	-0.09	0.02	0.01	0.03	0.00	-0.01	0.12	0.00	0.07	-0.03
pH	0.02	-0.00	0.01	0.02	-0.01	-0.00	-0.04	0.02	0.00	0.01
Total P	-0.20	0.09	0.01	0.01	0.02	0.01	0.33	-0.04	0.12	-0.07
Soluble P	0.00	0.03	0.00	-0.01	-0.00	0.01	0.01	-0.00	-0.01	0.00
Resin P	-0.01	-0.02	-0.01	-0.00	0.01	-0.00	0.02	-0.01	0.00	-0.01
PO4	-0.02	-0.00	0.01	0.03	-0.00	-0.01	0.01	0.02	0.03	-0.00
NH4	-0.00	0.02	0.00	0.01	-0.01	0.00	0.01	0.01	0.01	0.00
NO3	-0.04	0.13	0.02	-0.00	-0.02	0.03	0.09	-0.00	0.02	0.00
Yield	0.13	-0.04	-0.00	-0.02	-0.01	0.00	-0.20	0.02	-0.09	0.04

Manure 50kg P/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.18	0.05	0.06	0.05	0.12	0.05	-0.08	0.01	0.12	0.13
EC	-0.15	0.05	0.09	0.05	0.10	0.04	-0.06	0.01	0.12	0.12
pH	-0.02	-0.00	-0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01
Total P	0.32	0.00	0.04	0.00	-0.17	-0.02	0.30	0.00	-0.06	-0.08
Soluble P	-0.07	0.01	-0.01	0.02	0.04	0.02	-0.02	0.01	0.04	0.05
Resin P	-0.24	0.03	0.03	0.03	0.14	0.04	-0.17	0.01	0.10	0.12
PO4	-0.05	0.02	0.01	0.03	0.03	0.02	0.00	0.01	0.05	0.05
NH4	0.05	0.09	0.26	0.01	0.03	-0.01	0.04	-0.01	0.09	0.06
NO3	-0.02	0.04	0.09	0.02	0.03	0.01	0.00	-0.00	0.05	0.05
Yield	0.45	-0.02	0.05	-0.05	-0.24	-0.07	0.32	-0.02	-0.15	-0.18

Willow 50kg P/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.12	-0.00	0.21	0.11	0.03	0.28	-1.14	-0.33	0.54	3.68
EC	0.02	-0.01	0.03	0.02	0.00	0.04	-0.12	-0.05	0.08	0.54
pH	-0.01	0.01	-0.02	-0.03	-0.02	-0.03	0.11	0.04	-0.05	-0.33
Total P	-0.05	-0.06	0.09	-0.44	-0.77	-0.48	3.23	0.11	-0.12	-1.14
Soluble P	0.01	0.00	-0.00	0.08	0.12	0.08	-0.48	-0.03	0.04	0.28
Resin P	0.00	-0.00	-0.04	0.14	0.24	0.12	-0.77	-0.02	0.00	0.03
PO4	0.01	-0.01	-0.01	0.09	0.14	0.08	-0.44	-0.03	0.02	0.11
NH4	0.01	-0.00	0.01	-0.01	-0.04	-0.00	0.09	-0.02	0.03	0.21
NO3	0.00	0.01	-0.00	-0.01	-0.00	0.00	-0.06	0.01	-0.01	-0.00
Yield	0.00	0.00	0.01	0.01	0.00	0.01	-0.05	-0.01	0.02	0.12

Canola Meal 10t/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.01	-0.01	0.01	-0.00	0.01	-0.01	0.01	0.01	-0.01	0.00
EC	0.09	0.14	-0.11	0.04	0.01	0.10	-0.02	-0.06	0.14	-0.01
pH	-0.05	-0.05	0.06	-0.01	0.01	-0.05	0.03	0.03	-0.06	0.01
Total P	-0.08	-0.01	0.11	0.01	0.06	-0.05	0.10	0.03	-0.02	0.01
Soluble P	0.08	0.07	-0.14	0.03	0.00	0.09	-0.05	-0.05	0.10	-0.01
Resin P	-0.05	-0.01	0.01	0.02	0.06	0.00	0.06	0.01	0.01	0.01
PO4	0.01	0.04	-0.02	0.02	0.02	0.03	0.01	-0.01	0.04	-0.00
NH4	-0.11	-0.05	0.15	-0.02	0.01	-0.14	0.11	0.06	-0.11	0.01
NO3	0.09	0.17	-0.05	0.04	-0.01	0.07	-0.01	-0.05	0.14	-0.01
Yield	0.11	0.09	-0.11	0.01	-0.05	0.08	-0.08	-0.05	0.09	-0.01

Canola Hull 10t/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.01	0.00	0.02	-0.00	0.00	-0.00	0.00	0.00	-0.00	0.00
EC	-0.10	-0.11	-0.08	0.15	0.01	0.05	-0.07	-0.12	0.16	-0.00
pH	0.11	0.06	0.27	-0.06	0.06	-0.02	-0.00	0.18	-0.12	0.00
Total P	0.05	0.03	0.15	-0.03	-0.00	-0.03	0.08	-0.00	-0.07	0.00
Soluble P	-0.03	-0.02	-0.09	0.02	-0.00	0.02	-0.03	-0.02	0.05	-0.00
Resin P	0.05	0.00	0.19	0.02	0.04	-0.00	-0.00	0.06	0.01	0.00
PO4	-0.04	-0.06	0.04	0.10	0.02	0.02	-0.03	-0.06	0.15	-0.00
NH4	0.34	0.08	1.27	0.04	0.19	-0.09	0.15	0.27	-0.08	0.02
NO3	0.05	0.05	0.08	-0.06	0.00	-0.02	0.03	0.06	-0.11	0.00
Yield	0.11	0.05	0.34	-0.04	0.05	-0.03	0.05	0.11	-0.10	0.01

Manure 10t/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.05	-0.00	0.04	0.12	-0.03	0.05	0.03	-0.00	0.02	0.01
EC	-0.01	0.00	-0.01	0.09	0.02	0.01	0.08	-0.01	0.03	0.02
pH	-0.03	-0.01	-0.17	0.04	-0.07	-0.01	-0.07	0.06	-0.01	-0.00
Total P	0.01	0.01	0.04	0.15	0.10	-0.00	0.25	-0.07	0.08	0.03
Soluble P	-0.11	-0.01	0.20	0.23	-0.08	0.14	-0.00	-0.01	0.01	0.05
Resin P	0.10	0.01	0.04	-0.16	0.13	-0.08	0.10	-0.07	0.02	-0.03
PO4	-0.25	-0.01	0.01	0.65	-0.16	0.23	0.15	0.04	0.09	0.12
NH4	-0.04	0.01	0.86	0.01	0.04	0.20	0.04	-0.17	-0.01	0.04
NO3	0.01	0.00	0.01	-0.01	0.01	-0.01	0.01	-0.01	0.00	-0.00
Yield	0.11	0.01	-0.04	-0.25	0.10	-0.11	0.01	-0.03	-0.01	-0.05

Willow 10t/ha

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.03	0.11	0.05	-0.03	-0.03	0.02	0.02	0.01	0.07	0.35
EC	-0.03	0.10	0.19	0.10	0.03	0.06	-0.09	-0.04	0.10	0.07
pH	0.01	-0.03	-0.08	-0.05	-0.02	-0.02	0.05	0.02	-0.04	0.01
Total P	0.03	-0.08	-0.14	-0.10	-0.06	-0.06	0.12	0.05	-0.09	0.02
Soluble P	-0.01	0.05	0.10	0.06	0.02	0.03	-0.06	-0.02	0.06	0.02
Resin P	-0.01	0.02	0.03	0.04	0.03	0.02	-0.06	-0.02	0.03	-0.03
PO4	-0.02	0.08	0.22	0.13	0.04	0.06	-0.10	-0.05	0.10	-0.03
NH4	-0.03	0.16	0.31	0.22	0.03	0.10	-0.14	-0.08	0.19	0.05
NO3	-0.03	0.10	0.16	0.08	0.02	0.05	-0.08	-0.03	0.10	0.11
Yield	0.01	-0.03	-0.03	-0.02	-0.01	-0.01	0.03	0.01	-0.03	-0.03

Canola Meal 10t/ha & TSP

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.00	0.00	-0.00	-0.01	-0.02	0.00	0.00	-0.01	0.01	0.00
EC	-0.01	0.02	0.07	-0.03	-0.07	0.01	0.20	-0.03	0.12	0.01
pH	0.01	0.00	0.03	0.03	0.12	-0.02	-0.01	0.04	-0.03	-0.01
Total P	-0.01	0.23	-0.02	-0.16	0.26	-0.10	0.42	-0.01	0.20	0.00
Soluble P	-0.00	-0.08	0.07	0.05	-0.16	0.05	-0.10	-0.02	0.01	0.00
Resin P	0.01	0.20	-0.08	-0.04	0.61	-0.16	0.26	0.12	-0.07	-0.02
PO4	0.01	-0.11	0.14	0.11	-0.04	0.05	-0.16	0.03	-0.03	-0.01
NH4	0.00	-0.13	0.27	0.14	-0.08	0.07	-0.02	0.03	0.07	-0.00
NO3	-0.00	0.15	-0.13	-0.11	0.20	-0.08	0.23	0.00	0.02	0.00
Yield	0.00	-0.00	0.00	0.01	0.01	-0.00	-0.01	0.01	-0.01	-0.00

Canola Hull 10t/ha & TSP

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.02	0.01	0.04	-0.06	-0.04	-0.08	0.03	0.03	-0.02	0.03
EC	0.00	0.02	-0.25	0.10	0.17	0.14	-0.25	-0.19	0.40	-0.02
pH	-0.04	0.01	0.20	-0.04	-0.16	0.04	0.10	0.18	-0.19	0.03
Total P	0.00	-0.01	0.15	-0.11	-0.09	-0.20	0.18	0.10	-0.25	0.03
Soluble P	-0.01	0.02	-0.04	0.27	0.01	0.58	-0.20	0.04	0.14	-0.08
Resin P	0.04	-0.01	-0.18	0.05	0.15	0.01	-0.09	-0.16	0.17	-0.04
PO4	0.02	0.00	-0.07	0.15	0.05	0.27	-0.11	-0.04	0.10	-0.06
NH4	-0.04	0.01	0.23	-0.07	-0.18	-0.04	0.15	0.20	-0.25	0.04
NO3	-0.01	0.00	0.01	0.00	-0.01	0.02	-0.01	0.01	0.02	0.01
Yield	0.02	-0.01	-0.04	0.02	0.04	-0.01	0.00	-0.04	0.00	-0.02

Manure 10t/ha & TSP

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.01	-0.02	0.03	0.17	0.11	0.17	0.13	0.01	-0.02	0.02
EC	0.02	0.01	-0.01	-0.18	-0.14	-0.18	-0.11	-0.01	0.02	-0.02
pH	0.01	-0.03	0.05	0.19	0.06	0.19	0.14	0.02	-0.01	0.01
Total P	0.04	-0.23	0.60	1.53	0.77	1.18	1.78	0.14	-0.11	0.13
Soluble P	-0.06	-0.22	0.24	2.03	1.06	2.14	1.18	0.19	-0.18	0.17
Resin P	-0.11	-0.10	0.08	1.10	0.88	1.06	0.77	0.06	-0.14	0.11
PO4	-0.04	-0.25	0.39	2.08	1.10	2.03	1.53	0.19	-0.18	0.17
NH4	0.06	-0.08	0.26	0.39	0.08	0.24	0.60	0.05	-0.01	0.03
NO3	-0.01	0.04	-0.08	-0.25	-0.10	-0.22	-0.23	-0.03	0.01	-0.02
Yield	0.03	-0.01	0.06	-0.04	-0.11	-0.06	0.04	0.01	0.02	-0.01

Willow 10t/ha & TSP

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.00	0.00	0.02	-0.08	-0.11	-0.13	-0.00	0.06	-0.02	0.13
EC	0.05	0.00	0.01	-0.01	0.02	-0.02	-0.03	-0.00	0.01	-0.02
pH	0.10	0.04	0.12	-0.06	-0.01	-0.10	-0.06	0.07	-0.00	0.06
Total P	-0.39	-0.03	-0.07	0.23	0.02	0.35	0.25	-0.06	-0.03	-0.00
Soluble P	-0.54	-0.02	-0.01	0.44	0.18	0.66	0.35	-0.10	-0.02	-0.13
Resin P	-0.01	0.04	0.12	0.13	0.15	0.18	0.02	-0.01	0.02	-0.11
PO4	-0.35	-0.00	0.01	0.29	0.13	0.44	0.23	-0.06	-0.01	-0.08
NH4	0.15	0.10	0.34	0.01	0.12	-0.01	-0.07	0.12	0.01	0.02
NO3	0.06	0.03	0.10	-0.00	0.04	-0.02	-0.03	0.04	0.00	0.00
Yield	0.63	0.06	0.15	-0.35	-0.01	-0.54	-0.39	0.10	0.05	-0.00

Fig. D1. Haverhill soil covariance heat map showing the influence of residual soil factors on canola crop yield. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

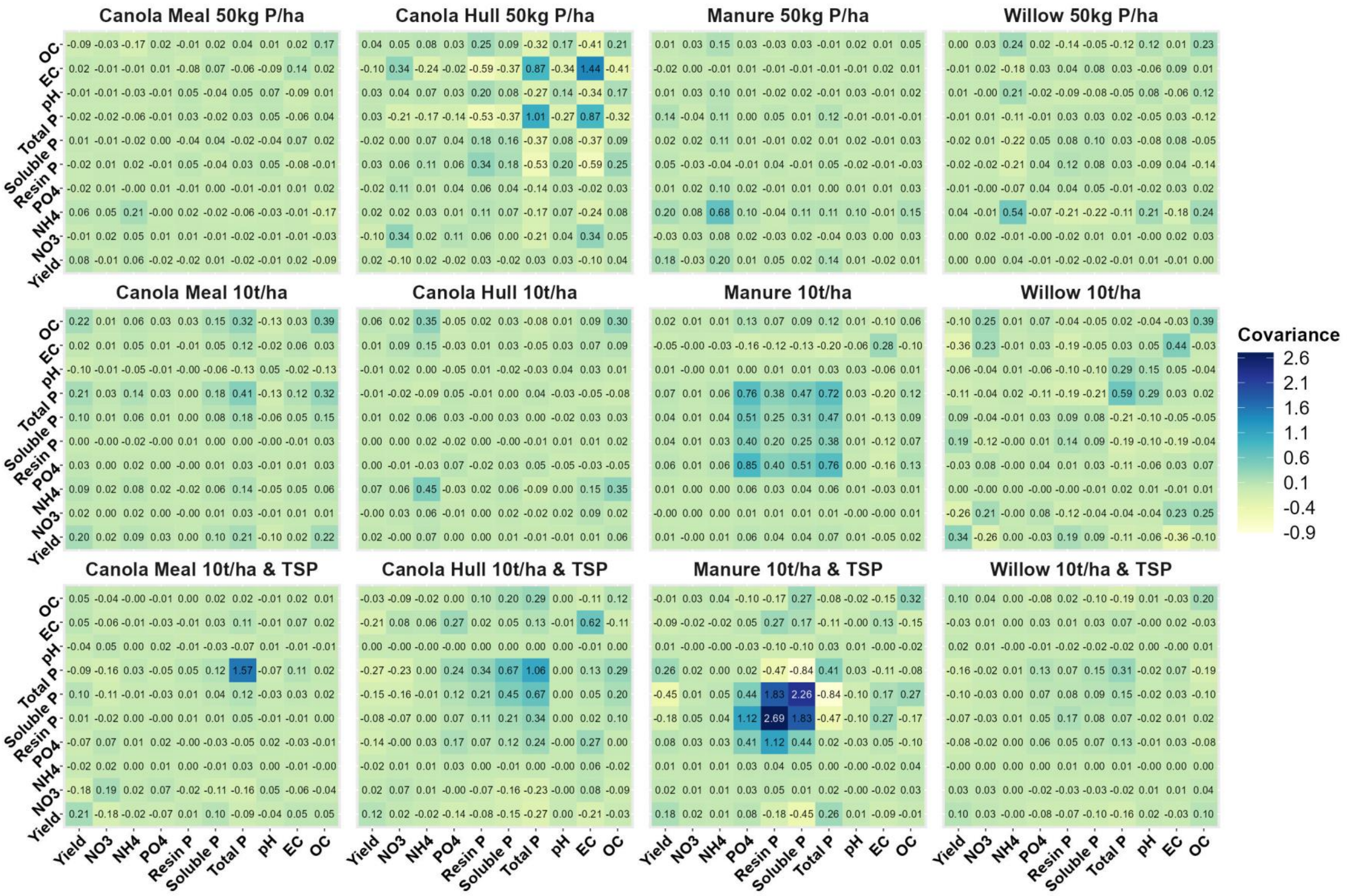


Fig. D2. Oxbow soil covariance heat map showing the influence of residual soil factors on canola crop yield. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

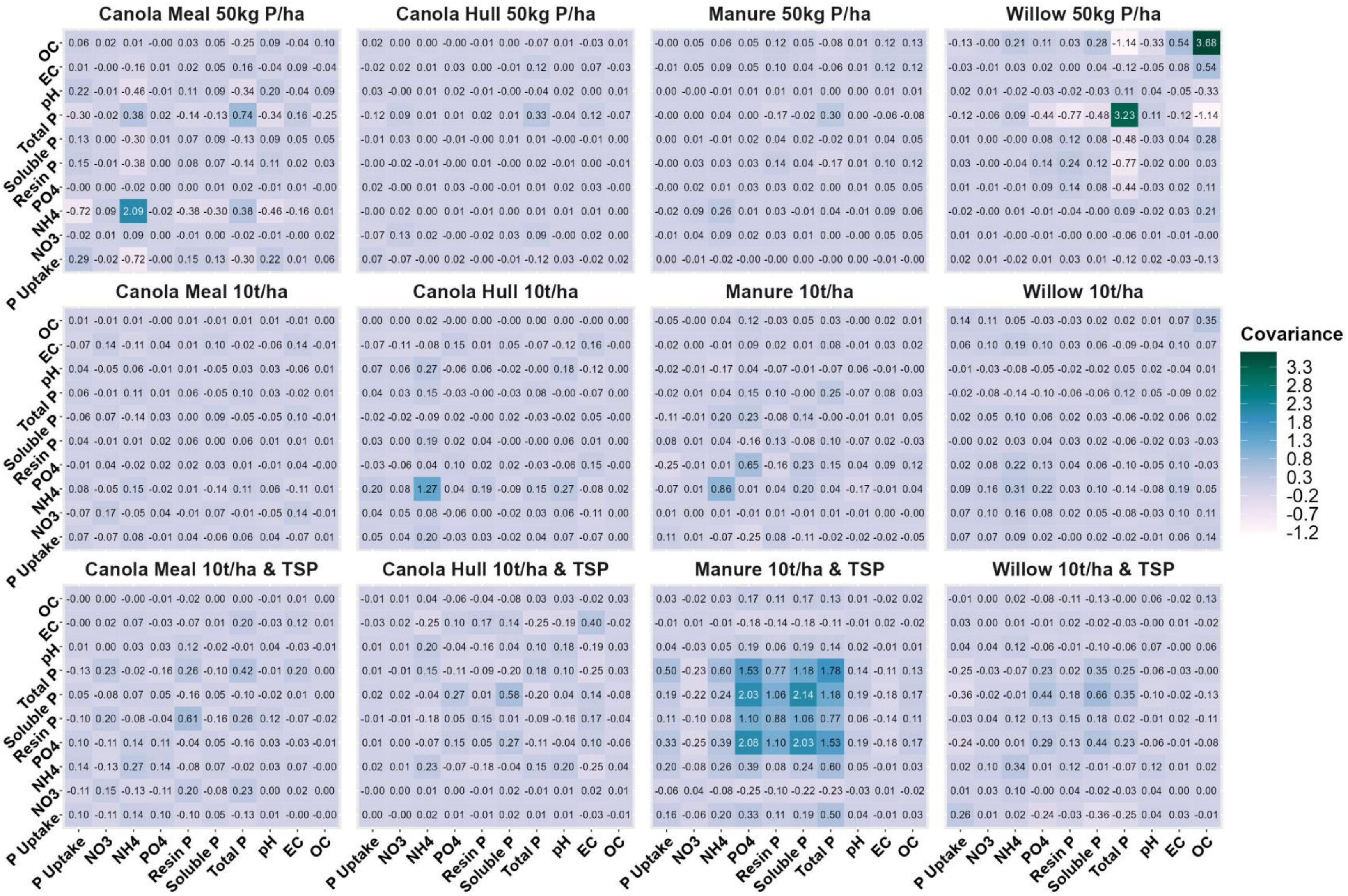
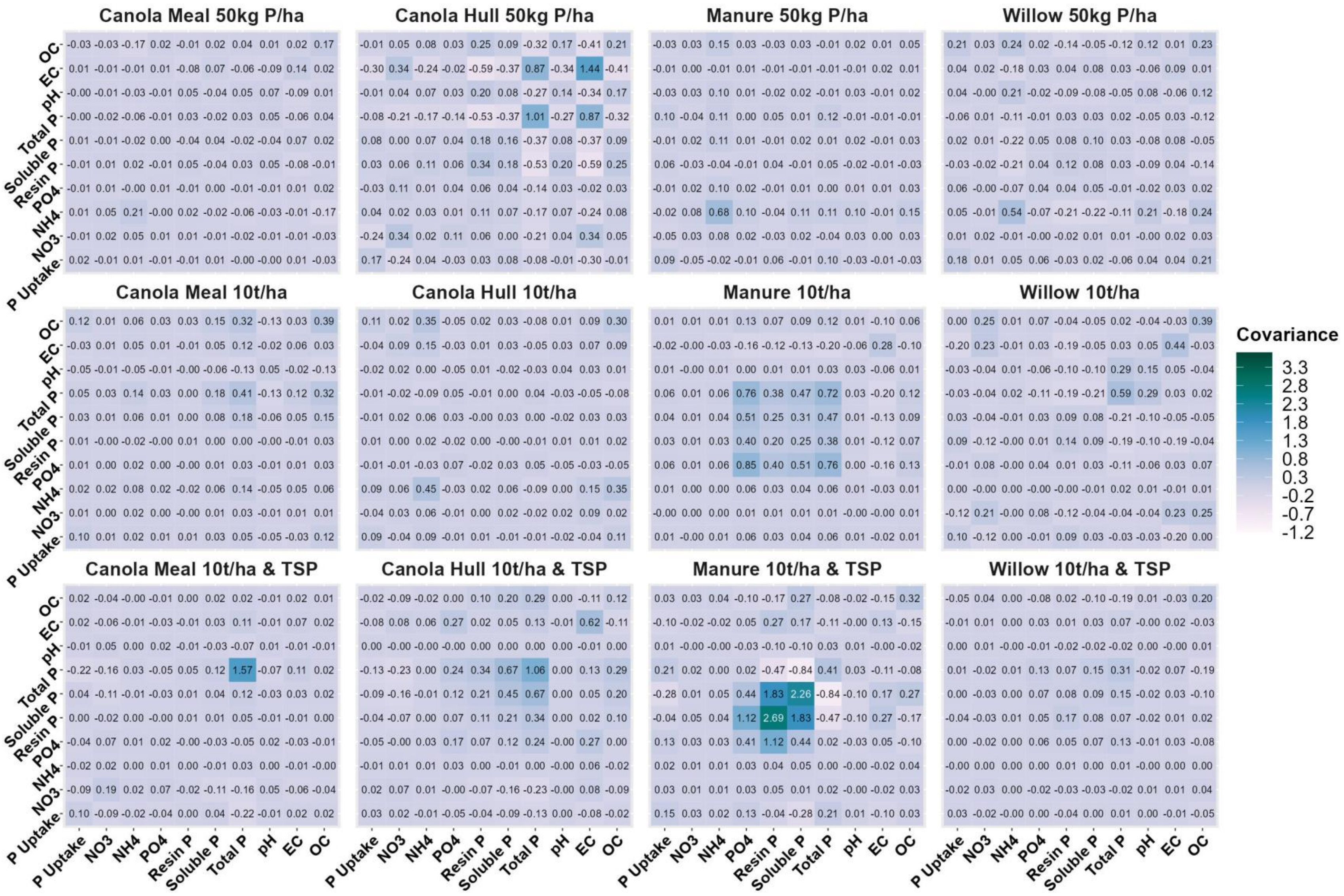


