PHOSPHORUS AVAILABILITY IN ORGANIC-CROPPED CHERNOZEMIC SOILS AS A FUNCTION OF STRUVITE APPLICATION TIMING AND GREEN MANURE CROP SPECIES

By

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ABSTRACT

Manushi Henagama Liyanage, M. Sc., The University of Manitoba, May 2024. Phosphorus availability in organic-cropped Chernozemic soils as a function of struvite application timing and green manure crop species. Advisors: Dr. Francis Zvomuya and Dr. Kimberley Schneider

Phosphorus (P) is an essential crop nutrient. Dwindling phosphate rock reserves essential for P fertilizer manufacture are increasingly necessitating P recovery from waste and its recycling in fertilizer products. Struvite ($MgNH_4.PO_4.6H_2O$), which is a slow-release fertilizer recovered from wastewater, holds potential as an alternative P fertilizer helping to close the P loop, particularly in organic crop production where soil P deficiency is pronounced. Research is needed to explore options for enhancing the dissolution dynamics of struvite and improving crop response, particularly in alkaline soils. Therefore, this thesis evaluated struvite for its capacity to supply plant-available P as affected by soil and different crop species in common crop rotations in the Canadian prairies. Field experiments conducted on alkaline soils in southern Manitoba under organic management examined the effect of struvite application timing and preceding green manure crop species on wheat crop response. A complementary growth room bioassay examined mechanisms controlling struvite-P mobilization as affected by struvite application timing and the presence of a buckwheat crop. Results from the field study demonstrated variability in responses of green manure species to struvite and the yield of a subsequent spring wheat crop. Response to struvite application was greater for buckwheat compared to field pea and faba bean. However, this differential response did not translate to a greater subsequent wheat crop response following struvite application to buckwheat. Applying struvite to the preceding green manures, compared to applying to the wheat crop did not produce a significant agronomic response in the wheat crop. Results from the growth room bioassay indicated no significant impact of a buckwheat crop on the availability to a subsequent crop of struvite-P applied to the buckwheat. Pre-seeding P application led to decreased cumulative P uptake by buckwheat from MAP relative to the at-seeding application of MAP but had no impact on P uptake from struvite. Our results suggest a lower agronomic response to struvite relative to MAP, regardless of timing of application. Although buckwheat appeared to be efficient in mobilizing struvite P, it may not effectively transfer sufficient P to support the growth of a following crop.

Keywords: Soil phosphorus, organic farming, alkaline soils, monoammonium phosphate

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FOREWORD

This thesis was prepared in manuscript format in compliance with the guidelines of the Department of Soil Science, University of Manitoba. The thesis has four chapters. Chapter 1 is a general introduction, providing background information and a review of the literature on phosphorus management in crop production, particularly elaborating on the potential fertilizer value of struvite in Canadian prairie organic cropping systems. Chapters 2 and 3 are separate research chapters structured as manuscripts for journal submissions. Chapter 2 focused on identifying green manure crop species that enhance P availability to a subsequent crop from struvite applied at strategic points in a common organic crop rotation in Manitoba. Chapter 3 focused on investigating strategies (preceding green manure crop, struvite application timing) of enhancing struvite P availability beyond the year of application. Chapter 4 is an overall synthesis providing a summary of research findings, implications of the results, and recommendations for future study.

Contribution of Authors

The contributions of the authors for Chapters 2 and 3 are as follows:

- Manushi Henagama Liyanage: Conducted experiments, collected and analyzed data, interpreted results, wrote the original manuscript draft
- Francis Zvomuya: Conceptualized the experiments, provided primary administration and supervision of the project, secured project funding, and reviewed and edited manuscript drafts
- Kim Schneider: Conceptualized the experiments, supervised the project, and reviewed and edited manuscript drafts
- Joanne Thiessen Martens: Conceptualized the experiments

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. GENERAL INTRODUCTION

1.1. Phosphorus in crop production

Providing adequate amounts of phosphorus (P) in the early stages of crop growth is essential, not only for ensuring early plant growth but also for maximizing yield at harvest (Grant et al. 2001). Phosphorus deficiency during the early stages can cause irreversible retardation of plant growth (Syers et al. 2008). Other deficiency symptoms include reduced tillering, low dry matter accumulation, low grain production, and delayed leaf emergence (Syers et al. 2008). Low P supply to plants can also hinder the utilization of other plant nutrients (Syers et al. 2008). The availability of soil N is enhanced as labile soil P concentration increases, which leads to improved growth of legumes (Parfitt et al. 2005). Phosphorus deficiency is globally a major concern that limits above-ground crop production (Hou et al. 2020). Phosphorus is the most likely plant nutrient after nitrogen that restricts crop development in the semi-arid parts of the Canadian prairies (Selles et al. 2011).

1.2. Phosphorus forms and their plant availability in agricultural soils

Despite its abundance in most soils, P tends to be deficient in the immediately plant-available (labile) forms, dominated by HPO_4^{2-} and $H_2PO_4^{-}$ species (orthophosphates) (Richardson 2001) present in the soil solution or weakly adsorbed to anion exchange sites (Havlin et al. 2016). Around 95 – 99 % of total P in the soil is in forms that are not immediately plant-available (Molla and Chowdhury 1984). The low mobility of phosphate ions in the soil is ascribed to this low availability, which necessitates the provision of an adequate supply of readily-accessible P in the P depletion zone to meet peak crop P demand (Bucher 2007; Syers et al. 2008). Therefore, regular replenishment of the plant-available P pool is essential (Richardson 2001; Mullins 2018). Managing chemical and biochemical processes of internal P cycling in soil, that is, mineralization-immobilization, dissolution-precipitation, sorption-desorption, and oxidation-reduction, is of paramount importance for maintaining soil solution P pools at optimum concentrations for plant growth (Sims and Sharpley 2005).

Havlin et al. (2016) categorized inorganic P (P_i) forms in soil into soil solution P, P weakly or strongly adsorbed to clay and other mineral surfaces, and strongly adsorbed and P-containing minerals. Solution P and weakly adsorbed P, which rapidly equilibrate with the soil solution through desorption, comprise the labile P_i pool, whereas non-labile P_i constitutes strongly adsorbed and mineral P, which equilibrate slowly (Sims and Sharpley 2005; Havlin et al. 2016). The concentrations of HPO_4^{2-} and $H_2PO_4^-$ ions in the soil solution are governed by soil pH. At pH 7.2, the concentrations of the two species are almost equal. At $pH > 7.2$, HPO_4^{2-} is the dominant species in the soil solution, whereas $H_2PO_4^-$ is the most abundant species at $pH < 7.2$. Inorganic P can react with other chemical constituents in the soil, including Ca, Mg, Mn, Al, and Fe, resulting in its low availability for plant uptake (Shen et al. 2011). This fixation/retention of these P_i forms depends on several factors of which pH is the most prominent. In acidic soil, P_i is typically bound to Fe or Al, whereas, in neutral and calcareous/alkaline soils, P_i is bound to Ca or Mg in high-Mg soils (Havlin et al. 2016). During the first year of application, plants utilize only approximately 20% of the P fertilizer applied due to its retention in the soil (Vance et al. 2003).