Fig. D3. ***Haverhill soil covariance heat map showing the influence of residual soil factors on crop P uptake. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.***



Canola Meal 50kg P/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.03	-0.03	-0.17	0.02	-0.01	0.02	0.04	0.01	0.02	0.17
EC	0.01	-0.01	-0.01	0.01	-0.08	0.07	-0.06	-0.09	0.14	0.02
pH	-0.00	-0.01	-0.03	-0.01	0.05	-0.04	0.05	0.07	-0.09	0.01
Total P	-0.00	-0.02	-0.06	-0.01	0.03	-0.02	0.03	0.05	-0.06	0.04
Soluble P	0.01	-0.01	-0.02	0.00	-0.04	0.04	-0.02	-0.04	0.07	0.02
Resin P	-0.01	0.01	0.02	-0.01	0.05	-0.04	0.03	0.05	-0.08	-0.01
PO4	-0.01	0.01	-0.00	0.01	-0.01	0.00	-0.01	-0.01	0.01	0.02
NH4	0.01	0.05	0.21	-0.00	0.02	-0.02	-0.06	-0.03	-0.01	-0.17
NO3	-0.01	0.02	0.05	0.01	0.01	-0.01	-0.02	-0.01	-0.01	-0.03
P Uptake	0.02	-0.01	0.01	-0.01	-0.01	0.01	-0.00	-0.00	0.01	-0.03

Canola Hull 50kg P/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.01	0.05	0.08	0.03	0.25	0.09	-0.32	0.17	-0.41	0.21
EC	-0.30	0.34	-0.24	-0.02	-0.59	-0.37	0.87	-0.34	1.44	-0.41
pH	-0.01	0.04	0.07	0.03	0.20	0.08	-0.27	0.14	-0.34	0.17
Total P	-0.08	-0.21	-0.17	-0.14	-0.53	-0.37	1.01	-0.27	0.87	-0.32
Soluble P	0.08	0.00	0.07	0.04	0.18	0.16	-0.37	0.08	-0.37	0.09
Resin P	0.03	0.06	0.11	0.06	0.34	0.18	-0.53	0.20	-0.59	0.25
PO4	-0.03	0.11	0.01	0.04	0.06	0.04	-0.14	0.03	-0.02	0.03
NH4	0.04	0.02	0.03	0.01	0.11	0.07	-0.17	0.07	-0.24	0.08
NO3	-0.24	0.34	0.02	0.11	0.06	0.00	-0.21	0.04	0.34	0.05
P Uptake	0.17	-0.24	0.04	-0.03	0.03	0.08	-0.08	-0.01	-0.30	-0.01

Manure 50kg P/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.03	0.03	0.15	0.03	-0.03	0.03	-0.01	0.02	0.01	0.05
EC	-0.01	0.00	-0.01	0.01	-0.01	-0.01	-0.01	-0.01	0.02	0.01
pH	-0.03	0.03	0.10	0.01	-0.02	0.02	-0.01	0.03	-0.01	0.02
Total P	0.10	-0.04	0.11	0.00	0.05	0.01	0.12	-0.01	-0.01	-0.01
Soluble P	-0.01	0.02	0.11	0.01	-0.01	0.02	0.01	0.02	-0.01	0.03
Resin P	0.06	-0.03	-0.04	-0.01	0.04	-0.01	0.05	-0.02	-0.01	-0.03
PO4	-0.01	0.02	0.10	0.02	-0.01	0.01	0.00	0.01	0.01	0.03
NH4	-0.02	0.08	0.68	0.10	-0.04	0.11	0.11	0.10	-0.01	0.15
NO3	-0.05	0.03	0.08	0.02	-0.03	0.02	-0.04	0.03	0.00	0.03
P Uptake	0.09	-0.05	-0.02	-0.01	0.06	-0.01	0.10	-0.03	-0.01	-0.03

Willow 50kg P/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.21	0.03	0.24	0.02	-0.14	-0.05	-0.12	0.12	0.01	0.23
EC	0.04	0.02	-0.18	0.03	0.04	0.08	0.03	-0.06	0.09	0.01
pH	0.04	-0.00	0.21	-0.02	-0.09	-0.08	-0.05	0.08	-0.06	0.12
Total P	-0.06	0.01	-0.11	-0.01	0.03	0.03	0.02	-0.05	0.03	-0.12
Soluble P	0.02	0.01	-0.22	0.05	0.08	0.10	0.03	-0.08	0.08	-0.05
Resin P	-0.03	-0.02	-0.21	0.04	0.12	0.08	0.03	-0.09	0.04	-0.14
PO4	0.06	-0.00	-0.07	0.04	0.04	0.05	-0.01	-0.02	0.03	0.02
NH4	0.05	-0.01	0.54	-0.07	-0.21	-0.22	-0.11	0.21	-0.18	0.24
NO3	0.01	0.02	-0.01	-0.00	-0.02	0.01	0.01	-0.00	0.02	0.03
P Uptake	0.18	0.01	0.05	0.06	-0.03	0.02	-0.06	0.04	0.04	0.21

Canola Meal 10t/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.12	0.01	0.06	0.03	0.03	0.15	0.32	-0.13	0.03	0.39
EC	-0.03	0.01	0.05	0.01	-0.01	0.05	0.12	-0.02	0.06	0.03
pH	-0.05	-0.01	-0.05	-0.01	-0.00	-0.06	-0.13	0.05	-0.02	-0.13
Total P	0.05	0.03	0.14	0.03	0.00	0.18	0.41	-0.13	0.12	0.32
Soluble P	0.03	0.01	0.06	0.01	0.00	0.08	0.18	-0.06	0.05	0.15
Resin P	0.01	-0.00	-0.02	-0.00	0.01	0.00	0.00	-0.00	-0.01	0.03
PO4	0.01	0.00	0.02	0.00	-0.00	0.01	0.03	-0.01	0.01	0.03
NH4	0.02	0.02	0.08	0.02	-0.02	0.06	0.14	-0.05	0.05	0.06
NO3	0.01	0.00	0.02	0.00	-0.00	0.01	0.03	-0.01	0.01	0.01
P Uptake	0.10	0.01	0.02	0.01	0.01	0.03	0.05	-0.05	-0.03	0.12

Canola Hull 10t/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.11	0.02	0.35	-0.05	0.02	0.03	-0.08	0.01	0.09	0.30
EC	-0.04	0.09	0.15	-0.03	0.01	0.03	-0.05	0.03	0.07	0.09
pH	-0.02	0.02	0.00	-0.05	0.01	-0.02	-0.03	0.04	0.03	0.01
Total P	-0.01	-0.02	-0.09	0.05	-0.01	0.00	0.04	-0.03	-0.05	-0.08
Soluble P	-0.01	0.02	0.06	0.03	-0.00	0.03	0.00	-0.02	0.03	0.03
Resin P	0.01	0.00	0.02	-0.02	0.00	-0.00	-0.01	0.01	0.01	0.02
PO4	-0.01	-0.01	-0.03	0.07	-0.02	0.03	0.05	-0.05	-0.03	-0.05
NH4	0.09	0.06	0.45	-0.03	0.02	0.06	-0.09	0.00	0.15	0.35
NO3	-0.04	0.03	0.06	-0.01	0.00	0.02	-0.02	0.02	0.09	0.02
P Uptake	0.09	-0.04	0.09	-0.01	0.01	-0.01	-0.01	-0.02	-0.04	0.11

Manure 10t/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.01	0.01	0.01	0.13	0.07	0.09	0.12	0.01	-0.10	0.06
EC	-0.02	-0.00	-0.03	-0.16	-0.12	-0.13	-0.20	-0.06	0.28	-0.10
pH	0.01	-0.00	0.01	0.00	0.01	0.01	0.03	0.03	-0.06	0.01
Total P	0.06	0.01	0.06	0.76	0.38	0.47	0.72	0.03	-0.20	0.12
Soluble P	0.04	0.01	0.04	0.51	0.25	0.31	0.47	0.01	-0.13	0.09
Resin P	0.03	0.01	0.03	0.40	0.20	0.25	0.38	0.01	-0.12	0.07
PO4	0.06	0.01	0.06	0.85	0.40	0.51	0.76	0.00	-0.16	0.13
NH4	0.01	0.00	0.00	0.06	0.03	0.04	0.06	0.01	-0.03	0.01
NO3	-0.00	0.00	0.00	0.01	0.01	0.01	0.01	-0.00	-0.00	0.01
P Uptake	0.01	-0.00	0.01	0.06	0.03	0.04	0.06	0.01	-0.02	0.01

Willow 10t/ha

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.00	0.25	0.01	0.07	-0.04	-0.05	0.02	-0.04	-0.03	0.39
EC	-0.20	0.23	-0.01	0.03	-0.19	-0.05	0.03	0.05	0.44	-0.03
pH	-0.03	-0.04	0.01	-0.06	-0.10	-0.10	0.29	0.15	0.05	-0.04
Total P	-0.03	-0.04	0.02	-0.11	-0.19	-0.21	0.59	0.29	0.03	0.02
Soluble P	0.03	-0.04	-0.01	0.03	0.09	0.08	-0.21	-0.10	-0.05	-0.05
Resin P	0.09	-0.12	-0.00	0.01	0.14	0.09	-0.19	-0.10	-0.19	-0.04
PO4	-0.01	0.08	-0.00	0.04	0.01	0.03	-0.11	-0.06	0.03	0.07
NH4	0.00	-0.00	0.00	-0.00	-0.00	-0.01	0.02	0.01	-0.01	0.01
NO3	-0.12	0.21	-0.00	0.08	-0.12	-0.04	-0.04	-0.04	0.23	0.25
P Uptake	0.10	-0.12	0.00	-0.01	0.09	0.03	-0.03	-0.03	-0.20	0.00

Canola Meal 10t/ha & TSP

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.02	-0.04	-0.00	-0.01	0.00	0.02	0.02	-0.01	0.02	0.01
EC	0.02	-0.06	-0.01	-0.03	-0.01	0.03	0.11	-0.01	0.07	0.02
pH	-0.01	0.05	0.00	0.02	-0.01	-0.03	-0.07	0.01	-0.01	-0.01
Total P	-0.22	-0.16	0.03	-0.05	0.05	0.12	1.57	-0.07	0.11	0.02
Soluble P	0.04	-0.11	-0.01	-0.03	0.01	0.04	0.12	-0.03	0.03	0.02
Resin P	0.00	-0.02	0.00	-0.00	0.01	0.01	0.05	-0.01	-0.01	0.00
PO4	-0.04	0.07	0.01	0.02	-0.00	-0.03	-0.05	0.02	-0.03	-0.01
NH4	-0.02	0.02	0.00	0.01	0.00	-0.01	0.03	0.00	-0.01	-0.00
NO3	-0.09	0.19	0.02	0.07	-0.02	-0.11	-0.16	0.05	-0.06	-0.04
P Uptake	0.10	-0.09	-0.02	-0.04	0.00	0.04	-0.22	-0.01	0.02	0.02

Canola Hull 10t/ha & TSP

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.02	-0.09	-0.02	0.00	0.10	0.20	0.29	0.00	-0.11	0.12
EC	-0.08	0.08	0.06	0.27	0.02	0.05	0.13	-0.01	0.62	-0.11
pH	0.00	-0.00	-0.00	-0.00	0.00	0.00	0.00	0.00	-0.01	0.00
Total P	-0.13	-0.23	0.00	0.24	0.34	0.67	1.06	0.00	0.13	0.29
Soluble P	-0.09	-0.16	-0.01	0.12	0.21	0.45	0.67	0.00	0.05	0.20
Resin P	-0.04	-0.07	0.00	0.07	0.11	0.21	0.34	0.00	0.02	0.10
PO4	-0.05	-0.00	0.03	0.17	0.07	0.12	0.24	-0.00	0.27	0.00
NH4	-0.01	0.01	0.01	0.03	0.00	-0.01	0.00	-0.00	0.06	-0.02
NO3	0.02	0.07	0.01	-0.00	-0.07	-0.16	-0.23	-0.00	0.08	-0.09
P Uptake	0.03	0.02	-0.01	-0.05	-0.04	-0.09	-0.13	0.00	-0.08	-0.02

Manure 10t/ha & TSP

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.03	0.03	0.04	-0.10	-0.17	0.27	-0.08	-0.02	-0.15	0.32
EC	-0.10	-0.02	-0.02	0.05	0.27	0.17	-0.11	-0.00	0.13	-0.15
pH	0.01	-0.00	-0.00	-0.03	-0.10	-0.10	0.03	0.01	-0.00	-0.02
Total P	0.21	0.02	0.00	0.02	-0.47	-0.84	0.41	0.03	-0.11	-0.08
Soluble P	-0.28	0.01	0.05	0.44	1.83	2.26	-0.84	-0.10	0.17	0.27
Resin P	-0.04	0.05	0.04	1.12	2.69	1.83	-0.47	-0.10	0.27	-0.17
PO4	0.13	0.03	0.03	0.41	1.12	0.44	0.02	-0.03	0.05	-0.10
NH4	0.02	0.01	0.01	0.03	0.04	0.05	0.00	-0.00	-0.02	0.04
NO3	0.03	0.01	0.01	0.03	0.05	0.01	0.02	-0.00	-0.02	0.03
P Uptake	0.15	0.03	0.02	0.13	-0.04	-0.28	0.21	0.01	-0.10	0.03

Willow 10t/ha & TSP

	P Uptake	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.05	0.04	0.00	-0.08	0.02	-0.10	-0.19	0.01	-0.03	0.20
EC	-0.01	0.01	0.00	0.03	0.01	0.03	0.07	-0.00	0.02	-0.03
pH	0.00	0.01	-0.00	-0.01	-0.02	-0.02	-0.02	0.00	-0.00	0.01
Total P	0.01	-0.02	0.01	0.13	0.07	0.15	0.31	-0.02	0.07	-0.19
Soluble P	0.00	-0.03	0.00	0.07	0.08	0.09	0.15	-0.02	0.03	-0.10
Resin P	-0.04	-0.03	0.01	0.05	0.17	0.08	0.07	-0.02	0.01	0.02
PO4	0.00	-0.02	0.00	0.06	0.05	0.07	0.13	-0.01	0.03	-0.08
NH4	-0.00	0.00	0.00	0.00	0.01	0.00	0.01	-0.00	0.00	0.00
NO3	-0.02	0.03	0.00	-0.02	-0.03	-0.03	-0.02	0.01	0.01	0.04
P Uptake	0.03	-0.02	-0.00	0.00	-0.04	0.00	0.01	0.00	-0.01	-0.05

Fig. D4. *Oxbow soil covariance heat map showing the influence of residual soil factors on crop P uptake. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.*

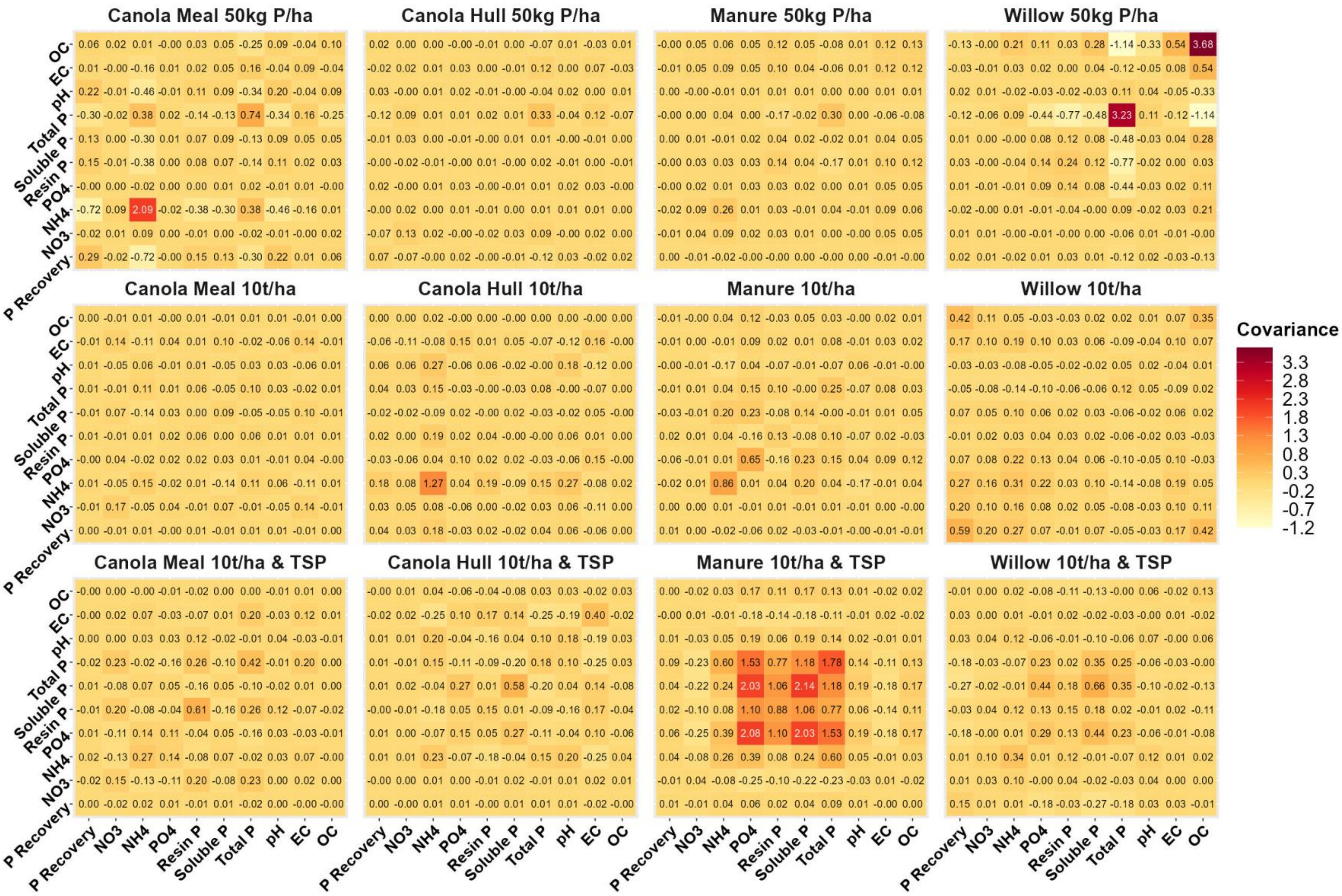
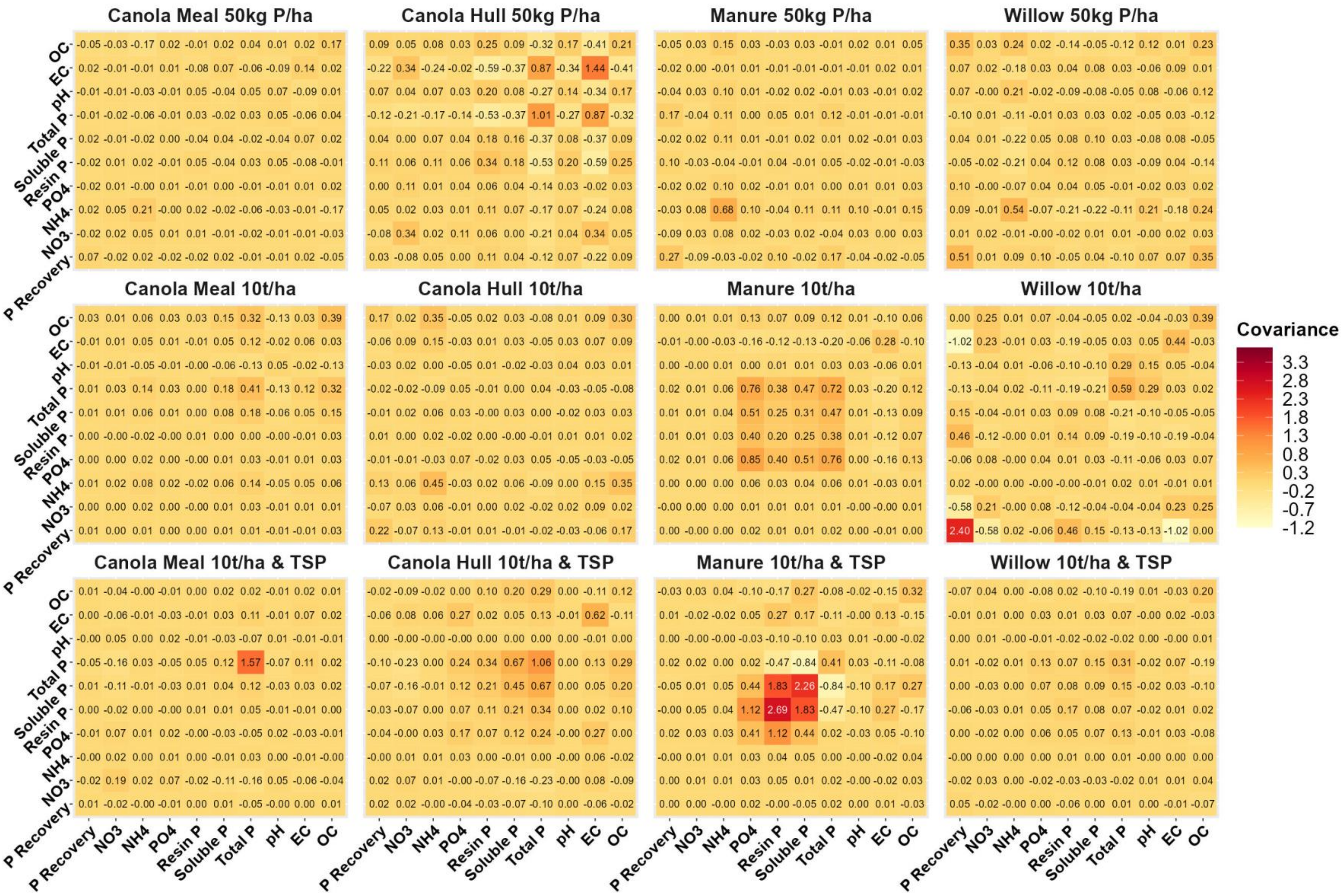


Fig. D5. Haverhill soil covariance heat map showing the influence of residual soil factors on crop P recovery. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.



Canola Meal 50kg P/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.05	-0.03	-0.17	0.02	-0.01	0.02	0.04	0.01	0.02	0.17
EC	0.02	-0.01	-0.01	0.01	-0.08	0.07	-0.06	-0.09	0.14	0.02
pH	-0.01	-0.01	-0.03	-0.01	0.05	-0.04	0.05	0.07	-0.09	0.01
Total P	-0.01	-0.02	-0.06	-0.01	0.03	-0.02	0.03	0.05	-0.06	0.04
Soluble P	0.02	-0.01	-0.02	0.00	-0.04	0.04	-0.02	-0.04	0.07	0.02
Resin P	-0.02	0.01	0.02	-0.01	0.05	-0.04	0.03	0.05	-0.08	-0.01
PO4	-0.02	0.01	-0.00	0.01	-0.01	0.00	-0.01	-0.01	0.01	0.02
NH4	0.02	0.05	0.21	-0.00	0.02	-0.02	-0.06	-0.03	-0.01	-0.17
NO3	-0.02	0.02	0.05	0.01	0.01	-0.01	-0.02	-0.01	-0.01	-0.03
P Recovery	0.07	-0.02	0.02	-0.02	-0.02	0.02	-0.01	-0.01	0.02	-0.05

Canola Hull 50kg P/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.09	0.05	0.08	0.03	0.25	0.09	-0.32	0.17	-0.41	0.21
EC	-0.22	0.34	-0.24	-0.02	-0.59	-0.37	0.87	-0.34	1.44	-0.41
pH	0.07	0.04	0.07	0.03	0.20	0.08	-0.27	0.14	-0.34	0.17
Total P	-0.12	-0.21	-0.17	-0.14	-0.53	-0.37	1.01	-0.27	0.87	-0.32
Soluble P	0.04	0.00	0.07	0.04	0.18	0.16	-0.37	0.08	-0.37	0.09
Resin P	0.11	0.06	0.11	0.06	0.34	0.18	-0.53	0.20	-0.59	0.25
PO4	0.00	0.11	0.01	0.04	0.06	0.04	-0.14	0.03	-0.02	0.03
NH4	0.05	0.02	0.03	0.01	0.11	0.07	-0.17	0.07	-0.24	0.08
NO3	-0.08	0.34	0.02	0.11	0.06	0.00	-0.21	0.04	0.34	0.05
P Recovery	0.03	-0.08	0.05	0.00	0.11	0.04	-0.12	0.07	-0.22	0.09

Manure 50kg P/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.05	0.03	0.15	0.03	-0.03	0.03	-0.01	0.02	0.01	0.05
EC	-0.02	0.00	-0.01	0.01	-0.01	-0.01	-0.01	-0.01	0.02	0.01
pH	-0.04	0.03	0.10	0.01	-0.02	0.02	-0.01	0.03	-0.01	0.02
Total P	0.17	-0.04	0.11	0.00	0.05	0.01	0.12	-0.01	-0.01	-0.01
Soluble P	-0.02	0.02	0.11	0.01	-0.01	0.02	0.01	0.02	-0.01	0.03
Resin P	0.10	-0.03	-0.04	-0.01	0.04	-0.01	0.05	-0.02	-0.01	-0.03
PO4	-0.02	0.02	0.10	0.02	-0.01	0.01	0.00	0.01	0.01	0.03
NH4	-0.03	0.08	0.68	0.10	-0.04	0.11	0.11	0.10	-0.01	0.15
NO3	-0.09	0.03	0.08	0.02	-0.03	0.02	-0.04	0.03	0.00	0.03
P Recovery	0.27	-0.09	-0.03	-0.02	0.10	-0.02	0.17	-0.04	-0.02	-0.05

Willow 50kg P/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.35	0.03	0.24	0.02	-0.14	-0.05	-0.12	0.12	0.01	0.23
EC	0.07	0.02	-0.18	0.03	0.04	0.08	0.03	-0.06	0.09	0.01
pH	0.07	-0.00	0.21	-0.02	-0.09	-0.08	-0.05	0.08	-0.06	0.12
Total P	-0.10	0.01	-0.11	-0.01	0.03	0.03	0.02	-0.05	0.03	-0.12
Soluble P	0.04	0.01	-0.22	0.05	0.08	0.10	0.03	-0.08	0.08	-0.05
Resin P	-0.05	-0.02	-0.21	0.04	0.12	0.08	0.03	-0.09	0.04	-0.14
PO4	0.10	-0.00	-0.07	0.04	0.04	0.05	-0.01	-0.02	0.03	0.02
NH4	0.09	-0.01	0.54	-0.07	-0.21	-0.22	-0.11	0.21	-0.18	0.24
NO3	0.01	0.02	-0.01	-0.00	-0.02	0.01	0.01	-0.00	0.02	0.03
P Recovery	0.51	0.01	0.09	0.10	-0.05	0.04	-0.10	0.07	0.07	0.35

Canola Meal 10t/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.03	0.01	0.06	0.03	0.03	0.15	0.32	-0.13	0.03	0.39
EC	-0.01	0.01	0.05	0.01	-0.01	0.05	0.12	-0.02	0.06	0.03
pH	-0.01	-0.01	-0.05	-0.01	-0.00	-0.06	-0.13	0.05	-0.02	-0.13
Total P	0.01	0.03	0.14	0.03	0.00	0.18	0.41	-0.13	0.12	0.32
Soluble P	0.01	0.01	0.06	0.01	0.00	0.08	0.18	-0.06	0.05	0.15
Resin P	0.00	-0.00	-0.02	-0.00	0.01	0.00	0.00	-0.00	-0.01	0.03
PO4	0.00	0.00	0.02	0.00	-0.00	0.01	0.03	-0.01	0.01	0.03
NH4	0.01	0.02	0.08	0.02	-0.02	0.06	0.14	-0.05	0.05	0.06
NO3	0.00	0.00	0.02	0.00	-0.00	0.01	0.03	-0.01	0.01	0.01
P Recovery	0.01	0.00	0.01	0.00	0.00	0.01	0.01	-0.01	-0.01	0.03

Canola Hull 10t/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.17	0.02	0.35	-0.05	0.02	0.03	-0.08	0.01	0.09	0.30
EC	-0.06	0.09	0.15	-0.03	0.01	0.03	-0.05	0.03	0.07	0.09
pH	-0.03	0.02	0.00	-0.05	0.01	-0.02	-0.03	0.04	0.03	0.01
Total P	-0.02	-0.02	-0.09	0.05	-0.01	0.00	0.04	-0.03	-0.05	-0.08
Soluble P	-0.01	0.02	0.06	0.03	-0.00	0.03	0.00	-0.02	0.03	0.03
Resin P	0.01	0.00	0.02	-0.02	0.00	-0.00	-0.01	0.01	0.01	0.02
PO4	-0.01	-0.01	-0.03	0.07	-0.02	0.03	0.05	-0.05	-0.03	-0.05
NH4	0.13	0.06	0.45	-0.03	0.02	0.06	-0.09	0.00	0.15	0.35
NO3	-0.07	0.03	0.06	-0.01	0.00	0.02	-0.02	0.02	0.09	0.02
P Recovery	0.22	-0.07	0.13	-0.01	0.01	-0.01	-0.02	-0.03	-0.06	0.17

Manure 10t/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.00	0.01	0.01	0.13	0.07	0.09	0.12	0.01	-0.10	0.06
EC	-0.01	-0.00	-0.03	-0.16	-0.12	-0.13	-0.20	-0.06	0.28	-0.10
pH	0.00	-0.00	0.01	0.00	0.01	0.01	0.03	0.03	-0.06	0.01
Total P	0.02	0.01	0.06	0.76	0.38	0.47	0.72	0.03	-0.20	0.12
Soluble P	0.01	0.01	0.04	0.51	0.25	0.31	0.47	0.01	-0.13	0.09
Resin P	0.01	0.01	0.03	0.40	0.20	0.25	0.38	0.01	-0.12	0.07
PO4	0.02	0.01	0.06	0.85	0.40	0.51	0.76	0.00	-0.16	0.13
NH4	0.00	0.00	0.00	0.06	0.03	0.04	0.06	0.01	-0.03	0.01
NO3	-0.00	0.00	0.00	0.01	0.01	0.01	0.01	-0.00	-0.00	0.01
P Recovery	0.00	-0.00	0.00	0.02	0.01	0.01	0.02	0.00	-0.01	0.00

Willow 10t/ha

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.00	0.25	0.01	0.07	-0.04	-0.05	0.02	-0.04	-0.03	0.39
EC	-1.02	0.23	-0.01	0.03	-0.19	-0.05	0.03	0.05	0.44	-0.03
pH	-0.13	-0.04	0.01	-0.06	-0.10	-0.10	0.29	0.15	0.05	-0.04
Total P	-0.13	-0.04	0.02	-0.11	-0.19	-0.21	0.59	0.29	0.03	0.02
Soluble P	0.15	-0.04	-0.01	0.03	0.09	0.08	-0.21	-0.10	-0.05	-0.05
Resin P	0.46	-0.12	-0.00	0.01	0.14	0.09	-0.19	-0.10	-0.19	-0.04
PO4	-0.06	0.08	-0.00	0.04	0.01	0.03	-0.11	-0.06	0.03	0.07
NH4	0.02	-0.00	0.00	-0.00	-0.00	-0.01	0.02	0.01	-0.01	0.01
NO3	-0.58	0.21	-0.00	0.08	-0.12	-0.04	-0.04	-0.04	0.23	0.25
P Recovery	2.40	-0.58	0.02	-0.06	0.46	0.15	-0.13	-0.13	-1.02	0.00

Canola Meal 10t/ha & TSP

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.01	-0.04	-0.00	-0.01	0.00	0.02	0.02	-0.01	0.02	0.01
EC	0.00	-0.06	-0.01	-0.03	-0.01	0.03	0.11	-0.01	0.07	0.02
pH	-0.00	0.05	0.00	0.02	-0.01	-0.03	-0.07	0.01	-0.01	-0.01
Total P	-0.05	-0.16	0.03	-0.05	0.05	0.12	1.57	-0.07	0.11	0.02
Soluble P	0.01	-0.11	-0.01	-0.03	0.01	0.04	0.12	-0.03	0.03	0.02
Resin P	0.00	-0.02	0.00	-0.00	0.01	0.01	0.05	-0.01	-0.01	0.00
PO4	-0.01	0.07	0.01	0.02	-0.00	-0.03	-0.05	0.02	-0.03	-0.01
NH4	-0.00	0.02	0.00	0.01	0.00	-0.01	0.03	0.00	-0.01	-0.00
NO3	-0.02	0.19	0.02	0.07	-0.02	-0.11	-0.16	0.05	-0.06	-0.04
P Recovery	0.01	-0.02	-0.00	-0.01	0.00	0.01	-0.05	-0.00	0.00	0.01

Canola Hull 10t/ha & TSP

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.02	-0.09	-0.02	0.00	0.10	0.20	0.29	0.00	-0.11	0.12
EC	-0.06	0.08	0.06	0.27	0.02	0.05	0.13	-0.01	0.62	-0.11
pH	0.00	-0.00	-0.00	-0.00	0.00	0.00	0.00	0.00	-0.01	0.00
Total P	-0.10	-0.23	0.00	0.24	0.34	0.67	1.06	0.00	0.13	0.29
Soluble P	-0.07	-0.16	-0.01	0.12	0.21	0.45	0.67	0.00	0.05	0.20
Resin P	-0.03	-0.07	0.00	0.07	0.11	0.21	0.34	0.00	0.02	0.10
PO4	-0.04	-0.00	0.03	0.17	0.07	0.12	0.24	-0.00	0.27	0.00
NH4	-0.00	0.01	0.01	0.03	0.00	-0.01	0.00	-0.00	0.06	-0.02
NO3	0.02	0.07	0.01	-0.00	-0.07	-0.16	-0.23	-0.00	0.08	-0.09
P Recovery	0.02	0.02	-0.00	-0.04	-0.03	-0.07	-0.10	0.00	-0.06	-0.02

Manure 10t/ha & TSP

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.03	0.03	0.04	-0.10	-0.17	0.27	-0.08	-0.02	-0.15	0.32
EC	0.01	-0.02	-0.02	0.05	0.27	0.17	-0.11	-0.00	0.13	-0.15
pH	0.00	-0.00	-0.00	-0.03	-0.10	-0.10	0.03	0.01	-0.00	-0.02
Total P	0.02	0.02	0.00	0.02	-0.47	-0.84	0.41	0.03	-0.11	-0.08
Soluble P	-0.05	0.01	0.05	0.44	1.83	2.26	-0.84	-0.10	0.17	0.27
Resin P	-0.00	0.05	0.04	1.12	2.69	1.83	-0.47	-0.10	0.27	-0.17
PO4	0.02	0.03	0.03	0.41	1.12	0.44	0.02	-0.03	0.05	-0.10
NH4	-0.00	0.01	0.01	0.03	0.04	0.05	0.00	-0.00	-0.02	0.04
NO3	0.00	0.01	0.01	0.03	0.05	0.01	0.02	-0.00	-0.02	0.03
P Recovery	0.00	0.00	-0.00	0.02	-0.00	-0.05	0.02	0.00	0.01	-0.03

Willow 10t/ha & TSP

	P Recovery	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.07	0.04	0.00	-0.08	0.02	-0.10	-0.19	0.01	-0.03	0.20
EC	-0.01	0.01	0.00	0.03	0.01	0.03	0.07	-0.00	0.02	-0.03
pH	0.00	0.01	-0.00	-0.01	-0.02	-0.02	-0.02	0.00	-0.00	0.01
Total P	0.01	-0.02	0.01	0.13	0.07	0.15	0.31	-0.02	0.07	-0.19
Soluble P	0.00	-0.03	0.00	0.07	0.08	0.09	0.15	-0.02	0.03	-0.10
Resin P	-0.06	-0.03	0.01	0.05	0.17	0.08	0.07	-0.02	0.01	0.02
PO4	0.00	-0.02	0.00	0.06	0.05	0.07	0.13	-0.01	0.03	-0.08
NH4	-0.00	0.00	0.00	0.00	0.01	0.00	0.01	-0.00	0.00	0.00
NO3	-0.02	0.03	0.00	-0.02	-0.03	-0.03	-0.02	0.01	0.01	0.04
P Recovery	0.05	-0.02	-0.00	0.00	-0.06	0.00	0.01	0.00	-0.01	-0.07

Fig. D6. Oxbow soil covariance heat map showing the influence of residual soil factors on crop P recovery. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

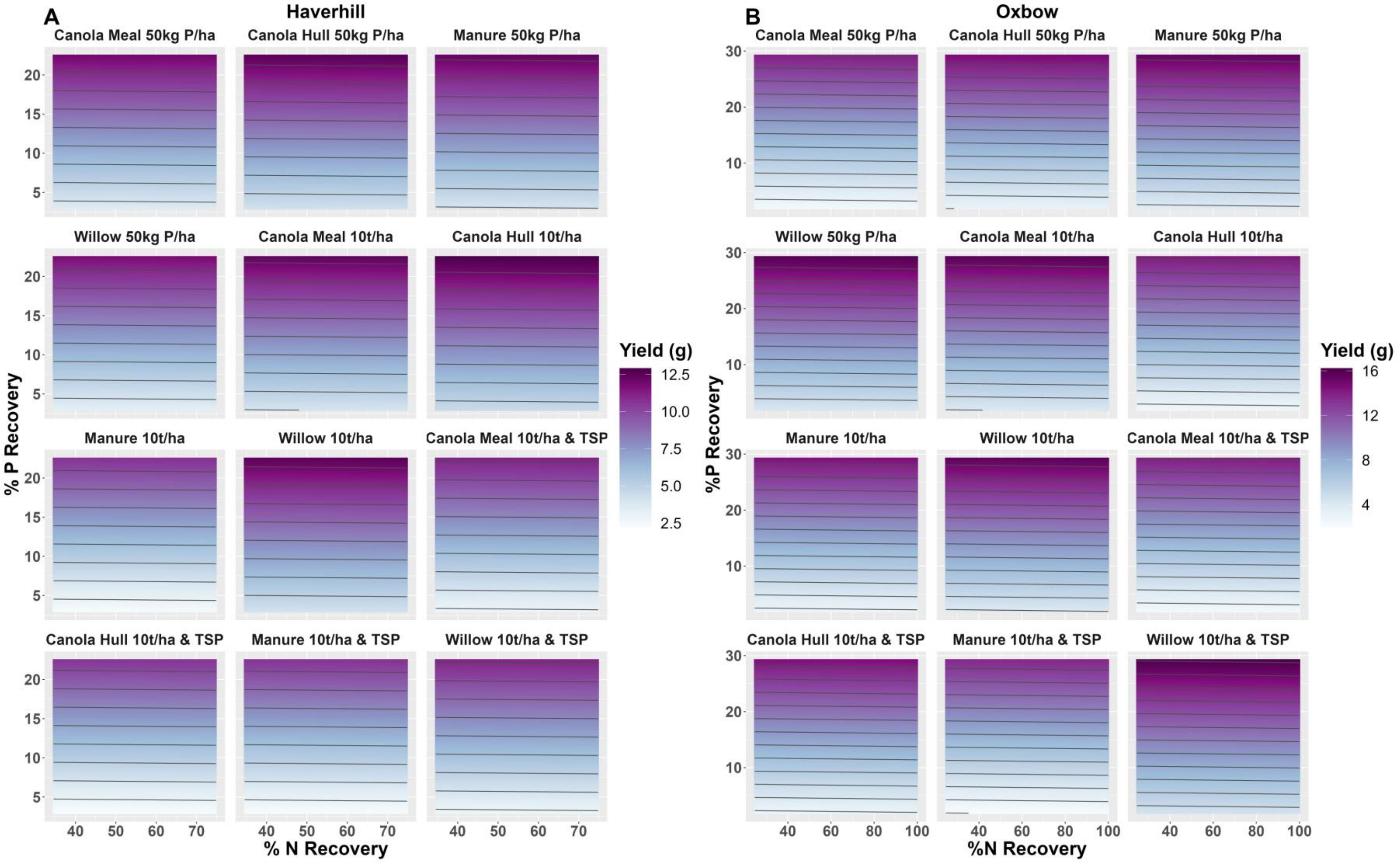
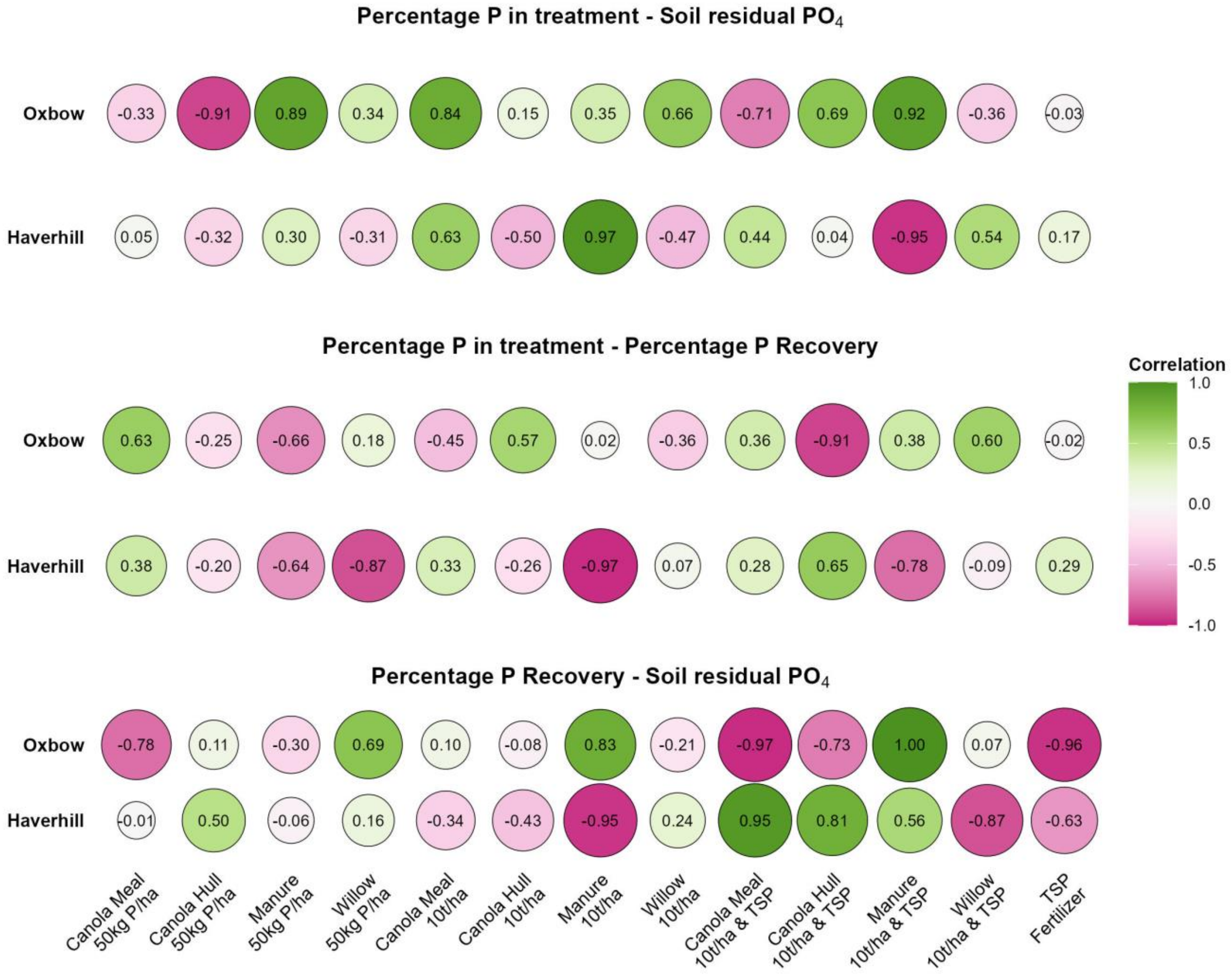


Fig. D7 The effect of the interaction between N and P recovery on canola yield in (A) Haverhill soil and (B) Oxbow soil. Darker colours indicate increased yield. Lines are set at 1g yield increments. The angle of the line indicates the relationship between N & P recovery – horizontal lines indicate no relationship, slanted down to the right indicate a positive relationship. There was almost no relationship between N and P in its effect on yield for either soil. P recovery had a much larger influence on crop yield than N recovery.