Biological and biochemical processes also contribute to plant availability of P to some extent via mineralization of organic P (P_o) (organic forms of soil P, and P in crop residues and soil organisms) (Frossard et al. 2016; Schneider et al. 2019). Organic P forms include orthophosphate monoesters (specifically inositol phosphate) and orthophosphate diesters, particularly DNA, RNA, phospholipids and phosphonates (Frossard et al. 2016).

1.3. Phosphorus fertilizers

Monoammonium phosphate ($NH_4H_2PO_4$, 11-52-0) is the most commonly used commercial P fertilizer in western Canada (Statistics Canada 2022). During the 2021/2022 growing season, 212,000 metric tonnes of MAP were shipped to the agricultural market in the Canadian prairies, accounting for 71% of the total shipments of MAP to Canada (Statistics Canada 2023). Other forms of fertilizer P used in Canada include ammonium phosphates such as diammonium phosphate ($(NH_4)_2HPO_4$, 18-46-0) and ammonium polyphosphate ($(NH_4)_3HP_2O_7$, 10-34-0), and calcium phosphates such as triple superphosphate ($Ca(H_2PO_4)_2$, 0-45-0) (Grant and Flaten 2019b; Havlin et al. 2016).

1.3. Phosphorus availability in Prairie organic crop production

Canadian prairie soils are typically characterized by high levels of total P but relatively low levels of plant-available P (Doyle and Cowell 1993 as cited by Selles et al. 2011). In general, soils under organic production systems are low in available P concentration compared to those under conventional cropping systems (Welsh et al. 2009; Reimer et al. 2020). When organic farms rely on biological N_2 fixation for deriving most of their N requirement, the availability of other nutrients, including P (Reimer et al. 2020), may be compromised. Plant-available soil P concentration under organic management across the Canadian prairies is generally low whereas plant-available N, S and K are mostly sufficient for most crops (Entz et al. 2001). Organic agriculture is based on four key principles, namely health, ecology, fairness, and care (IFOAM n.d.). that guide the regulation of the permitted substances allowed in organic farming. Commercially-available P amendments permitted for soil application in organic crop production in Canada include phosphate rock, animal manure, compost, livestock-derived products like bone meal, and plant-sourced products such as alfalfa pellets (Canadian General Standards Board 2021).

Phosphate rock is not recommended for neutral to alkaline soils because of its low reactivity. Therefore for those soils, P sources including compost, digestates, biosolids, and struvite are being explored for their potential, although commercially available struvite is not yet permitted for use in organic production in Canada (Möller et al. 2018). Many recycled P fertilizers show greater plant availability of P than phosphate rock (Möller et al. 2018).

1.4. The need for P recycling and recovery

Managing soil P in farming systems faces the grand challenge of supplying sufficient P to the crop while avoiding the adverse environmental impacts caused by the release of excess P into surface water (Withers et al. 2014). The need to improve P use efficiency is increasingly critical as global phosphate rock reserves are dwindling. Organic agriculture faces additional P-related management challenges, namely, the limited fertilizer options available for use in the sector. Phosphorus fertilizers are obtained predominantly from mined phosphate rock (Cordell et al. 2009). The mineral P reserves are not evenly distributed across the world (Villalba et al. 2008), with economically viable sources of rock phosphate being confined to a few countries (Childers et al. 2011). The exploitation of rock phosphate for fertilizer is expected to peak by 2030 (Cordell et al. 2009) and it is estimated that existing sources of economically extractable mineral P will become scanty or even depleted over the next 50 to 100 years (Cordell et al. 2009; Smil 2000; Shen et al. 2011). Once peak utilization is reached, the availability and affordability of P for manufacturing fertilizer will become a limiting factor for food supply and commodities. Consequently, the cost of P fertilization has gained attention worldwide, and the management of P nutrition has become a major concern in sustainable crop production.

Fertilizer P is a vital component in contemporary agricultural systems and at the same time, it is a major driving factor for eutrophication (Withers et al. 2014). Fertilizer application to achieve "insurance levels of plant-available P" is widely encouraged in most developed countries. Establishing and sustaining critical levels of soil P is the basis for most of the P fertilizer recommendation systems to increase crop productivity across the world (Macintosh et al. 2019). This critical level of P refers to the soil test P (STP) concentration that corresponds to 90-95 % of maximum crop yield (Manschadi et al. 2014). This strategy of feeding the soil to feed the crop is aimed at making sure P is not limiting the yield potential of crops. However, it leads to creating a "legacy of P accumulation" in soils, wastes, and sediments, which will eventually end up in surface waters (Withers et al. 2014). Furthermore, the geographical separation of crop and livestock production systems also results in a linear flow of P, with feed transferred to livestock, then excreted as manure onto soil, leading to excess P accumulation in soil (Sharpley et al. 2018). Therefore, according to Sharpley et al. (2018), even though P fertilization has enhanced the production of commercial food, fiber, and bioenergy, underpinning urbanization and population growth, "a conundrum of simultaneous P deficiencies and excesses" has emerged over the last 5-6 decades across national, regional, and local scales. During this period, public concerns have come to light about dwindling rock phosphate, which is a finite non-renewable resource, P use inefficiencies, and the ecological threat of excess P transport to freshwater and marine ecosystems worldwide (Sharpley et al. 2018). The inadequacies in reconnecting the agricultural P cycle result in poor water quality due to P loss-induced eutrophication, which exerts environmental pressure on wastewater treatment plants.

An evaluation of 12 different P waste streams revealed a general upward trend of annual per capita waste flow from 1961 to 2013 (Chen and Graedel 2016). Contamination of surface water with excess nutrients leads to eutrophication and potentially toxic algal blooms (Schneider et al. 2019). Eventually, this presents a risk to the survival of fish and other aquatic life and the health of water resources (Le Corre et al. 2009). The primary sources of agricultural P runoff include particulate P from soil erosion, and dissolved P desorbed from soil, fertilizer, and frozen plant residue. The predominant pathways for P leaving agricultural fields are mainly surface runoff and tile drainage, with subsurface lateral movement observed in certain areas (Reid et al., 2018). Phosphorus loss occurs in the Northern Great Plain region during cold winters, primarily due to snowmelt-induced runoff, and is attributed to the greater soil losses from snowmelt than rainfall-runoff, as well as prolonged soil-plant-water contact associated with snowmelt, leading to increased dissolved P losses (Tiessen et al. 2010).