A principal component analysis (PCA) of the variables analyzed showed that for the Haverhill soil, in order and direction of influence, residual water soluble P (+) and MK extractable PO_4 (+), N uptake (+) and residual NO_3 (-) had the largest effect on yield, while for the Oxbow soil, in order and direction of influence, P uptake (+), water soluble P (+), N uptake (+) and electrical conductivity (-) had the largest effect on yield. A covariance analysis showed a very slight negative relationship between P uptake and the residual soil characteristics.

Correlations between char P, P uptake and residual P:

The addition of char was correlated with residual soil P fractions measured in the post-harvest soils and P recovery in the crop. P recovery was also correlated to the residual soil P.



Percentage P in treatment - Soil residual PO_4

	Canola Meal 50kg P/ha	Canola Hull 50kg P/ha	Manure 50kg P/ha	Willow 50kg P/ha	Canola Meal 10t/ha	Canola Hull 10t/ha	Manure 10t/ha	Willow 10t/ha	Canola Meal 10t/ha & TSP	Canola Hull 10t/ha & TSP	Manure 10t/ha & TSP	Willow 10t/ha & TSP	TSP Fertilizer
Oxbow	-0.33	-0.91	0.89	0.34	0.84	0.15	0.35	0.66	-0.71	0.69	0.92	-0.36	-0.03
Haverhill	0.05	-0.32	0.30	-0.31	0.63	-0.50	0.97	-0.47	0.44	0.04	-0.95	0.54	0.17

Percentage P in treatment - Percentage P Recovery

	Canola Meal 50kg P/ha	Canola Hull 50kg P/ha	Manure 50kg P/ha	Willow 50kg P/ha	Canola Meal 10t/ha	Canola Hull 10t/ha	Manure 10t/ha	Willow 10t/ha	Canola Meal 10t/ha & TSP	Canola Hull 10t/ha & TSP	Manure 10t/ha & TSP	Willow 10t/ha & TSP	TSP Fertilizer
Oxbow	0.63	-0.25	-0.66	0.18	-0.45	0.57	0.02	-0.36	0.36	-0.91	0.38	0.60	-0.02
Haverhill	0.38	-0.20	-0.64	-0.87	0.33	-0.26	-0.97	0.07	0.28	0.65	-0.78	-0.09	0.29

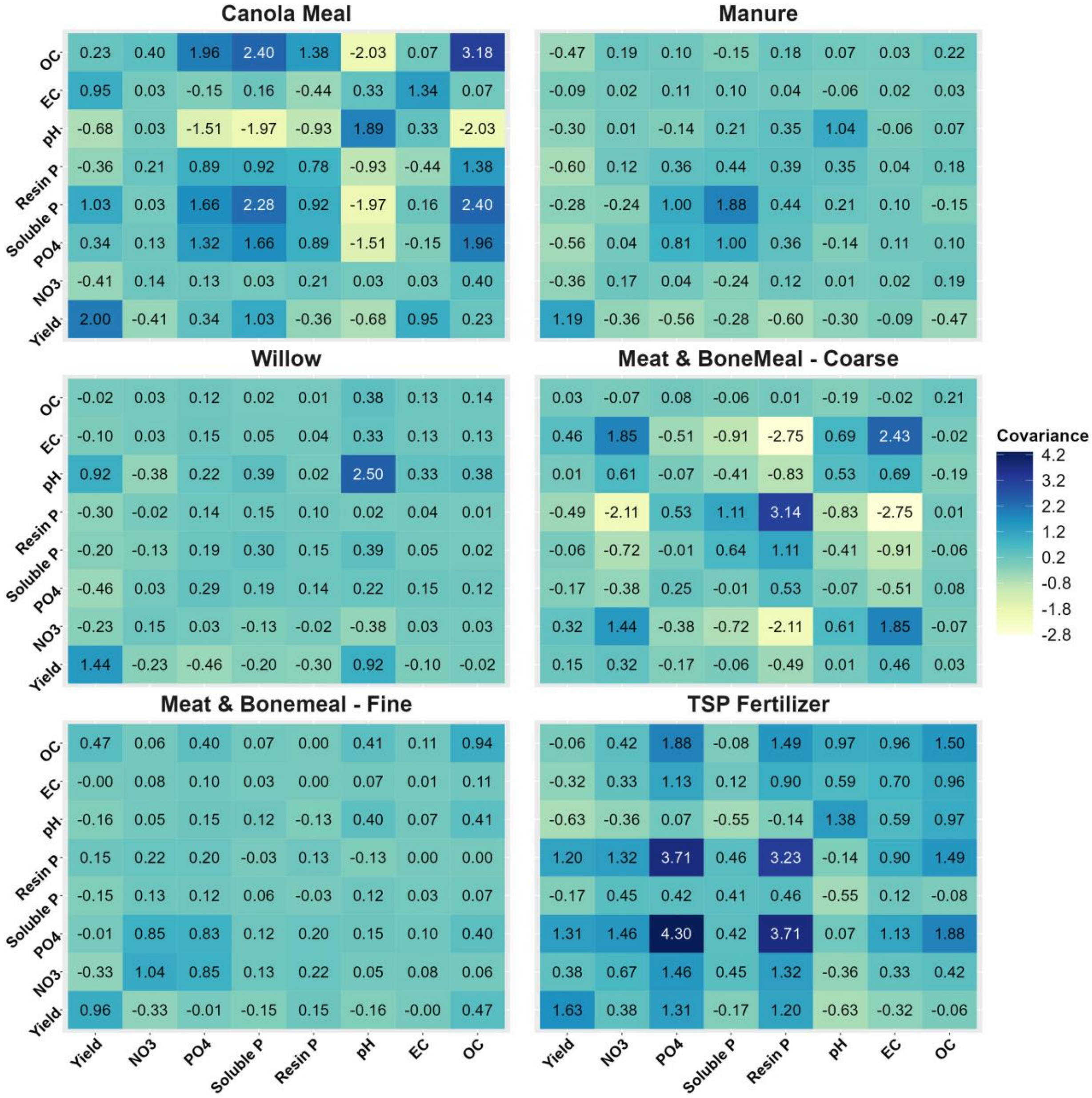
Percentage P Recovery - Soil residual PO_4

	Canola Meal 50kg P/ha	Canola Hull 50kg P/ha	Manure 50kg P/ha	Willow 50kg P/ha	Canola Meal 10t/ha	Canola Hull 10t/ha	Manure 10t/ha	Willow 10t/ha	Canola Meal 10t/ha & TSP	Canola Hull 10t/ha & TSP	Manure 10t/ha & TSP	Willow 10t/ha & TSP	TSP Fertilizer
Oxbow	-0.78	0.11	-0.30	0.69	0.10	-0.08	0.83	-0.21	-0.97	-0.73	1.00	0.07	-0.96
Haverhill	-0.01	0.50	-0.06	0.16	-0.34	-0.43	-0.95	0.24	0.95	0.81	0.56	-0.87	-0.63

Fig. D8. Correlation between the chars, residual soil PO_4 and P recovery in the Haverhill and Oxbow soils. Green indicates a positive correlation while pink indicates a negative correlation. Larger circles indicate larger correlations with |1| indicating a perfect correlation.

Wheat study

Small plot component



Canola Meal

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.23	0.40	1.96	2.40	1.38	-2.03	0.07	3.18
EC	0.95	0.03	-0.15	0.16	-0.44	0.33	1.34	0.07
pH	-0.68	0.03	-1.51	-1.97	-0.93	1.89	0.33	-2.03
Resin P	-0.36	0.21	0.89	0.92	0.78	-0.93	-0.44	1.38
Soluble P	1.03	0.03	1.66	2.28	0.92	-1.97	0.16	2.40
PO4	0.34	0.13	1.32	1.66	0.89	-1.51	-0.15	1.96
NO3	-0.41	0.14	0.13	0.03	0.21	0.03	0.03	0.40
Yield	2.00	-0.41	0.34	1.03	-0.36	-0.68	0.95	0.23

Manure

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.47	0.19	0.10	-0.15	0.18	0.07	0.03	0.22
EC	-0.09	0.02	0.11	0.10	0.04	-0.06	0.02	0.03
pH	-0.30	0.01	-0.14	0.21	0.35	1.04	-0.06	0.07
Resin P	-0.60	0.12	0.36	0.44	0.39	0.35	0.04	0.18
Soluble P	-0.28	-0.24	1.00	1.88	0.44	0.21	0.10	-0.15
PO4	-0.56	0.04	0.81	1.00	0.36	-0.14	0.11	0.10
NO3	-0.36	0.17	0.04	-0.24	0.12	0.01	0.02	0.19
Yield	1.19	-0.36	-0.56	-0.28	-0.60	-0.30	-0.09	-0.47

Willow

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.02	0.03	0.12	0.02	0.01	0.38	0.13	0.14
EC	-0.10	0.03	0.15	0.05	0.04	0.33	0.13	0.13
pH	0.92	-0.38	0.22	0.39	0.02	2.50	0.33	0.38
Resin P	-0.30	-0.02	0.14	0.15	0.10	0.02	0.04	0.01
Soluble P	-0.20	-0.13	0.19	0.30	0.15	0.39	0.05	0.02
PO4	-0.46	0.03	0.29	0.19	0.14	0.22	0.15	0.12
NO3	-0.23	0.15	0.03	-0.13	-0.02	-0.38	0.03	0.03
Yield	1.44	-0.23	-0.46	-0.20	-0.30	0.92	-0.10	-0.02

Meat & BoneMeal - Coarse

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.03	-0.07	0.08	-0.06	0.01	-0.19	-0.02	0.21
EC	0.46	1.85	-0.51	-0.91	-2.75	0.69	2.43	-0.02
pH	0.01	0.61	-0.07	-0.41	-0.83	0.53	0.69	-0.19
Resin P	-0.49	-2.11	0.53	1.11	3.14	-0.83	-2.75	0.01
Soluble P	-0.06	-0.72	-0.01	0.64	1.11	-0.41	-0.91	-0.06
PO4	-0.17	-0.38	0.25	-0.01	0.53	-0.07	-0.51	0.08
NO3	0.32	1.44	-0.38	-0.72	-2.11	0.61	1.85	-0.07
Yield	0.15	0.32	-0.17	-0.06	-0.49	0.01	0.46	0.03

Meat & Bonemeal - Fine

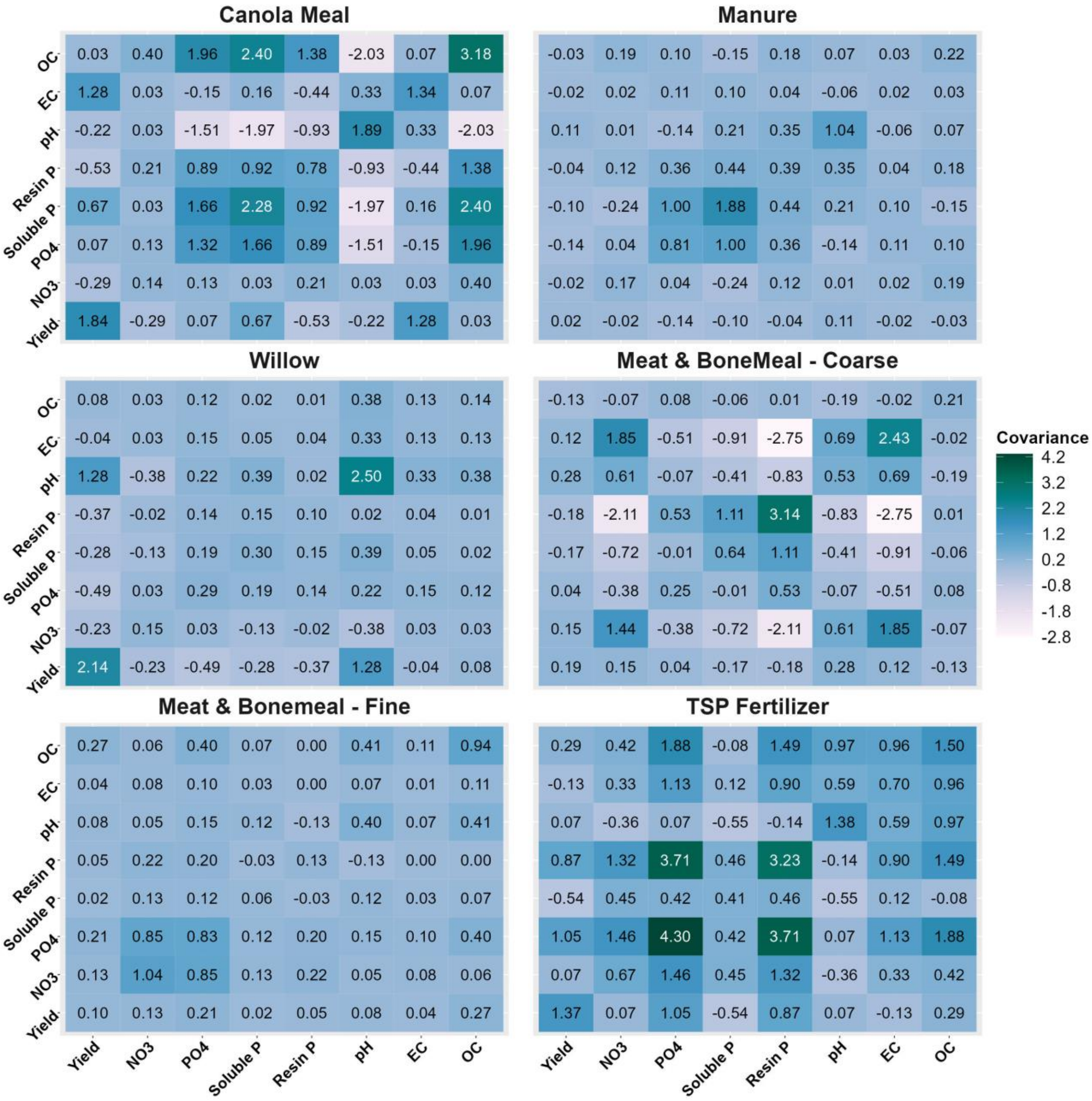
	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.47	0.06	0.40	0.07	0.00	0.41	0.11	0.94
EC	-0.00	0.08	0.10	0.03	0.00	0.07	0.01	0.11
pH	-0.16	0.05	0.15	0.12	-0.13	0.40	0.07	0.41
Resin P	0.15	0.22	0.20	-0.03	0.13	-0.13	0.00	0.00
Soluble P	-0.15	0.13	0.12	0.06	-0.03	0.12	0.03	0.07
PO4	-0.01	0.85	0.83	0.12	0.20	0.15	0.10	0.40
NO3	-0.33	1.04	0.85	0.13	0.22	0.05	0.08	0.06
Yield	0.96	-0.33	-0.01	-0.15	0.15	-0.16	-0.00	0.47

TSP Fertilizer

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.06	0.42	1.88	-0.08	1.49	0.97	0.96	1.50
EC	-0.32	0.33	1.13	0.12	0.90	0.59	0.70	0.96
pH	-0.63	-0.36	0.07	-0.55	-0.14	1.38	0.59	0.97
Resin P	1.20	1.32	3.71	0.46	3.23	-0.14	0.90	1.49
Soluble P	-0.17	0.45	0.42	0.41	0.46	-0.55	0.12	-0.08
PO4	1.31	1.46	4.30	0.42	3.71	0.07	1.13	1.88
NO3	0.38	0.67	1.46	0.45	1.32	-0.36	0.33	0.42
Yield	1.63	0.38	1.31	-0.17	1.20	-0.63	-0.32	-0.06

Fig. D9. Wheat study small plot component covariance heat map showing the influence of residual soil factors on crop yield. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship. Crop yield was severely affected by grasshoppers and the results from this covariance assessment may thus not accurately reflect the effect of the residual soil factors on yield.

A PCA of the variables analyzed showed that, in order and direction of influence, N uptake (+) and P uptake (+) (PC1) as well as EC (-) and NO_3 (-) (PC 2) had the largest effect on yield. When looking at the influence of the residual soil factors on yield for the individual treatments, other factors appear to have a stronger relationship to yield for the individual treatments.



Canola Meal

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.03	0.40	1.96	2.40	1.38	-2.03	0.07	3.18
EC	1.28	0.03	-0.15	0.16	-0.44	0.33	1.34	0.07
pH	-0.22	0.03	-1.51	-1.97	-0.93	1.89	0.33	-2.03
Resin P	-0.53	0.21	0.89	0.92	0.78	-0.93	-0.44	1.38
Soluble P	0.67	0.03	1.66	2.28	0.92	-1.97	0.16	2.40
PO4	0.07	0.13	1.32	1.66	0.89	-1.51	-0.15	1.96
NO3	-0.29	0.14	0.13	0.03	0.21	0.03	0.03	0.40
Yield	1.84	-0.29	0.07	0.67	-0.53	-0.22	1.28	0.03

Manure

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.03	0.19	0.10	-0.15	0.18	0.07	0.03	0.22
EC	-0.02	0.02	0.11	0.10	0.04	-0.06	0.02	0.03
pH	0.11	0.01	-0.14	0.21	0.35	1.04	-0.06	0.07
Resin P	-0.04	0.12	0.36	0.44	0.39	0.35	0.04	0.18
Soluble P	-0.10	-0.24	1.00	1.88	0.44	0.21	0.10	-0.15
PO4	-0.14	0.04	0.81	1.00	0.36	-0.14	0.11	0.10
NO3	-0.02	0.17	0.04	-0.24	0.12	0.01	0.02	0.19
Yield	0.02	-0.02	-0.14	-0.10	-0.04	0.11	-0.02	-0.03

Willow

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.08	0.03	0.12	0.02	0.01	0.38	0.13	0.14
EC	-0.04	0.03	0.15	0.05	0.04	0.33	0.13	0.13
pH	1.28	-0.38	0.22	0.39	0.02	2.50	0.33	0.38
Resin P	-0.37	-0.02	0.14	0.15	0.10	0.02	0.04	0.01
Soluble P	-0.28	-0.13	0.19	0.30	0.15	0.39	0.05	0.02
PO4	-0.49	0.03	0.29	0.19	0.14	0.22	0.15	0.12
NO3	-0.23	0.15	0.03	-0.13	-0.02	-0.38	0.03	0.03
Yield	2.14	-0.23	-0.49	-0.28	-0.37	1.28	-0.04	0.08

Meat & BoneMeal - Coarse

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.13	-0.07	0.08	-0.06	0.01	-0.19	-0.02	0.21
EC	0.12	1.85	-0.51	-0.91	-2.75	0.69	2.43	-0.02
pH	0.28	0.61	-0.07	-0.41	-0.83	0.53	0.69	-0.19
Resin P	-0.18	-2.11	0.53	1.11	3.14	-0.83	-2.75	0.01
Soluble P	-0.17	-0.72	-0.01	0.64	1.11	-0.41	-0.91	-0.06
PO4	0.04	-0.38	0.25	-0.01	0.53	-0.07	-0.51	0.08
NO3	0.15	1.44	-0.38	-0.72	-2.11	0.61	1.85	-0.07
Yield	0.19	0.15	0.04	-0.17	-0.18	0.28	0.12	-0.13

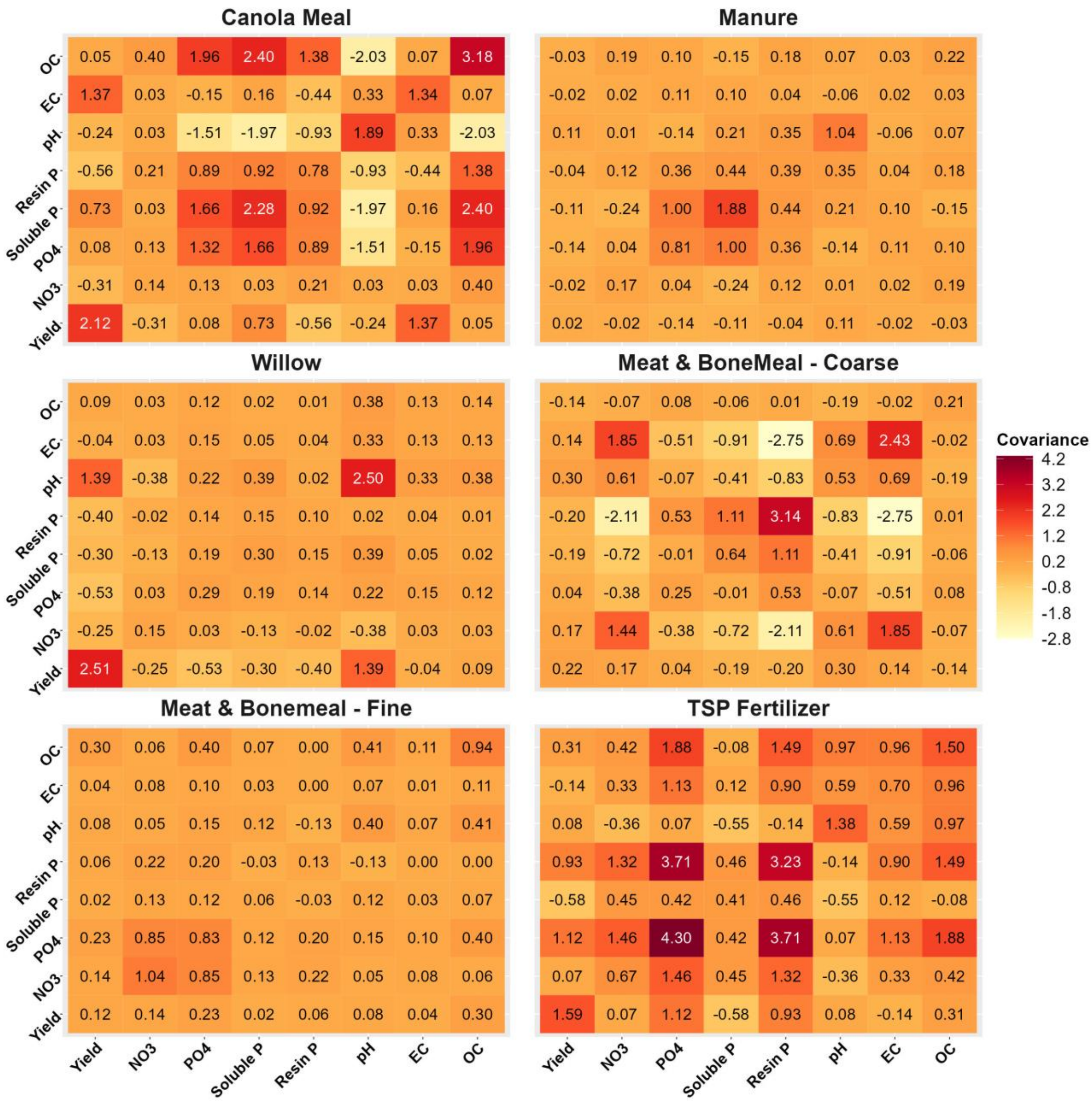
Meat & Bonemeal - Fine

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.27	0.06	0.40	0.07	0.00	0.41	0.11	0.94
EC	0.04	0.08	0.10	0.03	0.00	0.07	0.01	0.11
pH	0.08	0.05	0.15	0.12	-0.13	0.40	0.07	0.41
Resin P	0.05	0.22	0.20	-0.03	0.13	-0.13	0.00	0.00
Soluble P	0.02	0.13	0.12	0.06	-0.03	0.12	0.03	0.07
PO4	0.21	0.85	0.83	0.12	0.20	0.15	0.10	0.40
NO3	0.13	1.04	0.85	0.13	0.22	0.05	0.08	0.06
Yield	0.10	0.13	0.21	0.02	0.05	0.08	0.04	0.27

TSP Fertilizer

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.29	0.42	1.88	-0.08	1.49	0.97	0.96	1.50
EC	-0.13	0.33	1.13	0.12	0.90	0.59	0.70	0.96
pH	0.07	-0.36	0.07	-0.55	-0.14	1.38	0.59	0.97
Resin P	0.87	1.32	3.71	0.46	3.23	-0.14	0.90	1.49
Soluble P	-0.54	0.45	0.42	0.41	0.46	-0.55	0.12	-0.08
PO4	1.05	1.46	4.30	0.42	3.71	0.07	1.13	1.88
NO3	0.07	0.67	1.46	0.45	1.32	-0.36	0.33	0.42
Yield	1.37	0.07	1.05	-0.54	0.87	0.07	-0.13	0.29

Fig. D10. Wheat study small plot component covariance heat map showing the influence of residual soil factors on crop P uptake. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship. Crop yield was severely affected by grasshoppers and the results from this covariance assessment may thus not accurately reflect the effect of the residual soil factors on P uptake.


Canola Meal

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.05	0.40	1.96	2.40	1.38	-2.03	0.07	3.18
EC	1.37	0.03	-0.15	0.16	-0.44	0.33	1.34	0.07
pH	-0.24	0.03	-1.51	-1.97	-0.93	1.89	0.33	-2.03
Resin P	-0.56	0.21	0.89	0.92	0.78	-0.93	-0.44	1.38
Soluble P	0.73	0.03	1.66	2.28	0.92	-1.97	0.16	2.40
PO4	0.08	0.13	1.32	1.66	0.89	-1.51	-0.15	1.96
NO3	-0.31	0.14	0.13	0.03	0.21	0.03	0.03	0.40
Yield	2.12	-0.31	0.08	0.73	-0.56	-0.24	1.37	0.05

Manure

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.03	0.19	0.10	-0.15	0.18	0.07	0.03	0.22
EC	-0.02	0.02	0.11	0.10	0.04	-0.06	0.02	0.03
pH	0.11	0.01	-0.14	0.21	0.35	1.04	-0.06	0.07
Resin P	-0.04	0.12	0.36	0.44	0.39	0.35	0.04	0.18
Soluble P	-0.11	-0.24	1.00	1.88	0.44	0.21	0.10	-0.15
PO4	-0.14	0.04	0.81	1.00	0.36	-0.14	0.11	0.10
NO3	-0.02	0.17	0.04	-0.24	0.12	0.01	0.02	0.19
Yield	0.02	-0.02	-0.14	-0.11	-0.04	0.11	-0.02	-0.03

Willow

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.09	0.03	0.12	0.02	0.01	0.38	0.13	0.14
EC	-0.04	0.03	0.15	0.05	0.04	0.33	0.13	0.13
pH	1.39	-0.38	0.22	0.39	0.02	2.50	0.33	0.38
Resin P	-0.40	-0.02	0.14	0.15	0.10	0.02	0.04	0.01
Soluble P	-0.30	-0.13	0.19	0.30	0.15	0.39	0.05	0.02
PO4	-0.53	0.03	0.29	0.19	0.14	0.22	0.15	0.12
NO3	-0.25	0.15	0.03	-0.13	-0.02	-0.38	0.03	0.03
Yield	2.51	-0.25	-0.53	-0.30	-0.40	1.39	-0.04	0.09

Meat & BoneMeal - Coarse

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	-0.14	-0.07	0.08	-0.06	0.01	-0.19	-0.02	0.21
EC	0.14	1.85	-0.51	-0.91	-2.75	0.69	2.43	-0.02
pH	0.30	0.61	-0.07	-0.41	-0.83	0.53	0.69	-0.19
Resin P	-0.20	-2.11	0.53	1.11	3.14	-0.83	-2.75	0.01
Soluble P	-0.19	-0.72	-0.01	0.64	1.11	-0.41	-0.91	-0.06
PO4	0.04	-0.38	0.25	-0.01	0.53	-0.07	-0.51	0.08
NO3	0.17	1.44	-0.38	-0.72	-2.11	0.61	1.85	-0.07
Yield	0.22	0.17	0.04	-0.19	-0.20	0.30	0.14	-0.14

Meat & Bonemeal - Fine

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.30	0.06	0.40	0.07	0.00	0.41	0.11	0.94
EC	0.04	0.08	0.10	0.03	0.00	0.07	0.01	0.11
pH	0.08	0.05	0.15	0.12	-0.13	0.40	0.07	0.41
Resin P	0.06	0.22	0.20	-0.03	0.13	-0.13	0.00	0.00
Soluble P	0.02	0.13	0.12	0.06	-0.03	0.12	0.03	0.07
PO4	0.23	0.85	0.83	0.12	0.20	0.15	0.10	0.40
NO3	0.14	1.04	0.85	0.13	0.22	0.05	0.08	0.06
Yield	0.12	0.14	0.23	0.02	0.06	0.08	0.04	0.30

TSP Fertilizer

	Yield	NO3	PO4	Soluble P	Resin P	pH	EC	OC
OC	0.31	0.42	1.88	-0.08	1.49	0.97	0.96	1.50
EC	-0.14	0.33	1.13	0.12	0.90	0.59	0.70	0.96
pH	0.08	-0.36	0.07	-0.55	-0.14	1.38	0.59	0.97
Resin P	0.93	1.32	3.71	0.46	3.23	-0.14	0.90	1.49
Soluble P	-0.58	0.45	0.42	0.41	0.46	-0.55	0.12	-0.08
PO4	1.12	1.46	4.30	0.42	3.71	0.07	1.13	1.88
NO3	0.07	0.67	1.46	0.45	1.32	-0.36	0.33	0.42
Yield	1.59	0.07	1.12	-0.58	0.93	0.08	-0.14	0.31

Fig. D11. Wheat study small plot component covariance heat map showing the influence of residual soil factors on crop P recovery. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship. Crop yield was severely affected by grasshoppers and the results from this covariance assessment may thus not accurately reflect the effect of the residual soil factors on P recovery.

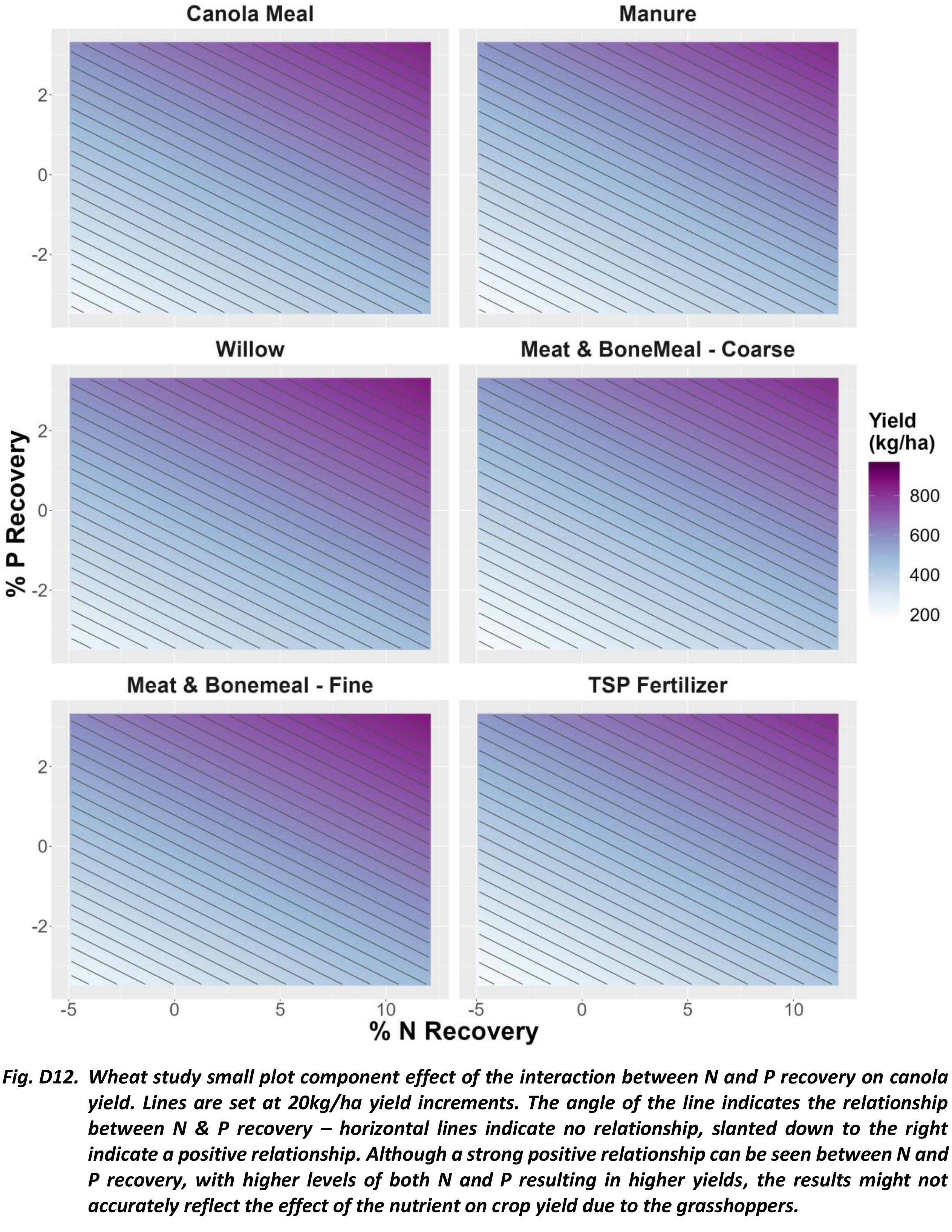


Fig. D12. Wheat study small plot component effect of the interaction between N and P recovery on canola yield. Lines are set at 20kg/ha yield increments. The angle of the line indicates the relationship between N & P recovery – horizontal lines indicate no relationship, slanted down to the right indicate a positive relationship. Although a strong positive relationship can be seen between N and P recovery, with higher levels of both N and P resulting in higher yields, the results might not accurately reflect the effect of the nutrient on crop yield due to the grasshoppers.

Correlations between char P, P uptake and residual P:

Although there were no statistically significant differences between residual PO_4 levels in the post-harvest soil, a correlation was done between the chars' P content and residual soil PO_4, P levels in the char and P recovery in the crop as well as P recovery and residual soil PO_4 (Fig. B1). The P content of the chars in all treatments except willow char (lowest P content) and the MBMA fine fraction (highest P content) were negatively correlated to the residual PO_4, indicating that the majority of the chars resulted in immobilization of P in the soil, with the TSP fertilizer showing the highest levels of immobilization. This is very different to what was seen in the canola study, where most chars resulted in increased PO_4 availability. All chars showed a negative correlation, indicating that increased levels of P in the chars resulted in decreased uptake, and likely decreased availability of P during the growing season. There doesn't appear to be a definitive relationship between the P recovery and the soil residual PO_4, likely as a result of the grasshoppers.

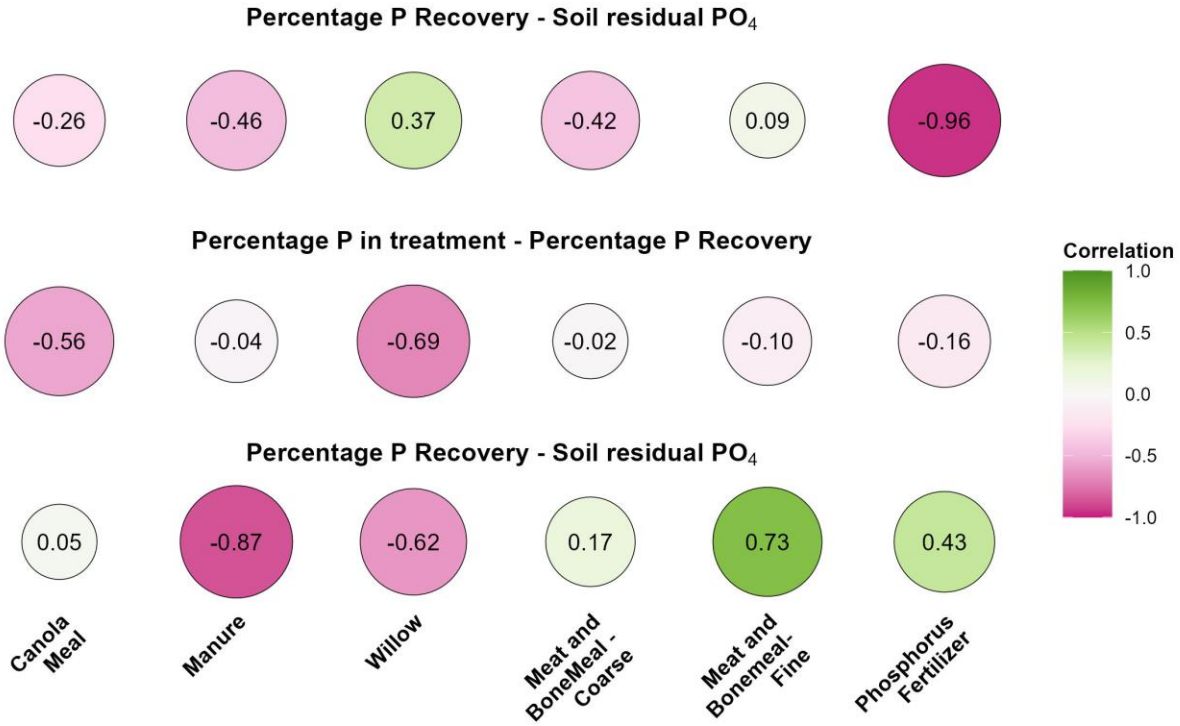
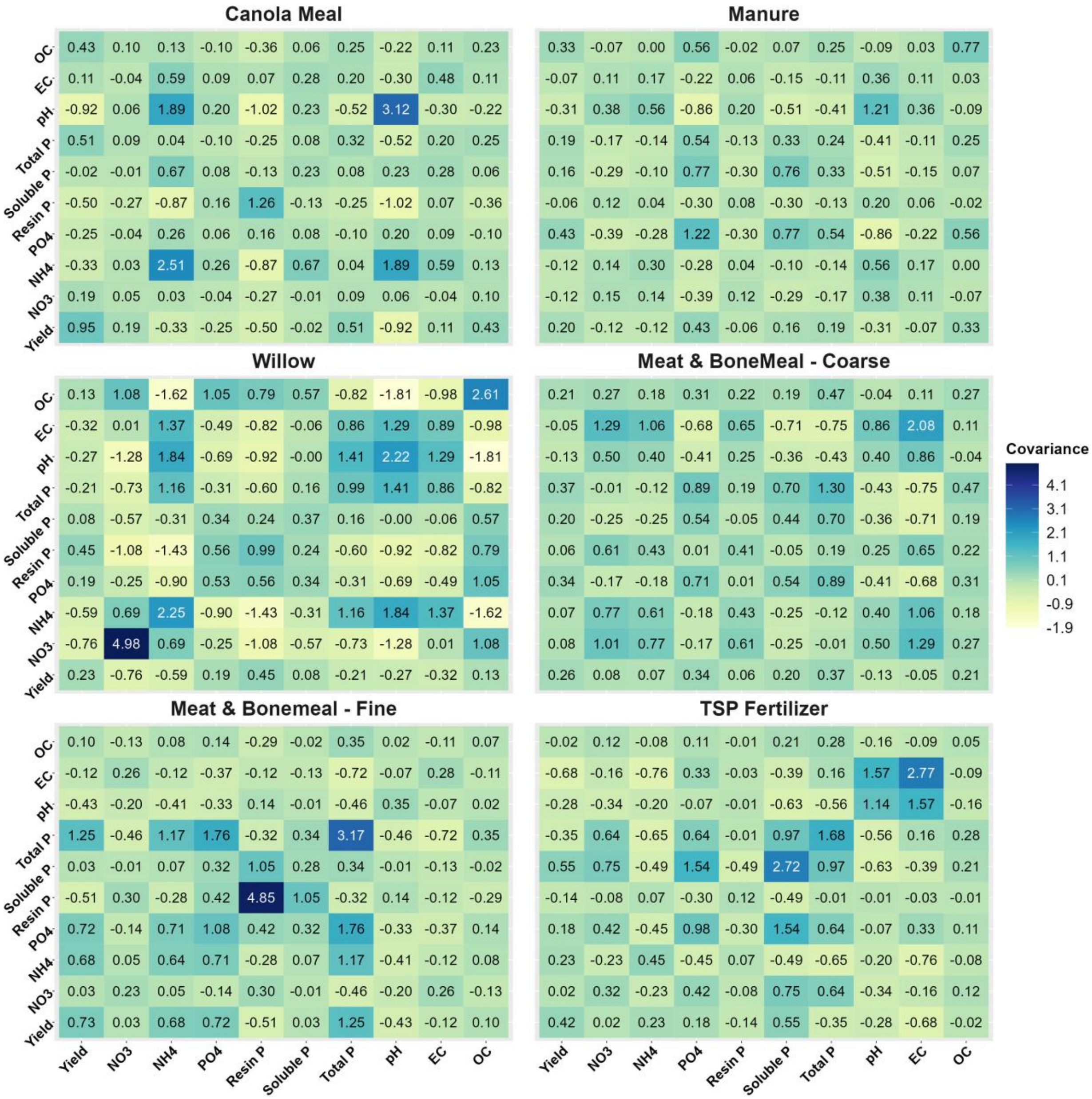


Fig. D13. Wheat study small plot component correlation between the chars, residual soil PO_4 and P recovery. Green indicates a positive correlation while pink indicates a negative correlation. Larger circles indicate larger correlations with |1| indicating a perfect correlation. Correlations including phosphorus uptake may not be meaningful due to the effect of the grasshoppers on the crop biomass and related P losses (see Section 3.4.2.1 of this thesis).