Schneider et al. (2019) highlighted the urgent need for increased P use efficiency (PUE) in agricultural systems to mitigate future impacts on the environment. Therefore, P management that targets increasing crop P use efficiency rather than feeding the soil is critical. A paradigm shift toward crop requirement-based nutrient supply instead of "insurance-based" fertilizer application is currently being promoted in modern farming systems (Withers et al. 2014). According to Grant and Flaten (2019)a, management of soil nutrients at suboptimal levels, rather than implementing soil conservation practices, is more effective for the Northern Great Plains region. Therefore, beneficial management practices such as the 4R nutrient stewardship strategy (right source, right rate, right time, and right place) for management of P fertilizers have a big role to play in sustainable crop production.

While continuing to follow classic principles of P management for sustainable crop production in the Northern Great Plains, i.e., P application at rates equivalent to the removal rate of P by crops, it is important to develop novel technologies to circulate "post-consumer P" back into agricultural production (Grant and Flaten 2019a). A closed-loop economy of P fertilization is needed, which can be achieved by increasing PUE of cropping systems through advances in crop breeding and cropping system designs that ensure reduced crop P demand and improved utilization of legacy P reserves, as well as through promoting recycling and recovery of P from waste streams (Schneider et al. 2019). It is widely perceived that P recycling and recovery from waste streams is crucial to sustainably manage the global P cycle (Chen and Graedel 2016; Cordell et al. 2011). Recycled P has a potential role in the sustainability of organic crop production in Canada because waste P generation is substantially greater than the P requirement of organic farmlands (Nicksy and Entz 2021). Factors including processing times and distinct manufacturing conditions, such as solution pH, temperature, and additives, regulate P bioavailability from recycled products and their efficacy as P fertilizers (Wollmann et al. 2018).

1.5. Struvite and the paradigm of slow-release phosphorus

1.5.1. What is struvite?

Slow-release fertilizers (SRF) are sources that release soil nutrients in a slower and more controlled manner compared to soluble fertilizers (Shaviv and Mikkelsen 1993). Therefore, slow-release fertilizers like struvite have benefits in addressing spatial and temporal susceptibility to eutrophication (Everaert et al. 2018). Waste treatment facilities have evolved aiming to remove N and P to comply with stringent regulations. This nutrient removal process, especially biological nutrient removal, results in increased concentrations of N, P, and Mg in the effluent, which in turn react to form struvite (Doyle and Parsons 2002). Spontaneous precipitation and scaling of struvite is a major maintenance and operational problem in waste treatment plants (Degryse et al. 2017; Doyle and Parsons 2002). Concurrently, precipitation of minerals or salts, such as struvite, from P-rich sources has become a popular way of recovering P from waste streams due to its potential benefit as a P fertilizer (de-Bashan and Bashan 2004; Le Corre et al. 2009). Struvite is a white crystalline substance composed of equimolar concentrations of PO_4^{3-}, Mg, and NH_4^+ (Doyle and

Parsons 2002; Jaffer et al. 2002; Yilmazel and Demirer 2011). The general reaction of struvite precipitation is as follows (Doyle and Parsons 2002):

$$Mg^{2+} + NH_4^{+} + H_nPO_4^{n-3} + 6H_2O \rightarrow MgNH_4PO_4{\bullet}6H_2O + nH^{+}$$

where *n* can take the values 0, 1, or 2.

This reaction is governed by pH, temperature, degree of supersaturation, and other ions, such as Ca^{2+}, present in the solution. The composition of pure struvite by mass is 39% phosphate (12.6% P), 7% ammonium (5.7% N), 10% magnesium, and 44% H_2O (Gell et al. 2011). The struvite product used in this study was Crystal Green® (5-28-0 with 10% Mg; Ostara Nutrient Recovery Technologies, Vancouver, BC, Canada), which is a high-purity granular fertilizer commercially available in Canada and other countries. Crystal Green® is recovered from municipal wastewater via the Pearl® process. Its P content is within the same range as MAP. Human waste-derived struvite is not currently permitted in organic farming in Canada, but plant and livestock-based struvite is already permitted (Canadian General Standards Board 2021). Struvite is known to have poor solubility in water (Bouropoulos and Koutsoukos 2000). The risk of P runoff from struvite is low compared to that from MAP (Everaert et al. 2018). The concentration of impurities and toxic metals such as Cd, Ni, Zn, and Cr in struvite is significantly lower when compared to triple superphosphate (Hall et al. 2020). These properties of struvite make it ideal as a promising source of P relative to highly soluble P sources. Struvite derived from different waste streams, such as sewage sludge (Mehta et al. 2018; Meyer et al. 2018; Vogel et al. 2015; Wollmann et al. 2018), dairy manure (Hilt et al. 2016), and swine manure (Ackerman et al. 2013; Katanda et al. 2016), with varying P contents, have been studied for their fertilizer value. While struvite is still being explored to see if it can supply adequate P to a range of crops despite its low solubility, the low water-solubility may help minimize eutrophication potential (Everaert et al. 2018; Mavhungu et al. 2021).

1.5.2. Dissolution and behavior of struvite in soil-plant systems

Struvite is sparingly soluble (1-5% solubility) in water (Achat et al. 2014; Cabeza et al. 2011), and its solubility decreases gradually as pH increases from 7 to 8.5 (Bhuiyan et al. 2007). While initial dissolution of struvite-P is strongly and negatively correlated with the initial solution pH, the latter has no impact on the equilibrium P concentration (Bhuiyan et al. 2007; Talboys et al. 2016). Only 6.6% of the P in struvite is water-soluble (Kratz et al. 2019). The water solubility of Crystal Green® is ~ 4% (Ostara Nutrient Recovery Technologies Inc.). The solubility of struvite in citrate is similar to the solubility of MAP in water and in water plus neutral ammonium citrate, but notably lower than the solubility of triple superphosphate (Hertzberger et al. 2020). Research comparing the citrate-solubility and water-solubility of different physical forms (granular and finely ground) of struvite derived from poultry manure, swine manure, and municipal wastewater suggests that chemical composition has a greater effect on the release of struvite P than physical composition (Rech et al. 2018). However, Degryse et al. (2017) and Talboys et al. (2016) reported higher pH-dependence of granular struvite dissolution. Meyer et al. (2018) concluded that water solubility underestimates plant P availability of potential P fertilizers whereas citrate solubility overestimates.