Controlled environment component



Canola Meal

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.43	0.10	0.13	-0.10	-0.36	0.06	0.25	-0.22	0.11	0.23
EC	0.11	-0.04	0.59	0.09	0.07	0.28	0.20	-0.30	0.48	0.11
pH	-0.92	0.06	1.89	0.20	-1.02	0.23	-0.52	3.12	-0.30	-0.22
Total P	0.51	0.09	0.04	-0.10	-0.25	0.08	0.32	-0.52	0.20	0.25
Soluble P	-0.02	-0.01	0.67	0.08	-0.13	0.23	0.08	0.23	0.28	0.06
Resin P	-0.50	-0.27	-0.87	0.16	1.26	-0.13	-0.25	-1.02	0.07	-0.36
PO4	-0.25	-0.04	0.26	0.06	0.16	0.08	-0.10	0.20	0.09	-0.10
NH4	-0.33	0.03	2.51	0.26	-0.87	0.67	0.04	1.89	0.59	0.13
NO3	0.19	0.05	0.03	-0.04	-0.27	-0.01	0.09	0.06	-0.04	0.10
Yield	0.95	0.19	-0.33	-0.25	-0.50	-0.02	0.51	-0.92	0.11	0.43

Manure

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.33	-0.07	0.00	0.56	-0.02	0.07	0.25	-0.09	0.03	0.77
EC	-0.07	0.11	0.17	-0.22	0.06	-0.15	-0.11	0.36	0.11	0.03
pH	-0.31	0.38	0.56	-0.86	0.20	-0.51	-0.41	1.21	0.36	-0.09
Total P	0.19	-0.17	-0.14	0.54	-0.13	0.33	0.24	-0.41	-0.11	0.25
Soluble P	0.16	-0.29	-0.10	0.77	-0.30	0.76	0.33	-0.51	-0.15	0.07
Resin P	-0.06	0.12	0.04	-0.30	0.08	-0.30	-0.13	0.20	0.06	-0.02
PO4	0.43	-0.39	-0.28	1.22	-0.30	0.77	0.54	-0.86	-0.22	0.56
NH4	-0.12	0.14	0.30	-0.28	0.04	-0.10	-0.14	0.56	0.17	0.00
NO3	-0.12	0.15	0.14	-0.39	0.12	-0.29	-0.17	0.38	0.11	-0.07
Yield	0.20	-0.12	-0.12	0.43	-0.06	0.16	0.19	-0.31	-0.07	0.33

Willow

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.13	1.08	-1.62	1.05	0.79	0.57	-0.82	-1.81	-0.98	2.61
EC	-0.32	0.01	1.37	-0.49	-0.82	-0.06	0.86	1.29	0.89	-0.98
pH	-0.27	-1.28	1.84	-0.69	-0.92	-0.00	1.41	2.22	1.29	-1.81
Total P	-0.21	-0.73	1.16	-0.31	-0.60	0.16	0.99	1.41	0.86	-0.82
Soluble P	0.08	-0.57	-0.31	0.34	0.24	0.37	0.16	-0.00	-0.06	0.57
Resin P	0.45	-1.08	-1.43	0.56	0.99	0.24	-0.60	-0.92	-0.82	0.79
PO4	0.19	-0.25	-0.90	0.53	0.56	0.34	-0.31	-0.69	-0.49	1.05
NH4	-0.59	0.69	2.25	-0.90	-1.43	-0.31	1.16	1.84	1.37	-1.62
NO3	-0.76	4.98	0.69	-0.25	-1.08	-0.57	-0.73	-1.28	0.01	1.08
Yield	0.23	-0.76	-0.59	0.19	0.45	0.08	-0.21	-0.27	-0.32	0.13

Meat & BoneMeal - Coarse

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.21	0.27	0.18	0.31	0.22	0.19	0.47	-0.04	0.11	0.27
EC	-0.05	1.29	1.06	-0.68	0.65	-0.71	-0.75	0.86	2.08	0.11
pH	-0.13	0.50	0.40	-0.41	0.25	-0.36	-0.43	0.40	0.86	-0.04
Total P	0.37	-0.01	-0.12	0.89	0.19	0.70	1.30	-0.43	-0.75	0.47
Soluble P	0.20	-0.25	-0.25	0.54	-0.05	0.44	0.70	-0.36	-0.71	0.19
Resin P	0.06	0.61	0.43	0.01	0.41	-0.05	0.19	0.25	0.65	0.22
PO4	0.34	-0.17	-0.18	0.71	0.01	0.54	0.89	-0.41	-0.68	0.31
NH4	0.07	0.77	0.61	-0.18	0.43	-0.25	-0.12	0.40	1.06	0.18
NO3	0.08	1.01	0.77	-0.17	0.61	-0.25	-0.01	0.50	1.29	0.27
Yield	0.26	0.08	0.07	0.34	0.06	0.20	0.37	-0.13	-0.05	0.21

Meat & Bonemeal - Fine

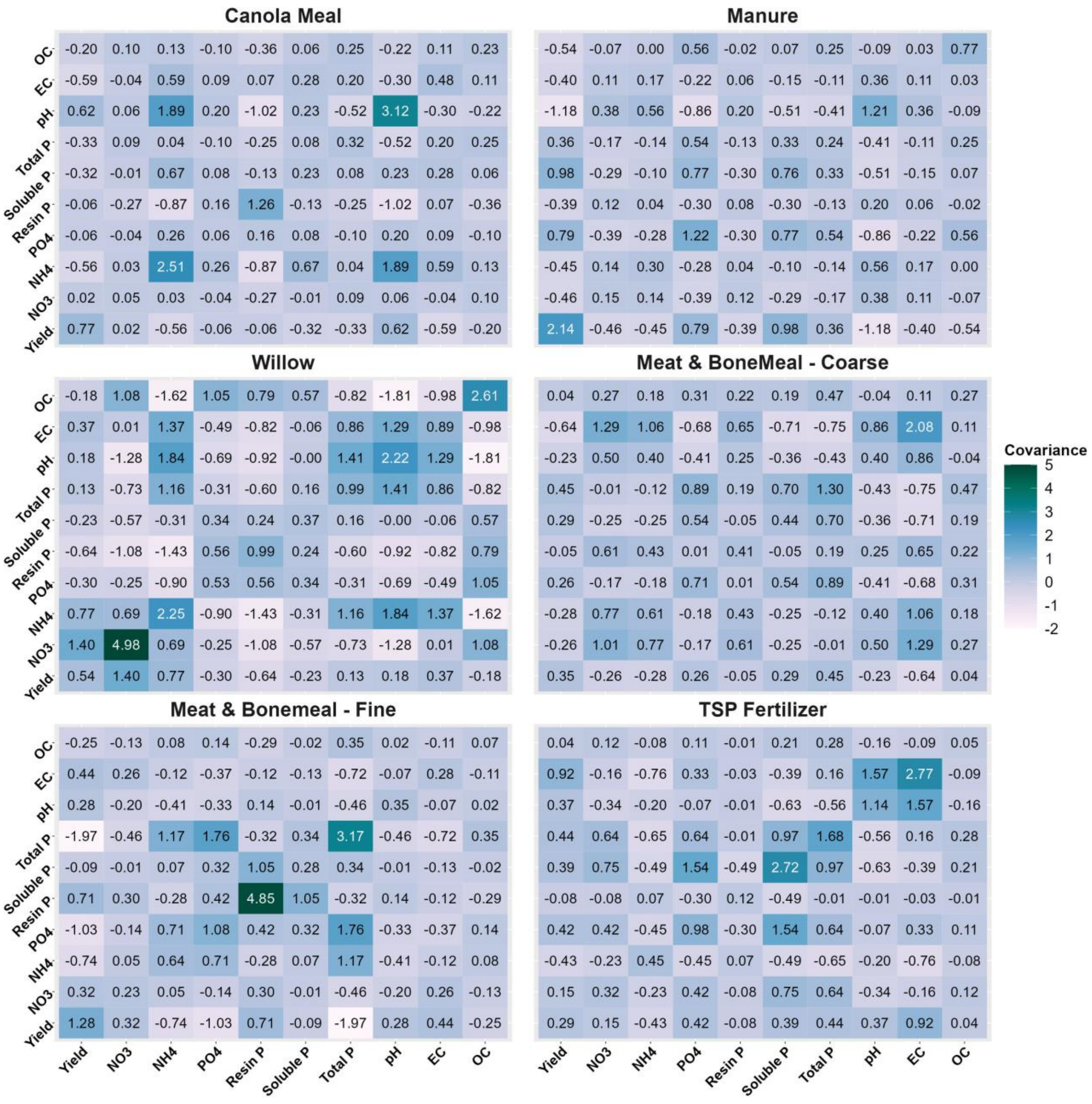
	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.10	-0.13	0.08	0.14	-0.29	-0.02	0.35	0.02	-0.11	0.07
EC	-0.12	0.26	-0.12	-0.37	-0.12	-0.13	-0.72	-0.07	0.28	-0.11
pH	-0.43	-0.20	-0.41	-0.33	0.14	-0.01	-0.46	0.35	-0.07	0.02
Total P	1.25	-0.46	1.17	1.76	-0.32	0.34	3.17	-0.46	-0.72	0.35
Soluble P	0.03	-0.01	0.07	0.32	1.05	0.28	0.34	-0.01	-0.13	-0.02
Resin P	-0.51	0.30	-0.28	0.42	4.85	1.05	-0.32	0.14	-0.12	-0.29
PO4	0.72	-0.14	0.71	1.08	0.42	0.32	1.76	-0.33	-0.37	0.14
NH4	0.68	0.05	0.64	0.71	-0.28	0.07	1.17	-0.41	-0.12	0.08
NO3	0.03	0.23	0.05	-0.14	0.30	-0.01	-0.46	-0.20	0.26	-0.13
Yield	0.73	0.03	0.68	0.72	-0.51	0.03	1.25	-0.43	-0.12	0.10

TSP Fertilizer

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.02	0.12	-0.08	0.11	-0.01	0.21	0.28	-0.16	-0.09	0.05
EC	-0.68	-0.16	-0.76	0.33	-0.03	-0.39	0.16	1.57	2.77	-0.09
pH	-0.28	-0.34	-0.20	-0.07	-0.01	-0.63	-0.56	1.14	1.57	-0.16
Total P	-0.35	0.64	-0.65	0.64	-0.01	0.97	1.68	-0.56	0.16	0.28
Soluble P	0.55	0.75	-0.49	1.54	-0.49	2.72	0.97	-0.63	-0.39	0.21
Resin P	-0.14	-0.08	0.07	-0.30	0.12	-0.49	-0.01	-0.01	-0.03	-0.01
PO4	0.18	0.42	-0.45	0.98	-0.30	1.54	0.64	-0.07	0.33	0.11
NH4	0.23	-0.23	0.45	-0.45	0.07	-0.49	-0.65	-0.20	-0.76	-0.08
NO3	0.02	0.32	-0.23	0.42	-0.08	0.75	0.64	-0.34	-0.16	0.12
Yield	0.42	0.02	0.23	0.18	-0.14	0.55	-0.35	-0.28	-0.68	-0.02

Fig. D14. Covariance heat map for the controlled environment component of the wheat study showing the influence of residual soil factors on crop yield. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

The PCA of the residual soil variables showed, in order and direction of influence that NH4-N (+)and PO_4 (+) (PC 1) and Resin P (-) (PC2) had the largest influence on yield.



Canola Meal

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.20	0.10	0.13	-0.10	-0.36	0.06	0.25	-0.22	0.11	0.23
EC	-0.59	-0.04	0.59	0.09	0.07	0.28	0.20	-0.30	0.48	0.11
pH	0.62	0.06	1.89	0.20	-1.02	0.23	-0.52	3.12	-0.30	-0.22
Total P	-0.33	0.09	0.04	-0.10	-0.25	0.08	0.32	-0.52	0.20	0.25
Soluble P	-0.32	-0.01	0.67	0.08	-0.13	0.23	0.08	0.23	0.28	0.06
Resin P	-0.06	-0.27	-0.87	0.16	1.26	-0.13	-0.25	-1.02	0.07	-0.36
PO4	-0.06	-0.04	0.26	0.06	0.16	0.08	-0.10	0.20	0.09	-0.10
NH4	-0.56	0.03	2.51	0.26	-0.87	0.67	0.04	1.89	0.59	0.13
NO3	0.02	0.05	0.03	-0.04	-0.27	-0.01	0.09	0.06	-0.04	0.10
Yield	0.77	0.02	-0.56	-0.06	-0.06	-0.32	-0.33	0.62	-0.59	-0.20

Manure

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.54	-0.07	0.00	0.56	-0.02	0.07	0.25	-0.09	0.03	0.77
EC	-0.40	0.11	0.17	-0.22	0.06	-0.15	-0.11	0.36	0.11	0.03
pH	-1.18	0.38	0.56	-0.86	0.20	-0.51	-0.41	1.21	0.36	-0.09
Total P	0.36	-0.17	-0.14	0.54	-0.13	0.33	0.24	-0.41	-0.11	0.25
Soluble P	0.98	-0.29	-0.10	0.77	-0.30	0.76	0.33	-0.51	-0.15	0.07
Resin P	-0.39	0.12	0.04	-0.30	0.08	-0.30	-0.13	0.20	0.06	-0.02
PO4	0.79	-0.39	-0.28	1.22	-0.30	0.77	0.54	-0.86	-0.22	0.56
NH4	-0.45	0.14	0.30	-0.28	0.04	-0.10	-0.14	0.56	0.17	0.00
NO3	-0.46	0.15	0.14	-0.39	0.12	-0.29	-0.17	0.38	0.11	-0.07
Yield	2.14	-0.46	-0.45	0.79	-0.39	0.98	0.36	-1.18	-0.40	-0.54

Willow

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.18	1.08	-1.62	1.05	0.79	0.57	-0.82	-1.81	-0.98	2.61
EC	0.37	0.01	1.37	-0.49	-0.82	-0.06	0.86	1.29	0.89	-0.98
pH	0.18	-1.28	1.84	-0.69	-0.92	-0.00	1.41	2.22	1.29	-1.81
Total P	0.13	-0.73	1.16	-0.31	-0.60	0.16	0.99	1.41	0.86	-0.82
Soluble P	-0.23	-0.57	-0.31	0.34	0.24	0.37	0.16	-0.00	-0.06	0.57
Resin P	-0.64	-1.08	-1.43	0.56	0.99	0.24	-0.60	-0.92	-0.82	0.79
PO4	-0.30	-0.25	-0.90	0.53	0.56	0.34	-0.31	-0.69	-0.49	1.05
NH4	0.77	0.69	2.25	-0.90	-1.43	-0.31	1.16	1.84	1.37	-1.62
NO3	1.40	4.98	0.69	-0.25	-1.08	-0.57	-0.73	-1.28	0.01	1.08
Yield	0.54	1.40	0.77	-0.30	-0.64	-0.23	0.13	0.18	0.37	-0.18

Meat & BoneMeal - Coarse

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.04	0.27	0.18	0.31	0.22	0.19	0.47	-0.04	0.11	0.27
EC	-0.64	1.29	1.06	-0.68	0.65	-0.71	-0.75	0.86	2.08	0.11
pH	-0.23	0.50	0.40	-0.41	0.25	-0.36	-0.43	0.40	0.86	-0.04
Total P	0.45	-0.01	-0.12	0.89	0.19	0.70	1.30	-0.43	-0.75	0.47
Soluble P	0.29	-0.25	-0.25	0.54	-0.05	0.44	0.70	-0.36	-0.71	0.19
Resin P	-0.05	0.61	0.43	0.01	0.41	-0.05	0.19	0.25	0.65	0.22
PO4	0.26	-0.17	-0.18	0.71	0.01	0.54	0.89	-0.41	-0.68	0.31
NH4	-0.28	0.77	0.61	-0.18	0.43	-0.25	-0.12	0.40	1.06	0.18
NO3	-0.26	1.01	0.77	-0.17	0.61	-0.25	-0.01	0.50	1.29	0.27
Yield	0.35	-0.26	-0.28	0.26	-0.05	0.29	0.45	-0.23	-0.64	0.04

Meat & Bonemeal - Fine

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	-0.25	-0.13	0.08	0.14	-0.29	-0.02	0.35	0.02	-0.11	0.07
EC	0.44	0.26	-0.12	-0.37	-0.12	-0.13	-0.72	-0.07	0.28	-0.11
pH	0.28	-0.20	-0.41	-0.33	0.14	-0.01	-0.46	0.35	-0.07	0.02
Total P	-1.97	-0.46	1.17	1.76	-0.32	0.34	3.17	-0.46	-0.72	0.35
Soluble P	-0.09	-0.01	0.07	0.32	1.05	0.28	0.34	-0.01	-0.13	-0.02
Resin P	0.71	0.30	-0.28	0.42	4.85	1.05	-0.32	0.14	-0.12	-0.29
PO4	-1.03	-0.14	0.71	1.08	0.42	0.32	1.76	-0.33	-0.37	0.14
NH4	-0.74	0.05	0.64	0.71	-0.28	0.07	1.17	-0.41	-0.12	0.08
NO3	0.32	0.23	0.05	-0.14	0.30	-0.01	-0.46	-0.20	0.26	-0.13
Yield	1.28	0.32	-0.74	-1.03	0.71	-0.09	-1.97	0.28	0.44	-0.25

TSP Fertilizer

	Yield	NO3	NH4	PO4	Resin P	Soluble P	Total P	pH	EC	OC
OC	0.04	0.12	-0.08	0.11	-0.01	0.21	0.28	-0.16	-0.09	0.05
EC	0.92	-0.16	-0.76	0.33	-0.03	-0.39	0.16	1.57	2.77	-0.09
pH	0.37	-0.34	-0.20	-0.07	-0.01	-0.63	-0.56	1.14	1.57	-0.16
Total P	0.44	0.64	-0.65	0.64	-0.01	0.97	1.68	-0.56	0.16	0.28
Soluble P	0.39	0.75	-0.49	1.54	-0.49	2.72	0.97	-0.63	-0.39	0.21
Resin P	-0.08	-0.08	0.07	-0.30	0.12	-0.49	-0.01	-0.01	-0.03	-0.01
PO4	0.42	0.42	-0.45	0.98	-0.30	1.54	0.64	-0.07	0.33	0.11
NH4	-0.43	-0.23	0.45	-0.45	0.07	-0.49	-0.65	-0.20	-0.76	-0.08
NO3	0.15	0.32	-0.23	0.42	-0.08	0.75	0.64	-0.34	-0.16	0.12
Yield	0.29	0.15	-0.43	0.42	-0.08	0.39	0.44	0.37	0.92	0.04

Fig. D15. Controlled environment component of the wheat study covariance heat map showing the influence of residual soil factors on crop P uptake. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

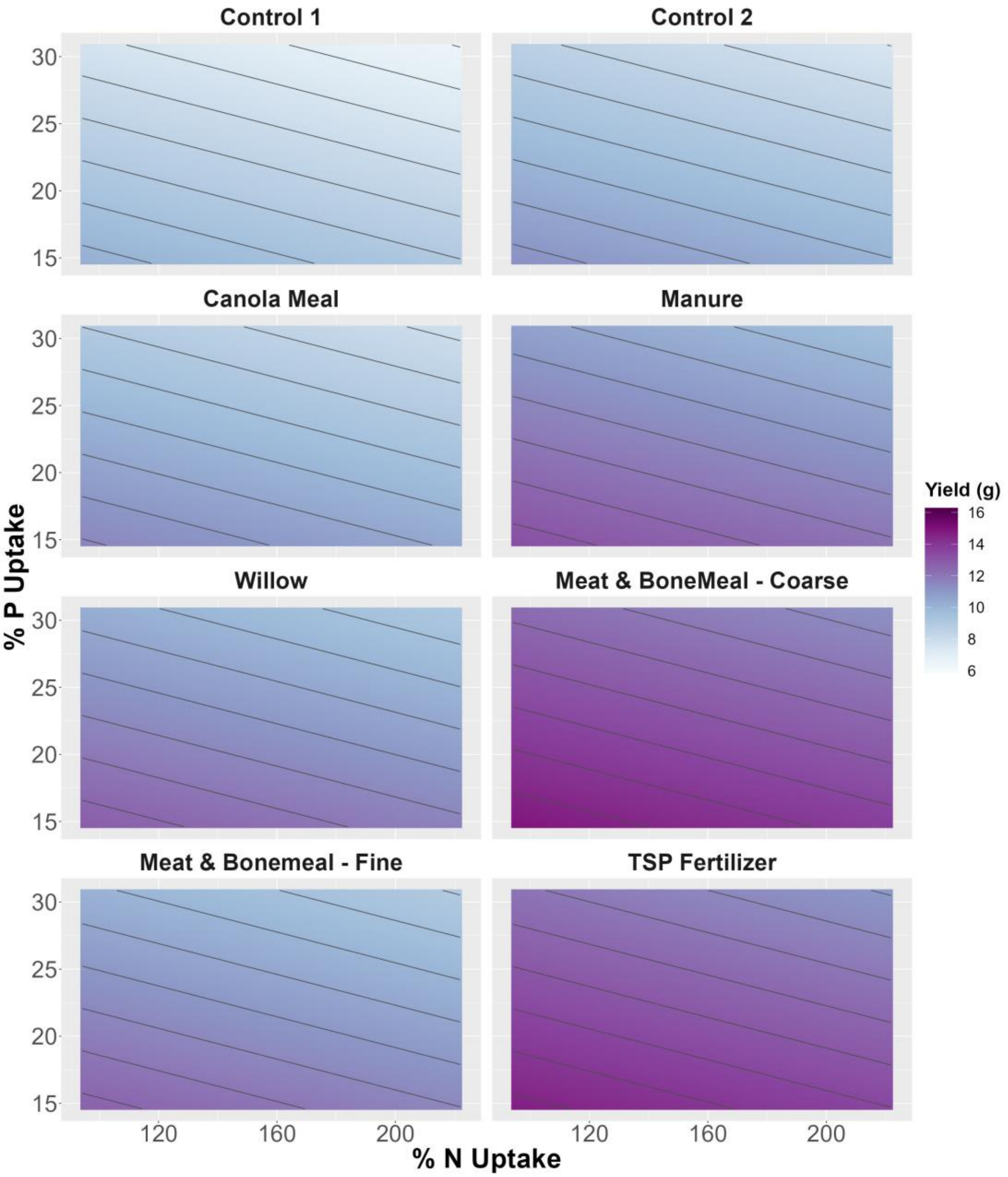


Fig. D16. Wheat study controlled environment component effect of the interaction between N and P recovery on wheat yield. Lines are set at 0.5g yield increments. The angle of the line indicates the relationship between N & P uptake. There was a moderately strong positive relationship between N and P.

Lower levels of both N and P uptake corresponded to higher yields in this study. This is in contrast to the findings of the small plot component of this study and is potentially indicative of the wheat having increased nutrient use efficiency compared to the canola, the nutrients being more bioavailable in the soil after the char had aged, or general soil and plant health under the optimal conditions in the growth chamber as well as the ageing of the char.

Correlations between char P, P uptake and residual P:

A correlation between the char P and soil residual PO_4 showed that all treatments except the canola meal char and the P fertilizer resulted in immobilization of P in the soil (Fig B2). Canola meal char has an especially high positive correlation, showing that the char P contributed to high P levels in the soil. The correlation between P uptake and the char P showed low plant availability for the canola meal char, likely linked to more P in the solid phase and less dissolved P when looking at the char P/PO_4 correlation. The willow char and MBMA coarse fraction both showed low plant available P, while manure char, MBMA fine fraction and TSP fertilizer showed higher levels of available P as expected. Canola meal char, willow char and MBMA fine fraction showed expected trends in the correlation between P uptake and soil PO_4. Manure char, MBMA coarse fraction and P fertilizer had moderate positive correlations between P uptake and residual PO_4 levels, likely indicating that too much P was added. The correlation pattern is very different from that seen in the field component, possibly indicating that the ageing of char influenced the P dynamics in the soil.

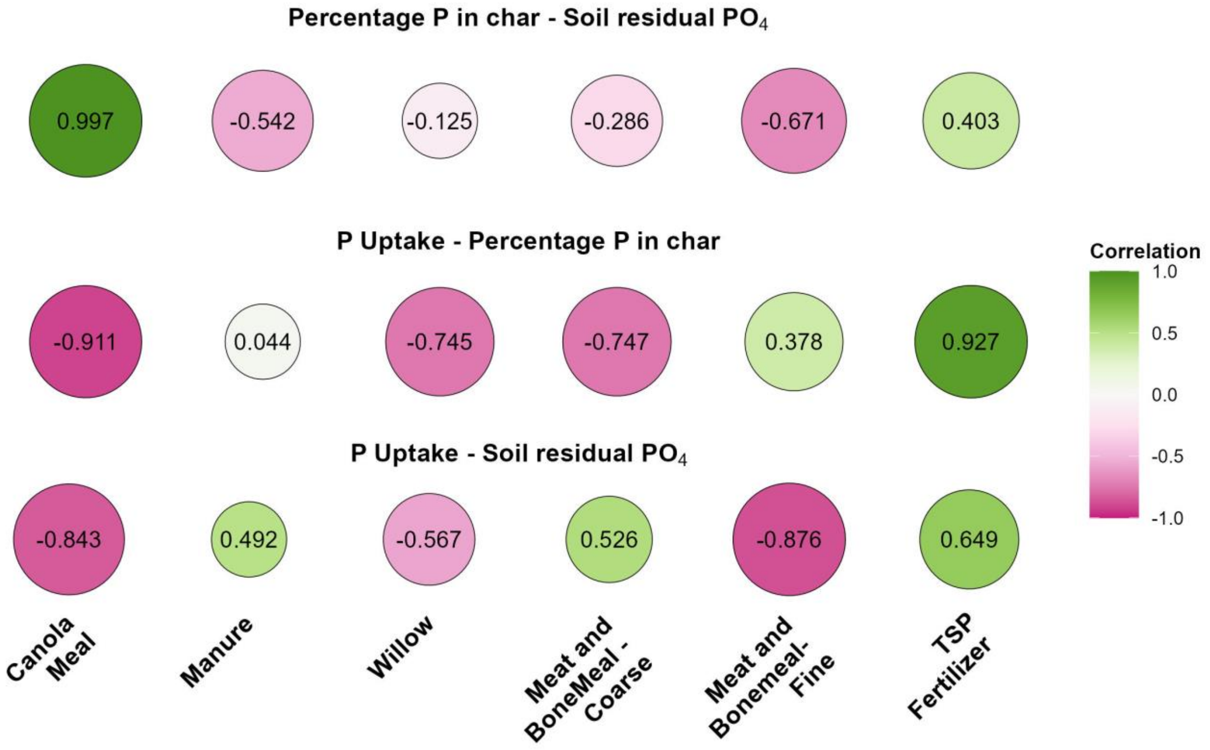


Fig. D17. Correlation between the chars, residual soil PO_4 and P recovery in the controlled environment core component of the wheat study. Green indicates a positive correlation while pink indicates a negative correlation. Larger circles indicate larger correlations with |1| indicating a perfect correlation.

2022 field study

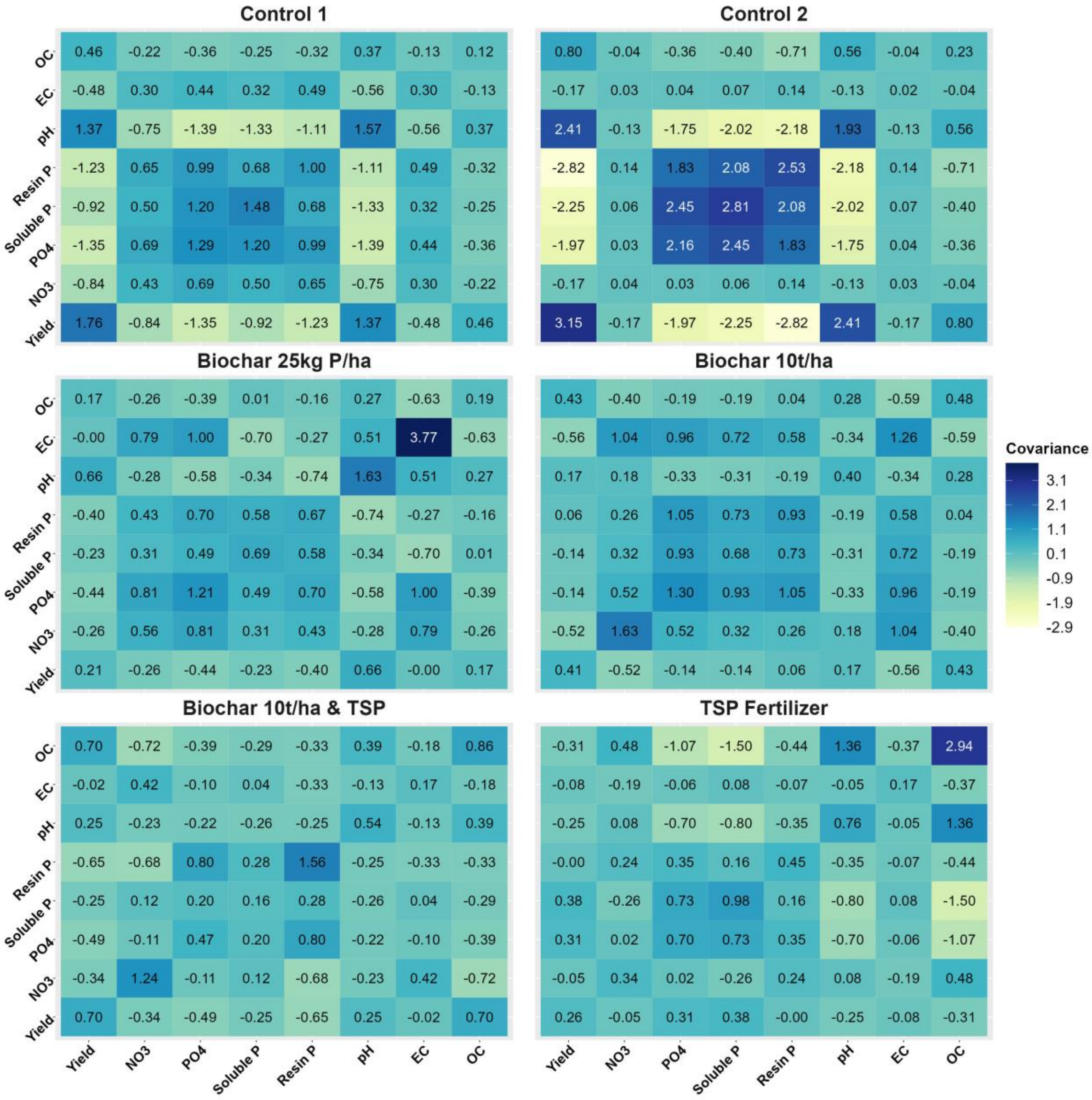


Fig. D18. Soil covariance heat map for the 2022 field study showing the influence of residual soil factors on crop yield. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

A PCA indicated that all variables measured had the same eigen loadings for the first component – residual soil variables used in the PCA were limited to the 0-10cm depth. For the second component, in order and direction of influence, nitrogen recovery (+) was the highest followed by all soil residual variables (+) except for NO_3. limited covariance between yield and the residual soil nutrients and characteristics.

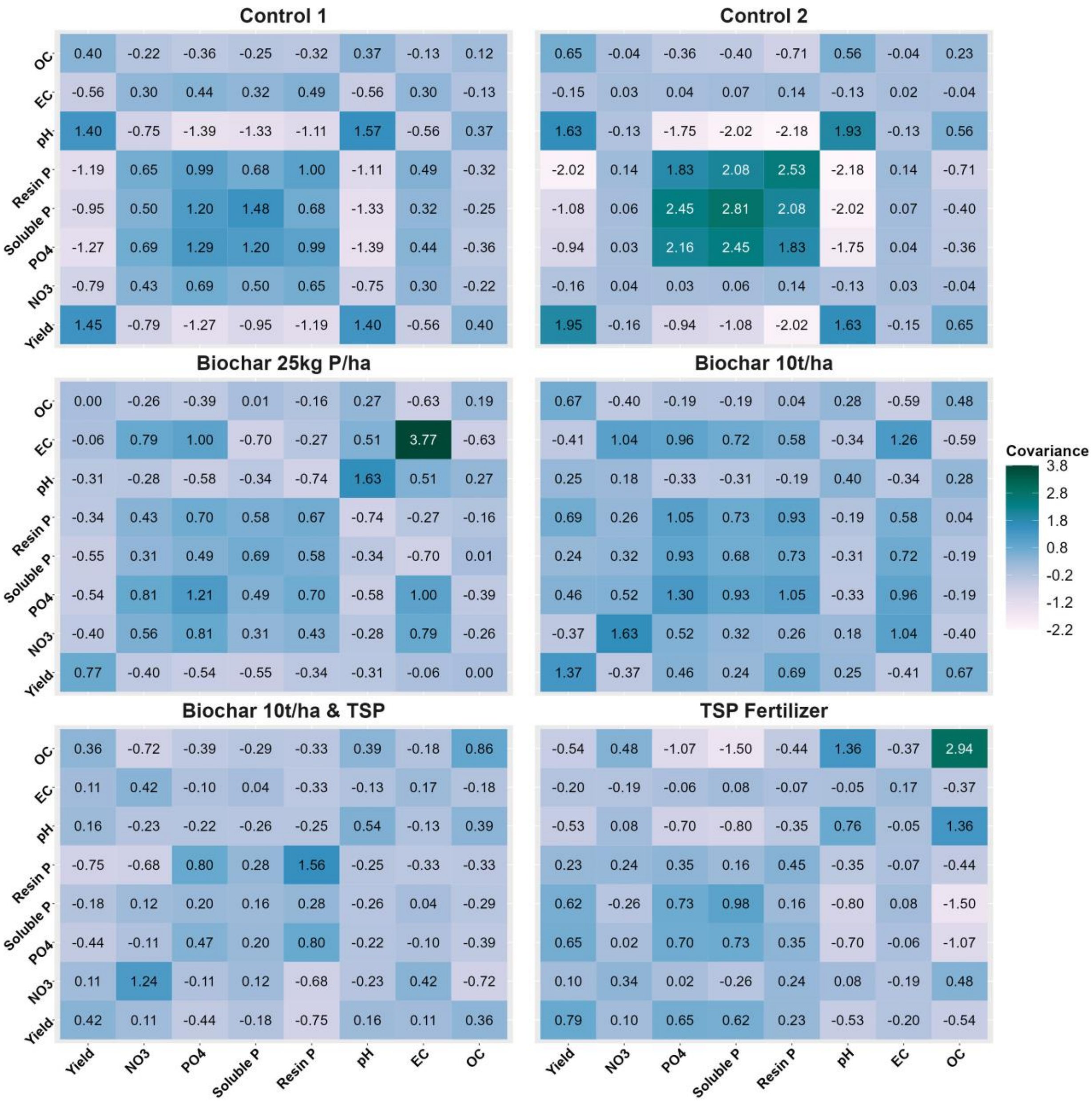


Fig. D19. 2022 field study covariance heat map showing the influence of residual soil factors on crop P uptake. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

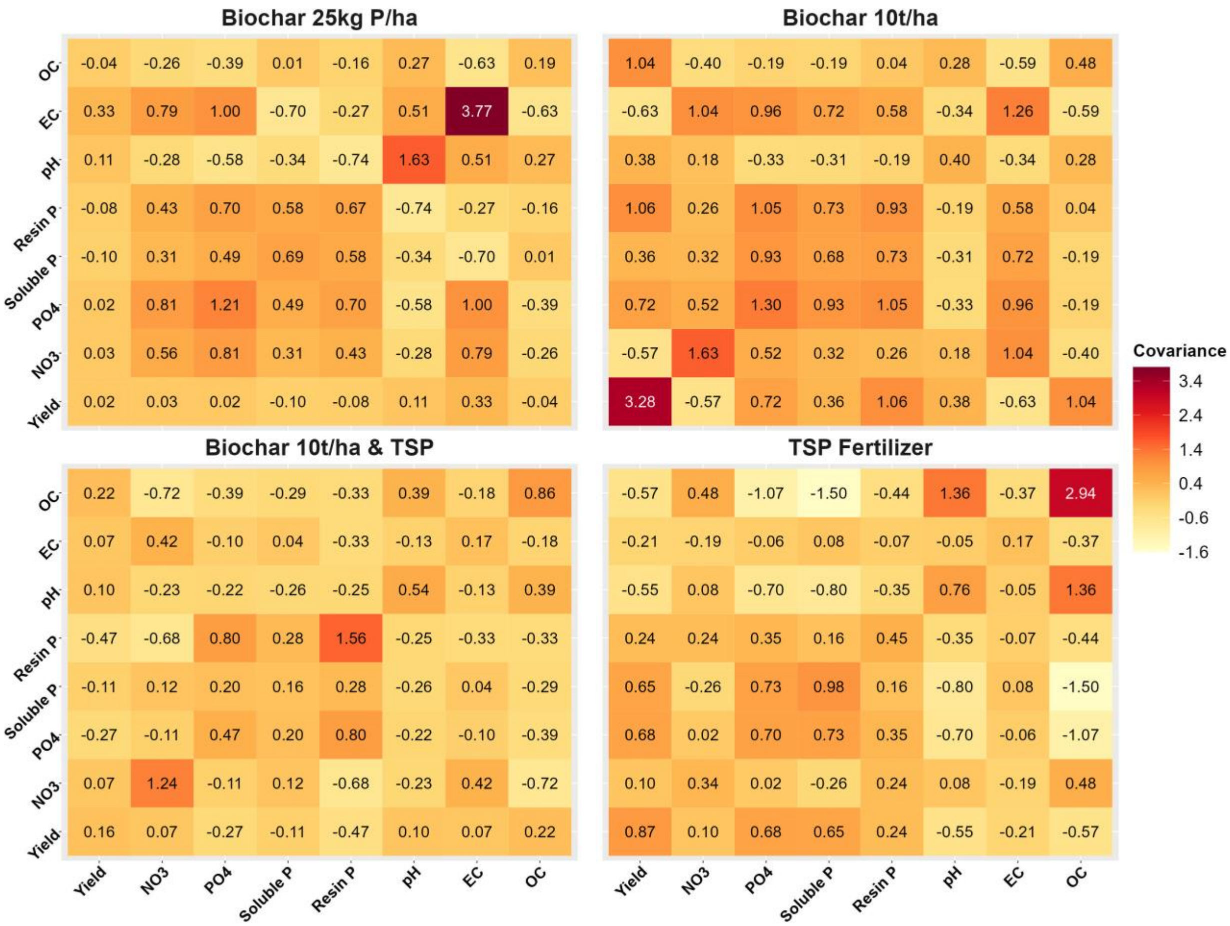


Fig. D20. 2022 field study covariance heat map showing the influence of residual soil factors on crop P recovery. Darker colours indicate a stronger positive relationship while lighter colours show a strong negative relationship.

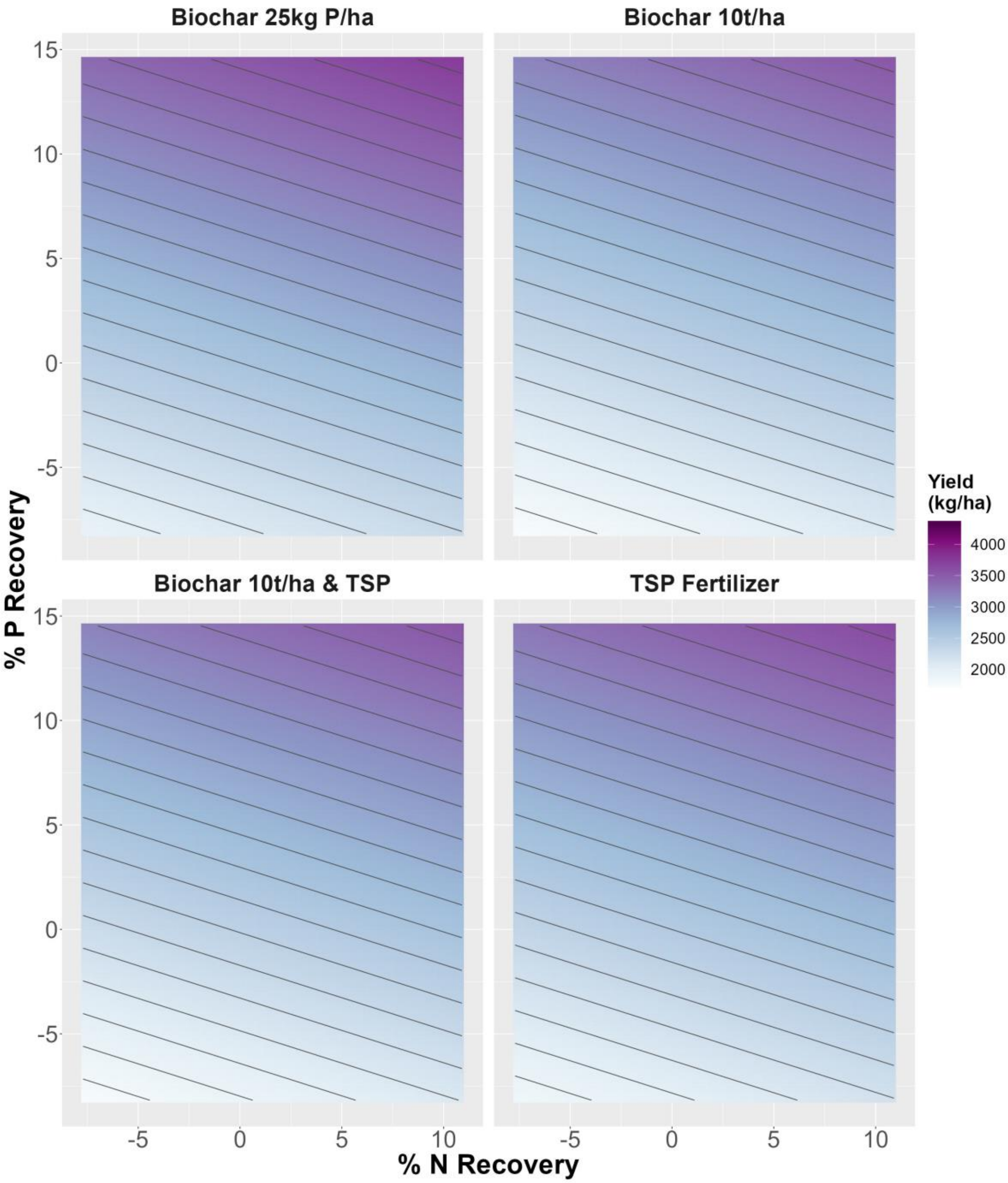


Fig. D21. 2022 field study showing the effect of the interaction between N and P recovery on canola yield. Lines are set at 100kg/ha yield increments. The angle of the line indicates the relationship between N & P recovery. There was a moderately strong positive relationship between N and P.

APPENDIX E: SOIL-WATER RELATIONS

Wheat study controlled environment component: leachate

The calculation to determine concentration of a nutrient in leachate in µg per gram of soil, requires the volume of water leached. During the experiment, 12 of the samples across all treatments except control 2 and MBMA fine fraction had minor water losses which may have skewed the data presented in Table 3.15. As noted in Section 3.5.2, the standard error of leachate data is remarkably high compared to the means, which may be as a result of the water losses. Although there were no statistically significant differences between the treatments for NO_3 in leachate, it should be noted that the standard error is very large in comparison to the means, contrasting the significance seen in the ANOVA test. For NO_3, willow char and MBMA fine fraction had the highest mean amounts of NO_3 removed from the soil through leaching, while the N content of these two amendments was very low (1.4% and 0.24% respectively), exceeding only the MBMA coarse fraction's N content (0.2%). Apart from these two chars, all other chars had lower NO_3 levels that were similar to control 2. Lower values than the controls observed for some of the chars may reflect that these chars had some positive effect on reducing NO_3 losses in leachate through enhancing plant uptake as well as possible sorption. All chars had higher NH_4 levels in leachate than the two controls, but only canola meal char and MBMA coarse fraction were significantly different from control 1.

This links up with the correlation between the leachate P fraction and the residual soil PO_4 (Fig. E1). Negative correlations indicate higher levels of leachate PO_4 is linked to lower levels of soil residual PO_4, which could be an indication that soil P was in the labile pool rather than the soluble pool. Positive correlation on the other hand indicates that pools of soluble P was easily leached but also recalcitrant in the soil. The MBMA coarse fraction performed the worst in terms of preventing P losses in leachate, followed by the MBMA fine fraction and willow char. The P fertilizer did slightly better than control 2, neither of these showing much of a correlation between the leachate and soil P. Canola meal char and manure char performed moderately good and on par with control 1. It should be noted that the correlations do not take into account the actual levels, which differ vastly between the treatments and controls. The difference between control 1 and control 2 can possibly be attributed to the interaction with other added nutrients that resulted in increased immobilization in control 2, while the poor performance of the MBMA fractions and willow char is likely similarly linked to interactions with other nutrients, or the lack thereof.