The dissolution of struvite in soil is also thought to depend on soil properties, including pH and P retention capacity, and on crop-specific P acquisition mechanisms. Acidic soil pH favors the dissolution of granular struvite and subsequent P uptake by the plant (Degryse et al. 2017; Hertzberger et al. 2020), although Achat et al. (2014) reported similar effectiveness of TSP and finely ground struvite mixed into soil, regardless of soil pH. In alkaline soil, the dissolution of finely ground struvite has been shown to be more rapid than that of granular struvite (Degryse et al. 2017; Everaert et al. 2017). Soil P retention capacity, which varies with soil texture (Ige et al. 2005), may also impact struvite solubilization (Degryse et al. 2017), as has been demonstrated for other P fertilizers (Duminda et al. 2016).

1.5.3. Agronomic performance of struvite

Different perspectives have emerged from recent research on the value of struvite as a P fertilizer. A number of studies (e.g., Katanda et al. 2016; Robles-Aguilar et al. 2019; Talboys et al. 2016; Vogel et al. 2015) have demonstrated that, in low pH soils, struvite could be as effective as high-solubility, commercial P fertilizers. Wollmann et al. (2018) reported greater maize dry matter yield and shoot P accumulation from struvite products relative to phosphate rock and other sewage-sludge-derived P fertilizers (Mephrec, pyrolysis coal, and Mg-containing sewage sludge ash). Residual P effects of struvite application on biomass yield could be expected in subsequent years, suggesting that struvite might be a multi-year P source (Katanda et al. 2016; Thiessen Martens et al. 2022; Vogel et al. 2015; Wollmann et al. 2018). Nonetheless, other studies have demonstrated inferior crop response to struvite, especially in alkaline soils (Ackerman et al. 2013; Hilt et al. 2016; Mehta et al. 2018; Nicksy et al. 2022). Degryse et al. (2017) concluded that the agronomic response to struvite was similar to MAP when struvite was ground and incorporated into the soil rather than the granular application, which is usually the common practice in agriculture. Some research suggests that mixing struvite with a readily soluble P source, such as chemical fertilizer (which is not applicable in organic farming) (Benjannet et al. 2020; Hertzberger et al. 2020) or composted manure (Thiessen Martens et al. 2022) would optimize its agronomic effectiveness.

Slow-release P fertilizers have the potential to ensure sustainable crop production in low-P soils via reduced P immobilization and increased recovery of applied fertilizer P, reduction in storm runoff of P immediately after application, and reduced need for allocation of photosynthates to complex strategies of soil P acquisition (root proliferation, exudation or mycorrhizal symbiosis) (Talboys et al. 2016). Thus, the slow-release properties shared by various types of struvite ensure a long-term P supply for plants while assuring P sufficiency during critical growth stages (Withers et al. 2014). This is crucial to the sustenance of optimal crop yields at reduced P application rates, hence minimal impacts on the aquatic environment (Talboys et al. 2016).

1.5.4. Optimization of struvite application in crop sequences

The dissolution dynamics and agronomic value of struvite depend on factors such as the extraction processes employed in struvite recovery from waste streams, crop species, and soil characteristics (Schneider et al. 2019). Therefore agronomic research on optimizing struvite application (rate, timing, and placement) needs to consider struvite's interactions with crop P acquisition processes under varying soil conditions (i.e., soil-struvite-plant interactions) in relation to crop rotation (Schneider et al. 2019; Thiessen Martens et al. 2022). Thiessen Martens et al. (2022) reported crop biomass and grain yield benefits at higher struvite application rates beyond the general recommendations in Manitoba, emphasizing the importance of determining optimum application rates. Multi-year residual P benefits from struvite application emphasize the capacity to augment soil P dynamics through P fertilizer application in a crop rotation at specific strategic points (Schneider et al. 2019).

1.6. Plant uptake of phosphorus

1.6.1. Phosphorus efficiency indices

Phosphorus use efficiency (PUE) is the total biomass or yield produced per unit mass of P taken up by the crop (Hammond et al. 2009). This index can be divided into two components: P acquisition efficiency (PAE) and P utilization efficiency (PUTIL) (Mendes et al. 2014). Acquisition efficiency is the ability of plants to acquire soil nutrients, in other words, the ratio of the amount of a nutrient taken up by the plant to the amount of that nutrient available in the soil (Mendes et al. 2014). Utilization efficiency relates to the internal metabolic processes that the taken-up nutrients undergo inside the plants. For cereals/grains, this is calculated by dividing the grain weight by the nutrient taken up by the plant (Mendes et al. 2014; Parentoni et al. 2012). Of the two indices, PAE is strongly correlated with PUE while PUTIL shows a relatively low correlation with PUE (Mendes et al. 2014).

1.6.2. Plant and microbial processes of P uptake

Plant roots absorb P_i from the soil solution in the form of orthophosphate, mostly as $H_2PO_4^-$ but also as HPO_4^{2-} to some extent. The plant availability of P_i depends on soil characteristics like the soil solution P_i concentration and the soil's capacity to replenish solution P_i. Plant traits such as the root volume and the spread of the root system within the soil and its effectiveness at taking up P also dictate crop P availability (Syers et al. 2008). Richardson et al. (2011) broadly categorized strategies deployed by plants and soil microorganisms for increased PUE as (i) root-foraging strategies, (ii) soil P mining strategies and (iii) strategies that enhance internal plant P utilization efficiency. Topsoil foraging strategies include genotypic adaptations for increased PAE in low-P soils, including shallower basal root growth angles, increased adventitious rooting, and lateral root proliferation according to localized soil P availability (Lynch and Brown 2001). Phosphorus mining strategies improve P mobilization from sparingly available organic and inorganic P pools and thereby decelerate net P accumulation when fertilizer is applied in P-sorbing soils (Richardson et al. 2011). The role of plant root and microbial exudation of organic anions and protons in the mobilization of relatively immobile P is well documented (Arcand and Schneider 2006; Frossard et al. 2016; Lynch and Brown 2001; Richardson et al. 2011). Organic acids exuded by plant roots commonly exist in their fully dissociated state as anions, which play a role in acidifying the rhizosphere. Consequently, root-induced acidification is rather a result of the exudation of organic anions (carboxylates) (Arcand and Schneider 2006). The organic anions include citrate, malate, and oxalate and their release is triggered by soil P_i deficiency and sometimes by Al^{3+} toxicity (Ryan et al. 2001; Vance et al. 2003). Symbiosis with mycorrhizal fungi is another way of modifying root architecture to access a larger volume of soil beyond the rhizosphere (Bucher 2007; Frossard et al. 2016). Symbiosis with Arbuscular mycorrhizal fungi (AMF) increases the efficiency of P uptake relative to plant roots alone (Schneider et al. 2019). Some plants uptake P_i effectively from P-limited environments through mechanisms such as the exudation of phosphatase enzymes that hydrolyze organic P, and the activation of high-affinity transporters of Pi (Frossard et al. 2016; Hinsinger 2001; Lynch and Brown 2001). These contributing factors are likely due to the differences in P acquisition between different crop species.

1.6.3. Green manure crops and phosphorus supply to subsequent crops

Green manure is a plant component that is incorporated into soil when it is still green or at its maturity (Soil Science Society of America 1997). Green manure is introduced to cropping systems with the primary objective of amending soil and providing nutrients to a succeeding crop. In general, green manuring provides various benefits for the sustainability of agricultural systems, such as increasing soil organic matter content and sometimes soil fertility levels, reducing soil erosion, improving weed control, retention of soil nutrients, and improving the physical, chemical, and biological properties of soil (Fageria 2007). It is a strategy for improving economic viability while minimizing the negative impacts of agriculture on the environment (Cherr et al. 2006). Therefore, green manuring is of paramount importance in organic agriculture. Green manure species are thought to benefit organic crop rotations by ameliorating soil N (Entz et al. 2001).

Incorporating a green crop with higher N content will increase soil N availability for the next crop in an organic rotation. Grazing can further increase N availability by the end of the green manure phase (Cicek et al. 2014). Advancement of cropping system design is one of the strategies for optimizing PUE, and P-mobilizing crops, such as green manure crops, can play a significant role (Schneider et al. 2019). However, the effectiveness of green manure crops at mobilizing recalcitrant P and to increasing P availability to a subsequent crop will depend on soil P status and crop combinations (Schneider et al. 2019). Available P is transferred from green manures to main crops through different mechanisms, including tissue P decomposition and mineralization, rhizosphere modification by root exudation, and the abundance and activity of soil microbes, especially AMF (Hallama et al. 2019). Main crop response to cover crops is more evident in cropping systems under low available P_i (Hallama et al. 2019). Therefore, potential benefits of cover crops could be greater in organic agricultural systems where available P_i is typically low. Vaisman et al. (2011) elaborated on how tillage intensity mediates soil nutrient availability following green manure crops in organic rotations. Reduced tillage resulted in relatively low soil N availability in late fall, thereby reducing the susceptibility to leaching. Fabaceae (legumes) provide the best cover cropping regardless of the growing environment (Hallama et al. 2019), likely be due to improved soil N fertility through atmospheric N_2 fixation and disruption of soil-borne disease cycles (Nuruzzaman et al. 2005). In a pot experiment, Nuruzzaman et al. (2015) found that biomass and P uptake of a wheat crop were greatest following faba bean, intermediate following field pea, and lowest following white lupin (*Lupinus albus* L.) despite the latter two crops producing significantly greater amounts of carboxylate. Faba bean has the morphological advantage of an extensive root system with higher P content and root mass ratio that enables access to a larger pool of relatively immobile P_o. Buckwheat exhibits an alkaline uptake pattern of nutrients (higher ratio of cation to anion uptake) (Arcand and Schneider 2006), is an excellent organic anion exuder (Arcand et al. 2010; Talboys et al. 2016), and is very effective in mobilizing Ca-phosphate in calcareous soils (Boglaienko et al. 2014). In Manitoba, the second most popular cover crop preceding forage establishment is buckwheat (Entz et al. 2001).

Despite the significant role of green manure crops as an alternative to mineral fertilizers, especially in organic agriculture, green crops alone may not provide sufficient nutrient levels for optimum economic yield. Therefore, the most appropriate technique to supply essential nutrients to a successive crop adequately is to supplement green manuring with mineral fertilizer. This would be a sustainable approach as it considerably reduces the rates of inorganic fertilizer application in conventional agriculture (Fageria and Filho 2007). Furthermore, the dissolution of struvite P and P supply to a subsequent crop can be influenced by unique rhizosphere mechanisms and crop-specific strategies of P acquisition (Schneider et al. 2019). Some green manure species have demonstrated a high potential to improve P recovery from struvite. For example, struvite resulted in better growth of a buckwheat *(Fagopyrum esculentum*) crop relative to spring wheat, an observation which was attributed to greater production of carboxylates by buckwheat (Talboys et al. 2016). A narrow-leaf lupine (*Lupinus angustifolius*) crop responded to struvite fertilizer better than to soluble P fertilizer at acidic pH by increasing specific root length, leading to greater tissue P concentration and P uptake efficiency, and at neutral pH by increasing the exudation of carboxylates (Robles-Aguilar et al. 2019). Wollmann et al. (2018) suggested that a red clover crop would mobilize P from struvite for its use as well as for a subsequent maize crop.

1.7. Research objectives

Struvite is gaining attention in diverse agricultural settings on regional and global scales as a promising P fertilizer with a low degree of impact on the environment. However, the efficacy of struvite varies widely under different cropping systems since struvite-soil-crop dynamics control the dissolution of struvite and subsequent plant P uptake. There is a need to elucidate the mechanisms underlying crop P availability and residual benefits from struvite in organic crop rotations. Therefore, the overall objective of this study was to investigate the impact of struvite and its interactions with soil and different green manure crop species on soil P dynamics and crop productivity in organically-managed agricultural systems in the Northern Great Plains region where soil test P concentrations are typically low. Specific objectives of the study were to (i) determine the main and interactive effects of a preceding green manure crop species and the source and application timing of P fertilizer on soil P dynamics and the agronomic performance of spring wheat in green manure-spring wheat crop rotations (Chapter 2), (ii) determine the impact of soil type, source of P, pre-seeding application of P fertilizer, the presence of a buckwheat crop, and their interactive effects on the residual P concentration of a low-P soil, and (iii) determine the effect of pre-seeding P fertilizer application on the supply rate of P in soil fertilized with struvite vs. MAP (Chapter 3).

1.8. Thesis layout

This thesis layout follows the guidelines of the Department of Soil Science, University of Manitoba. The thesis is outlined in four chapters, including Chapter 1, which is a general literature review, two research chapters (Chapter 2 and Chapter 3) written in manuscript format, and Chapter 4, which is the overall synthesis of the study.

Chapter 2: Agronomic response of spring wheat to struvite: Effect of preceding green manure crop;

Chapter 3: Struvite application timing effect on phosphorus availability and recovery by buckwheat in chernozemic soils.