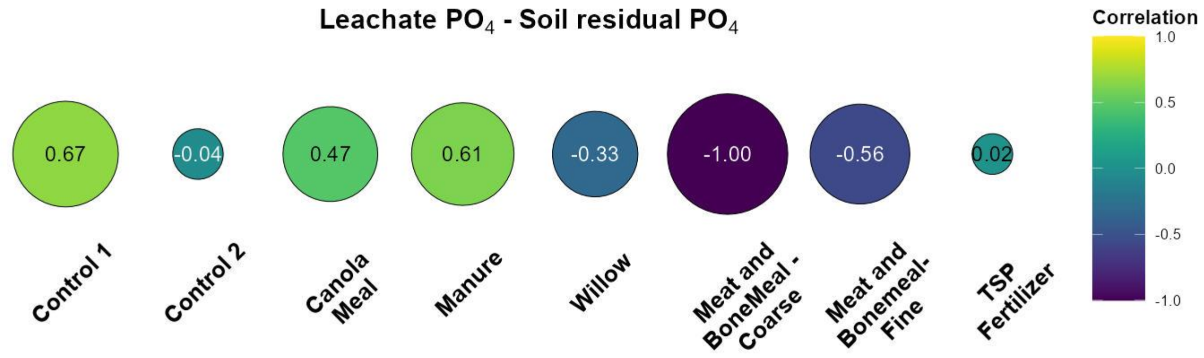


Fig. E1. Wheat study controlled environment component correlation of leachate PO$_4$ and residual soil PO$_4$, showing the ability of different chars in reducing PO$_4$ in leachate. Lighter colours indicate a positive correlation while darker colours indicate a negative correlation. Larger circles indicate larger correlations with |1| indicating a perfect correlation.

More studies have been done on the ability of biochars to reduce N in leachate than P, with more positive results in terms of reducing N concentrations in leachate (Ding *et al.,* 2010; Knowles *et al*., 2011; Troy *et al.,* 2014; Bradley *et al*., 2015; Shabaan *et al.,* 2018; Huang *et al*., 2021; Ghodszad *et al.,* 2021). Only willow char and MBMA fine fraction showed increased NO$_3$ levels compared to control 2 (Fig. E2). The canola meal char, manure char and MBMA coarse fraction were well below the control levels indicating that these chars were able to reduce the amount of soluble N in the soil. Canola meal char had the highest N content (7.66%) while the residual NO$_3$ levels were relatively low with corresponding low levels of leachate NO$_3$. The residual NH$_4$ levels for canola meal char were the highest of all treatments, corresponding to very high leachate NH$_4$ levels, which is likely linked to the high N content of the char. All char NH$_4$ leachate concentrations were higher than that of the control, with willow char showing the most potential to reduce NH$_4$ losses, in contrast to having the worst performance in reducing NO$_3$ losses. Overall, the chars used in this study showed potential to decrease NO$_3$ losses in leachate, but at the same time increase NH$_4$ concentrations. Shabaan *et al*. (2018) in a review study noted various chars' ability to increase NO$_3$ and NH$_4$ retention in soil, with NO$_3$ retention possibly linked to chemical adsorption through functional groups, aromatic ring carbonyl and hydroxyl groups, instead of by physical adsorption. They also noted that immobilization and ionic exchange have been identified in other studies as the primary retention mechanisms and that some studies showed decreased N retention.

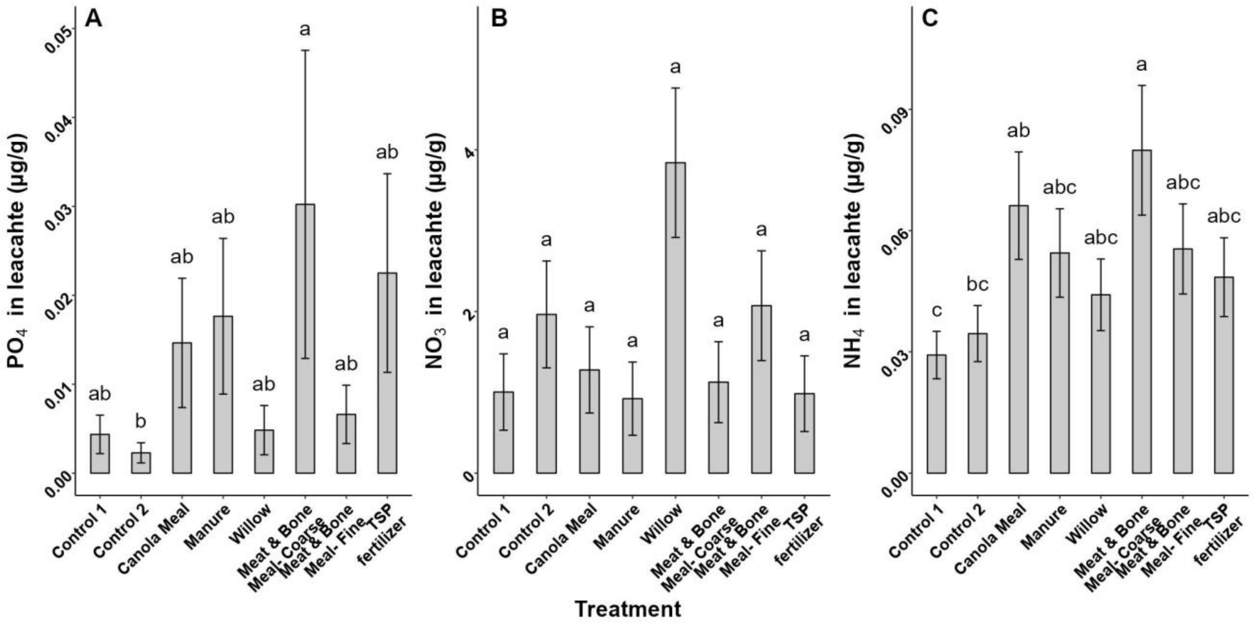


Fig. E2. ***Wheat study controlled environment component leachate experiment results. Values are microgram nutrient leached per gram of soil in the cores. Letters indicate significant differences between means for a Tukey HSD multi-treatment comparison. Error bars are standard error.***

<u>2022 field study</u>

<u>Snowmelt runoff</u>

Nitrogen load in the large plot snowmelt experiment showed no significant differences between treatments, most likely due to a very large standard error for all variables (Fig. E3). Overall, the addition of P, both in the char and TSP fertilizer reduced the NO_3 load in the runoff. The post-harvest soil test NO_3 in these treatments were higher compared to the controls, indicating that the chars or the addition of P decreases the likelihood of NO_3 entering the snowmelt runoff. Resin NH_4 and resin NO_3 were not measured in the post-harvest soils and can thus not be compared. However, the resin measurements do not indicate the same consistent pattern. The biochar 10t/ha treatment was the most effective in reducing N load based on the resin measurements, while the 10t/ha & TSP treatment increased the resin test load compared to the controls.

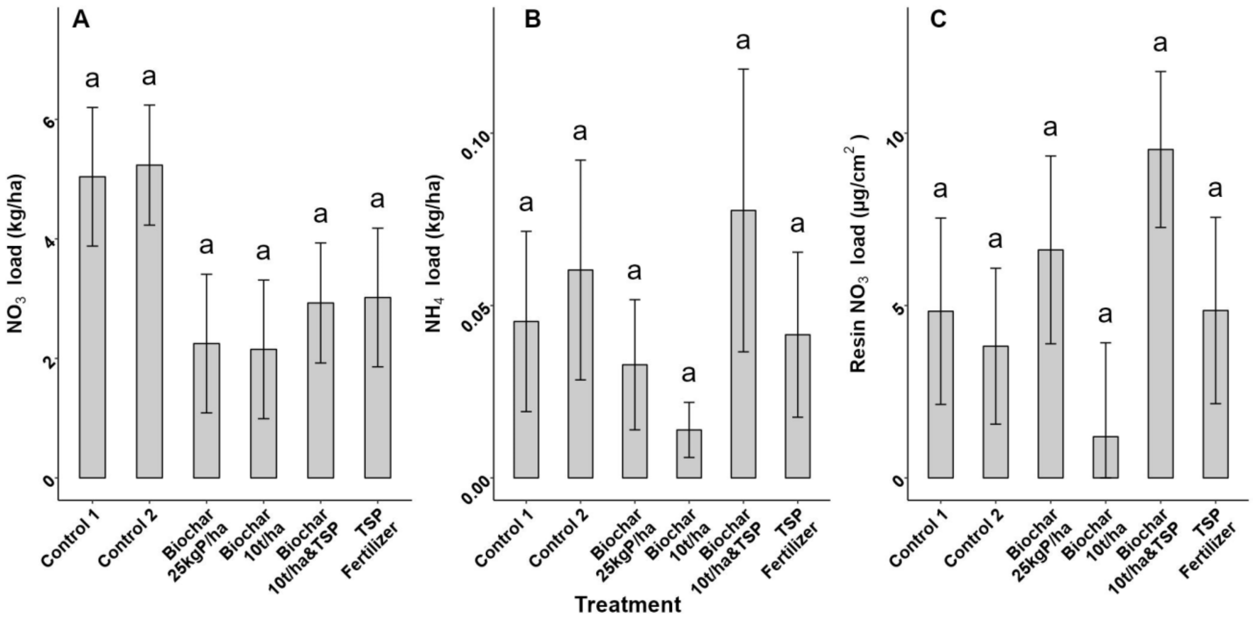


Fig. E3. ***2022 field study nitrogen load from the snowmelt experiment. Letters indicate significant differences between means for a Tukey HSD multi-treatment comparison. Error bars are standard error.***

Infiltration

The Philip two term model is one of a number of available models for analysing hydraulic parameters related to infiltration. It was chosen for this study for the sake of simplicity and as it was one of the models with the fewest parameters to be estimated based on available data. It should be noted that the infiltration experiment was done using the double ring infiltrometer falling head technique with a limited volume of water (10cm head) added to the inner ring. Time measurements were taken up to either the point where the water fully infiltrated, or in the case of slower samples, to a time limit of approximately three hours (see Table E1). As such, some or all of the samples likely didn't reach the point where the first term of the model became negligible, and the second term became fully dominant. Rather, it is estimated that the experiment reached a point partway between the two terms. This can be visually observed in Fig. E4.

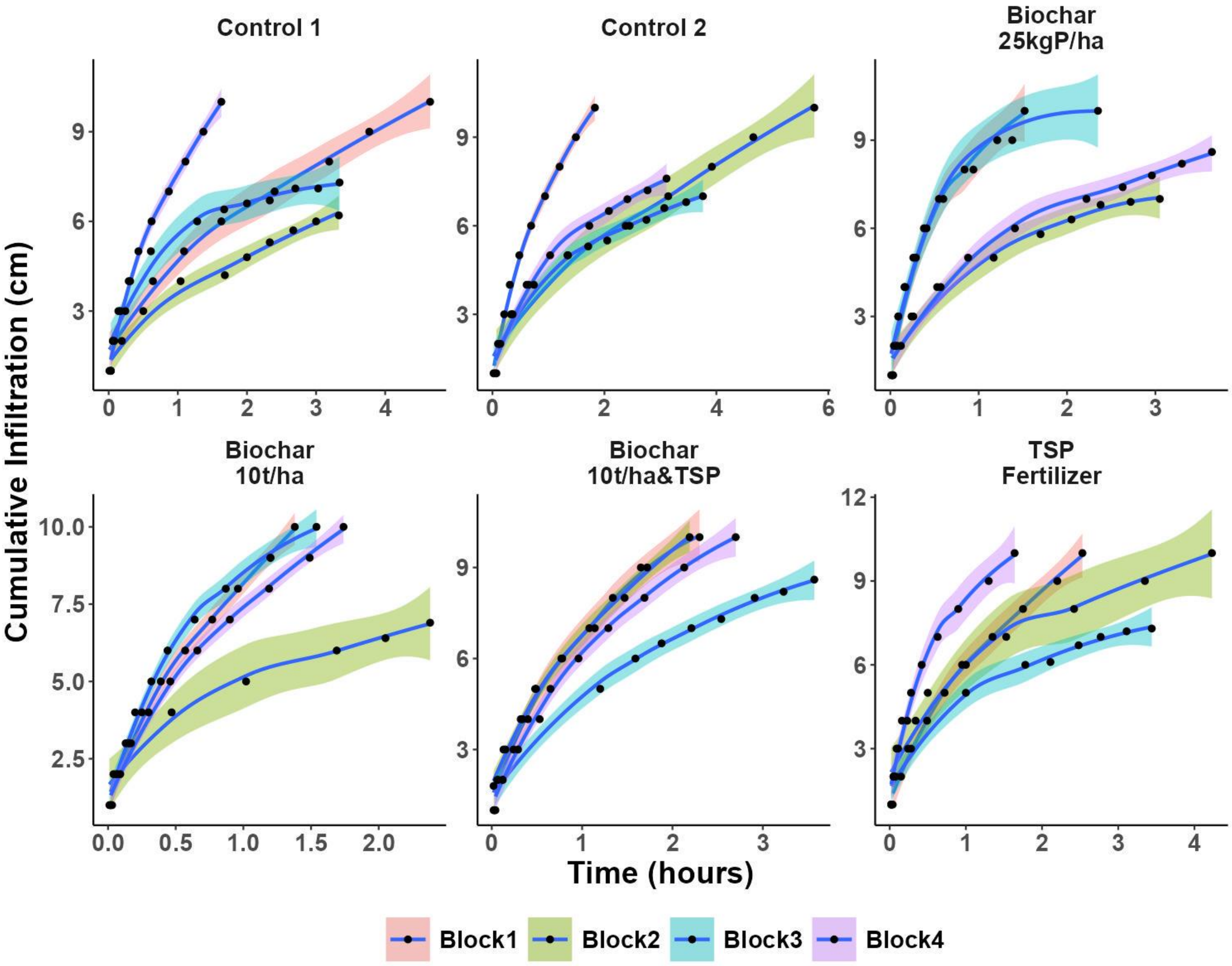


Fig. E4. 2022 field study raw infiltration data showing cumulative infiltration (cm) plotted against time (hours) per treatment. Coloured bands represent standard error. Based on these plots, along with the quartile ranges of the initial and final infiltration rates, control 1 block 4, control 2 block 1 and biochar 10t/ha block 2 were removed as outliers for the predictive modelling.

Table E1 ***Raw infiltration data for each plot showing time (T) in hours, Infiltration (I) and Cumulative Infiltration (CI) in centimetres.***

Treatment	**Block 1**			**Block 2**			**Block 3**			**Block 4**		
	T	***I***	***CI***	***T***	***I***	***CI***	***T***	***I***	***CI***	***T***	***I***	***CI***
Control 1	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0
Control 1	0.1	8.0	2.0	0.2	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0
Control 1	0.2	7.0	3.0	0.5	7.0	3.0	0.1	7.0	3.0	0.2	7.0	3.0
Control 1	0.6	6.0	4.0	1.0	6.0	4.0	0.3	6.0	4.0	0.3	6.0	4.0
Control 1	1.1	5.0	5.0	1.7	5.8	4.2	0.6	5.0	5.0	0.4	5.0	5.0
Control 1	1.6	4.0	6.0	2.0	5.2	4.8	1.3	4.0	6.0	0.6	4.0	6.0
Control 1	2.4	3.0	7.0	2.3	4.7	5.3	1.7	3.6	6.4	0.9	3.0	7.0
Control 1	3.2	2.0	8.0	2.7	4.3	5.7	2.0	3.4	6.6	1.1	2.0	8.0
Control 1	3.8	1.0	9.0	3.0	4.0	6.0	2.3	3.3	6.7	1.4	1.0	9.0
Control 1	4.7	0.0	10.0	3.3	3.8	6.2	2.7	2.9	7.1	1.6	0.0	10.0
Control 1							3.0	2.9	7.1			
Control 1							3.3	2.7	7.3			
Control 2	0.0	9.0	1.0	0.1	9.0	1.0	0.0	9.0	1.0	0.1	9.0	1.0
Control 2	0.1	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0
Control 2	0.2	7.0	3.0	0.4	7.0	3.0	0.4	7.0	3.0	0.3	7.0	3.0
Control 2	0.3	6.0	4.0	0.7	6.0	4.0	0.7	6.0	4.0	0.6	6.0	4.0
Control 2	0.5	5.0	5.0	1.4	5.0	5.0	1.3	5.0	5.0	1.0	5.0	5.0
Control 2	0.7	4.0	6.0	2.5	4.0	6.0	1.7	4.7	5.3	1.7	4.0	6.0
Control 2	0.9	3.0	7.0	3.1	3.0	7.0	2.1	4.5	5.5	2.1	3.5	6.5
Control 2	1.2	2.0	8.0	3.9	2.0	8.0	2.4	4.0	6.0	2.4	3.1	6.9
Control 2	1.5	1.0	9.0	4.7	1.0	9.0	2.8	3.8	6.2	2.8	2.8	7.2
Control 2	1.8	0.0	10.0	5.8	0.0	10.0	3.1	3.4	6.6	3.1	2.4	7.6
Control 2							3.5	3.2	6.8			
Control 2							3.8	3.0	7.0			
Biochar 25kg P/ha	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0
Biochar 25kg P/ha	0.1	8.0	2.0	0.1	8.0	2.0	0.0	8.0	2.0	0.1	8.0	2.0
Biochar 25kg P/ha	0.1	7.0	3.0	0.3	7.0	3.0	0.1	7.0	3.0	0.2	7.0	3.0
Biochar 25kg P/ha	0.2	6.0	4.0	0.6	6.0	4.0	0.2	6.0	4.0	0.5	6.0	4.0
Biochar 25kg P/ha	0.3	5.0	5.0	1.2	5.0	5.0	0.3	5.0	5.0	0.9	5.0	5.0
Biochar 25kg P/ha	0.4	4.0	6.0	1.7	4.2	5.8	0.4	4.0	6.0	1.4	4.0	6.0
Biochar 25kg P/ha	0.6	3.0	7.0	2.1	3.7	6.3	0.6	3.0	7.0	2.2	3.0	7.0
Biochar 25kg P/ha	0.8	2.0	8.0	2.4	3.2	6.8	0.9	2.0	8.0	2.6	2.6	7.4
Biochar 25kg P/ha	1.2	1.0	9.0	2.7	3.1	6.9	1.4	1.0	9.0	3.0	2.2	7.8

Treatment	Block 1			Block 2			Block 3			Block 4		
	T	*I*	*CI*	*T*	*I*	*CI*	*T*	*I*	*CI*	*T*	*I*	*CI*
Biochar 25kg P/ha	1.5	0.0	10.0	3.1	3.0	7.0	2.4	0.0	10.0	3.3	1.8	8.2
Biochar 25kg P/ha										3.6	1.4	8.6
Biochar 10t/ha	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0
Biochar 10t/ha	0.1	8.0	2.0	0.0	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0
Biochar 10t/ha	0.2	7.0	3.0	0.2	7.0	3.0	0.1	7.0	3.0	0.2	7.0	3.0
Biochar 10t/ha	0.3	6.0	4.0	0.5	6.0	4.0	0.2	6.0	4.0	0.3	6.0	4.0
Biochar 10t/ha	0.4	5.0	5.0	1.0	5.0	5.0	0.3	5.0	5.0	0.5	5.0	5.0
Biochar 10t/ha	0.6	4.0	6.0	1.7	4.0	6.0	0.4	4.0	6.0	0.7	4.0	6.0
Biochar 10t/ha	0.8	3.0	7.0	2.1	3.6	6.4	0.6	3.0	7.0	0.9	3.0	7.0
Biochar 10t/ha	1.0	2.0	8.0	2.4	3.1	6.9	0.9	2.0	8.0	1.2	2.0	8.0
Biochar 10t/ha	1.2	1.0	9.0				1.2	1.0	9.0	1.5	1.0	9.0
Biochar 10t/ha	1.4	0.0	10.0				1.5	0.0	10.0	1.7	0.0	10.0
Biochar 10t/ha & TSP	0.0	9.0	1.0	0.0	9.0	1.8	0.0	9.0	1.0	0.0	9.0	1.0
Biochar 10t/ha & TSP	0.1	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0
Biochar 10t/ha & TSP	0.2	7.0	3.0	0.1	7.0	3.0	0.3	7.0	3.0	0.2	7.0	3.0
Biochar 10t/ha & TSP	0.3	6.0	4.0	0.3	6.0	4.0	0.5	6.0	4.0	0.4	6.0	4.0
Biochar 10t/ha & TSP	0.5	5.0	5.0	0.5	5.0	5.0	1.2	5.0	5.0	0.7	5.0	5.0
Biochar 10t/ha & TSP	0.8	4.0	6.0	0.8	4.0	6.0	1.6	4.0	6.0	1.0	4.0	6.0
Biochar 10t/ha & TSP	1.1	3.0	7.0	1.1	3.0	7.0	1.9	3.5	6.5	1.3	3.0	7.0
Biochar 10t/ha & TSP	1.3	2.0	8.0	1.5	2.0	8.0	2.2	3.0	7.0	1.7	2.0	8.0
Biochar 10t/ha & TSP	1.7	1.0	9.0	1.7	1.0	9.0	2.5	2.7	7.3	2.1	1.0	9.0
Biochar 10t/ha & TSP	2.3	0.0	10.0	2.2	0.0	10.0	2.9	2.0	8.0	2.7	0.0	10.0
Biochar 10t/ha & TSP							3.2	1.8	8.2			
Biochar 10t/ha & TSP							3.6	1.4	8.6			
TSP fertilizer	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0	0.0	9.0	1.0
TSP fertilizer	0.2	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0	0.1	8.0	2.0
TSP fertilizer	0.3	7.0	3.0	0.1	7.0	3.0	0.2	7.0	3.0	0.1	7.0	3.0
TSP fertilizer	0.3	6.0	4.0	0.2	6.0	4.0	0.5	6.0	4.0	0.2	6.0	4.0
TSP fertilizer	0.7	5.0	5.0	0.5	5.0	5.0	1.0	5.0	5.0	0.3	5.0	5.0
TSP fertilizer	1.0	4.0	6.0	1.0	4.0	6.0	1.8	4.0	6.0	0.4	4.0	6.0
TSP fertilizer	1.4	3.0	7.0	1.5	3.0	7.0	2.1	3.9	6.1	0.6	3.0	7.0
TSP fertilizer	1.8	2.0	8.0	2.4	2.0	8.0	2.5	3.3	6.7	0.9	2.0	8.0
TSP fertilizer	2.2	1.0	9.0	3.4	1.0	9.0	2.8	3.0	7.0	1.3	1.0	9.0
TSP fertilizer	2.5	0.0	10.0	4.2	0.0	10.0	3.1	2.8	7.2	1.6	0.0	10.0
TSP fertilizer							3.4	2.7	7.3			