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2. AGRONOMIC RESPONSE OF SPRING WHEAT TO STRUVITE: EFFECT OF PRECEDING GREEN MANURE CROP

2.1. Abstract

Green manure crops (GMC) exhibit a variety of phosphorus (P) acquisition mechanisms that can increase the plant availability of P from sparingly soluble sources, such as struvite ($NH_4MgPO_4 \cdot 6H_2O$). This study examined the response of spring wheat to factorial combinations of P source (struvite and monoammonium phosphate (MAP)) and timing of application (previous year and current year) as affected by the preceding GMC (faba bean, buckwheat and field pea) at two organically-managed field sites (Libau and Notre Dame) in southern Manitoba. A control (no P fertilizer) was included for comparison. Fertilizers were applied in a band with the seed. Results showed no response of wheat to a preceding GMC species or to P application at Notre Dame where background soil P concentration was moderately high. Buckwheat exhibited greater capacity to access struvite-P than field pea and faba bean, but did not increase subsequent wheat grain yield.Struvite application to a preceding field pea or faba bean crop increased wheat yield relative to the unamended control. Averaged across GMC and P sources, P application to the previous GMC increased wheat yield and grain P uptake relative to P application to the current wheat crop. Overall, while struvite showed the potential to increase wheat productivity and cumulative P uptake relative to unamended soil, it did not perform as well as MAP. These results will inform the formulation of strategies for optimizing yields and overall struvite-P use efficiency based on the timing of struvite application in organic cropping systems in Manitoba.

Key words: monoammonium phosphate, soil phosphorus, organic farming

2.2. Introduction

Phosphorus (P) is an essential macronutrient for plant growth and development. The role of P is inextricable from global water, energy and food security (Jarvie et al. 2015; Macintosh et al. 2019). However, only a small fraction (13-17 %) of the P used in agriculture reaches the food chain (Vaccari et al. 2019). Roughly 20 million tonnes of P are extracted annually for food production (Jupp et al. 2021) and approximately 2 million tonnes end up in waste streams (Cordell et al. 2009). Phosphorus recovery from waste streams is mostly inefficient, with only ~10 % of P in human waste circulated back to agriculture (Elser and Bennett 2011). Implications of these inefficiencies in global P cycling on water quality have been recognized, particularly with respect to excess P losses and enrichment of aquatic systems, causing eutrophication (Jarvie et al. 2015; Schneider et al. 2019). The over-reliance of the human food chain on P may also lead to the exhaustion of rock phosphate reserves (Withers et al. 2014), a finite non-renewable source confined only to a few geographic regions (Cordell et al. 2009). Increasing P use efficiency (PUE) in crop production, as well as P recovery from waste streams such as waste water and livestock manure, alongside the recycling of P by utilizing recovered P in agricultural production, are approaches to the sustainable management of global P cycling (Chen and Graedel 2016; Cordell et al. 2009; Simpson et al. 2011; Withers et al. 2014).

Phosphorus management in agricultural soils should aim at increasing crop PUE at the farm scale, coupled with initiatives aimed at a circular economy for P at a broader regional scale (Schneider et al., 2019). Slow-release P fertilizers such as struvite show promise for improving PUE in crop production while alleviating adverse environmental impacts of P fertilizers arising from P transport to aquatic systems. The slow-release properties of such fertilizers offer a reduced risk of eutrophication in freshwater systems by reducing P losses through leaching and surface runoff

(Everaert et al. 2018). Although published field-scale research is scanty, some studies have shown a reduced potential for environmental P loss from struvite relative to soluble P fertilizers such as MAP (Everaert et al. 2018; Vivekananthan et al. 2024). Plant availability of struvite P in the soil is governed by soil properties, struvite characteristics, and plant P acquisition strategies. In previous studies, crop response to struvite has been similar to the response to soluble P fertilizers, especially in neutral and acidic soils (Katanda et al. 2016; Robles-Aguilar et al. 2019; Talboys et al. 2016; Vivekanathan et al. 2024; Vogel et al. 2015). Phosphate rock (PR) is less soluble and considered less efficient as a P source in alkaline soils, which have high concentrations of calcium phosphate (Rahman et al. 2014).

Agricultural crops manifest diverse capabilities of mobilizing P from sparingly soluble soil P pools and fertilizers (Schneider et al. 2019). Crop-specific processes of certain grain crops, cover crops, and green manure crops enhance soil P availability to succeeding crops, depending on soil characteristics. Therefore, interactions of struvite with strategies of crop P acquisition in crop rotations warrant further study (Schneider et al. 2019). In alkaline soils, struvite generally showed a relatively low crop response (Ackerman et al. 2013; Hilt et al. 2016; Mehta et al. 2018). However, in a field study on an alkaline, low P soil in Manitoba, Canada, Thiessen Martens et al. (2022) observed a moderate response of spring wheat (*Triticum aestivum* L.) to the application of struvite because grain yield and P uptake were greater from struvite at slightly high application rates relative to unfertilized plots. Therefore, it is important to further study the potential of struvite as a P source for organic wheat production in Manitoba. In 2020, wheat was the most widely cultivated organic cereal grain crop by acreage in the Canadian Prairie region (49% of total organic cereal grain acreage).

Previous studies have shown that green manure crops (GMC) can enhance the availability of struvite P for subsequent crops (Talboys et al. 2016; Thiessen Martens et al. 2022; Wollmann et al. 2018). Green manure crops play a pivotal role in organic crop rotations by providing nutrients to successive crops, modification of soil structure, and suppression of weeds and crop pests (Krauss et al. 2010). Slow nutrient release upon decomposition of green manure crop residues can closely match plant P uptake patterns, thus offering sustained nutrient supply to the main crop (Cavigelli and Thien 2003). A recent field survey showed that green manure crops are incorporated consistently in organic crop rotations on the Canadian prairies (Entz et al. 2001). Previous studies have shown that green manure crop species, such as buckwheat (*Fagopyrum esculentum*), field pea (*Pisum sativum* L.) and faba bean (*Vicia faba* L.), have the potential to supply P to a subsequent crop through distinct mechanisms (Doolette et al. 2019; Nuruzzaman et al. 2005; Talboys et al. 2016).

Phosphorus deficiency is common in agricultural soils globally, even where total soil P concentrations are not necessarily low (Zhu et al. 2002). The prevalence of P deficiency in Canadian soils under organic management is well documented (Entz et al. 2001; Knight et al. 2010; Schneider et al. 2016, 2017). In high-yield hay production systems, when exported P is not replaced, available P can be depleted (Welsh et al. 2009). However, recalcitrant soil P pools under organic systems can be comparable to those in conventional systems (Welsh et al. 2009). Therefore, in such systems, making recalcitrant soil P more plant-available and increasing P supply from sparingly soluble fertilizers like struvite can reduce the need for inorganic fertilizer application (Withers et al. 2014). Residual P availability from struvite beyond the year of application has been demonstrated by several past studies (Katanda et al. 2016; Thiessen Martens et al. 2022; Vogel et al. 2015; Wollmann et al. 2018). Therefore, optimizing the timing of application of struvite and other P fertilizers in crop rotations shows promise in improving soil P efficiency (Schneider et al. 2019).

Given the extent of P deficiency on organic farms, coupled with the prospects for legislative approval of struvite use in organic agriculture, there is a need to examine the agronomic potential of struvite, particularly on calcareous soils in Manitoba, Canada. Therefore, this field experiment focused on evaluating the agronomic responses of a wheat crop to three preceding green manure crop species, with different P amendments (struvite and conventional MAP fertilizer) applied at strategic points in crop rotations common in Canadian prairies organic cropping systems. The study examined the potential of green manure crop species to enhance the release of P from struvite in alkaline soils in Manitoba. The specific objective was to determine the main and interactive effects of the preceding green manure crop species and the source and application timing of P fertilizer on soil P dynamics and the agronomic performance of spring wheat in a green manure-spring wheat crop rotation. We hypothesized that (1) struvite application to the preceding green manure crop in the rotation would increase the grain yield, above-ground biomass production, P uptake and P efficiency of a subsequent wheat crop as well as the residual soil P concentration, and the response may vary depending on the green manure crop species.

2.3. Materials and Methods

2.3.1. Study Sites

The study was set up in 2021 on field plots from a previous experiment that was initiated in 2020 near Libau (50°14'28.5"N 96°43'44.0"W) and Notre Dame (49°34'08.2"N 98°45'20.9"W) in southern Manitoba, Canada. The region is characterized by a humid continental climate with mild summers and precipitation throughout the year. The soil was a Gleyed Rego Black Chernozem

(Udic Boroll under the USDA Soil Taxonomy) at Libau and an Orthic Dark Grey Chernozem (Boralfic Boroll) at Notre Dame.

Both fields had been managed according to Canadian organic production standards for more than 10 yr even though they were not certified organic. The Libau site had been under alfalfa grass hay production since 2005 until conversion to annual cropping in 2017. The Notre Dame site was under continuous alfalfa-grass hay production for almost nine years before establishment of the study plots in 2020.

2.3.2. Experimental layout and treatment application

The experiment was laid out as a randomized complete block design with four blocks (representing replicates) and a split-plot treatment structure. The main plot factor was the preceding (2020) green manure crop (GMC) species (buckwheat (*Fagopyrum esculentum*), faba bean (*Vicia faba* L.) and field pea (*Pisum sativum* L.)) and the subplot factor was the P fertilizer treatment (Table 2.1): no P (Control), struvite applied in 2020 (Str1), monoammonium phosphate (MAP) applied in 2020 (MAP1), struvite applied in 2021 (Str2) and MAP applied in 2021 (MAP2). The subplot size was 8 m long × 2 m wide.

Table 2.1 Phosphorus fertilizer treatments

Source of P	Timing of application	P fertilizer treatment
No-P	-	Control
Struvite	2020	Str1
MAP	2020	MAP1
Struvite	2021	Str2
MAP	2021	MAP2

Green manure crop species indicated above were established during the spring of 2020 at Libau (50°14'28.5"N 96°43'44.0"W) and Notre Dame (49°34'08.2"N 98°45'20.9"W). Green manure crops were seeded at Libau and Notre Dame on 29 May and on 12 June 2020 respectively using a Fabro plot-scale double-disc drill (Swift Machinery Co., Swift Current, SK) with ~ 15 cm row spacing. Green manures were incorporated in late summer. Hard red spring wheat ('Cardale' variety) (*Triticum aestivum* L.) was established during the spring of 2021 in plots that had been under the spring 2020-seeded GMC species. Plots were seeded for spring wheat on 25 May at Libau and on 28 May at Notre Dame using a JT-A10 air-drill seeder (R-Tech Industries Ltd. Homewood, MB) with ~ 20 cm row spacing. Struvite and MAP were placed directly in the seed row of both the green manure crops in 2020 and the wheat crop in 2021 at a rate of 30 kg P ha^{-1} (68.7 kg P_2O_5 ha^{-1}), which was above the recommended application rate in the region. The high rate reflected findings from a previous study at the Libau site, which suggested that wheat would respond to struvite rates greater than 40 kg P ha^{-1}, which was the highest rate tested in the study (Thiessen Martens et al. 2022). Organic crop production standards were maintained throughout the study, except for P fertilizer application. A chronological sequence of field operations is shown in Fig. 2.1.

2.3.3. Sample collection and analysis

Soil samples for baseline soil characterization were collected from the 0-15 and 15-60 cm layers at each site in spring 2020 prior to GMC seeding. Post-harvest soil samples (8 cores per plot) were taken from the 0-15 cm layer and composited. Before laboratory analysis, samples were carefully inspected, and any remnants of struvite granules were removed to ensure accurate results. The samples were air-dried and sieved through a 2-mm sieve prior to analysis for $NaHCO_3$ – extractable (Olsen) P (Olsen et al. 1954). A subsample (1 g) of the soil was extracted in 20 mL of 0.5 M $NaHCO_3$ at pH 8.5 (Frank et al. 2015) and analyzed for Olsen P concentration by spectrophotometry using a flow-injection analyzer (FIA Lab, FIAlyzer-1000).

Green manure crop aboveground biomass was harvested during the late summer from one-meter sections of three adjacent rows at two locations in each plot (a total of 6 m per plot). Weeds were separated from the green manure biomass samples. Both the green manure biomass and the weeds were then dried at ~ 65 °C for 48 h and weighed separately. Before grinding, the separated weed and green manure biomass samples were recombined. Subsamples were ground to a particle size of < 2 mm using a Wiley mill (Thomas Scientific). Wheat aboveground biomass samples were collected during the hard dough stage from 1 m sections of two adjacent rows at two locations in each plot (a total of 4 m per plot). Samples were cut at ~1 cm height from the ground using a hand sickle. Wheat was harvested in August 2021 using a plot combine. Grain samples were collected from each plot and their fresh weights (grain yield) and moisture contents were measured onsite. Aboveground biomass samples were dried following the same procedure used for the green manure crop samples and weighed for wheat biomass yield determination. Subsamples of the aboveground biomass were ground (< 2 mm) using a Wiley mill (Thomas Scientific) and those of grain were pulverized using a coffee grinder. The ground green manure and wheat crop samples were analyzed for P concentration by inductively coupled plasma–optical emission spectroscopy (ICP-OES) (Perkin Elmer, Waltham, MA). Subsamples of wheat biomass and grain were analyzed for total N concentration by the Dumas Combustion method using a thermal conductivity detector (Elementar, rapid N cube) (Jones et al. 1990). Wheat grain protein concentration was calculated by multiplying total grain N concentration by a factor of 5.7 (McDonald 1977).

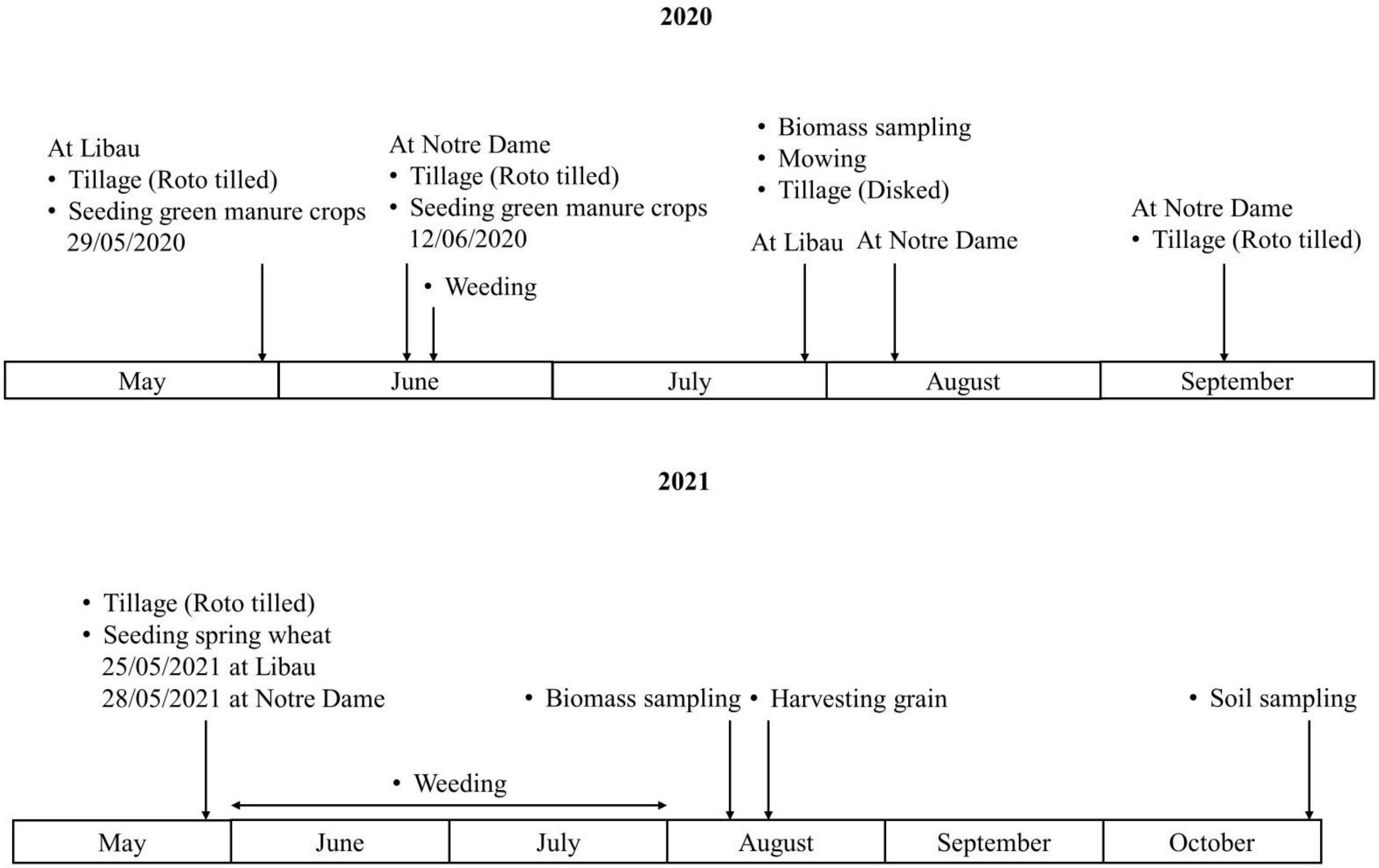

Figure 2.1 Chronological sequence of field operations in 2020 and 2021 at Libau and Notre Dame.

2.3.4. Calculations

Phosphorus accumulation in the grain and in the aboveground biomass were calculated by multiplying the respective P concentrations by the corresponding dry weights of these plant tissues. Apparent P recovery efficiency (PRE, %) for applied struvite and MAP in wheat aboveground biomass was calculated as:

$$PRE = \frac{PU_f - PU_0}{P_{app}} \times 100\ \% \qquad [1]$$

where PU_f (kg ha^{-1}) is P uptake in the fertilized plots, PU_0 (kg ha^{-1}) is P uptake in the unfertilized plots, and P_{app} (kg ha^{-1}) is the P rate (Syers et al. 2008).

Agronomic P use efficiency (AE, g DM mg^{-1} P) was calculated as:

$$\mathrm{AE} = \frac{\mathrm{DMY_f} - \mathrm{DMY_0}}{\mathrm{P_{app}}} \qquad [2]$$

where DMY is aboveground dry matter yield (DMY) and subscripts f and 0 refer to fertilized and unfertilized plots, respectively (Syers et al. 2008).

Phosphorus utilization efficiency (UE, g DM mg P^{-1}) was calculated as:

$$\mathrm{UE} = \frac{\mathrm{DMY_f} - \mathrm{DMY_0}}{\mathrm{PU_f} - \mathrm{PU_0}} \qquad [3]$$

(Fageria et al. 2013)

2.3.5. Statistical Analysis

Analysis of variance was conducted using the generalized linear mixed model procedure (PROC GLIMMIX) in SAS® (version 9.4, SAS OnDemand for Academics; SAS Institute, Cary, NC) to determine treatment effects on green manure yield, tissue P concentration, P uptake, weed biomass weight, wheat aboveground biomass, grain yield, tissue P accumulation, P efficiency indices, and residual soil Olsen P concentration after wheat harvest. Fertilizer treatment (P source for the green manure data and P source × timing for the wheat data) and GMC species were modeled as fixed factors while block and GMC × block were modelled as random effects. Treatment means were compared using Tukey's multiple comparison procedure at $\alpha = 0.05$. All crop measurements followed a normal distribution (Shapiro-Wilk's W-statistic > 0.9), and residual Olsen P concentration at Libau followed a lognormal distribution. Phosphorus recovery efficiency (PRE) in wheat was analyzed as a normal distribution since the presence of negative values precluded the use of a beta distribution in the analysis. The test of homoscedasticity indicated unequal variances for wheat dry matter yield, grain yield, biomass P uptake, grain P concentration, biomass concentration, grain protein concentration, biomass N uptake, and soil Olsen P concentration; the RANDOM_residual_/Group statement was therefore specified in the GLIMMIX model along with the Satterthwaite denominator degrees of freedom method (DDFM = Satterthwaite).

2.4. Results and Discussion

2.4.1. Weather

Monthly and seasonal precipitation and average air temperature data for the study sites are presented in Fig. 2.2 and Table 2.2, respectively. During the growing season (May-August) in 2021, Libau received 180 mm and Notre-Dame received 234 mm of rainfall. Both 2020 (the preceding GMC year) and 2021 were dry relative to the 30-yr average precipitation at the two sites Fig. 2.2).

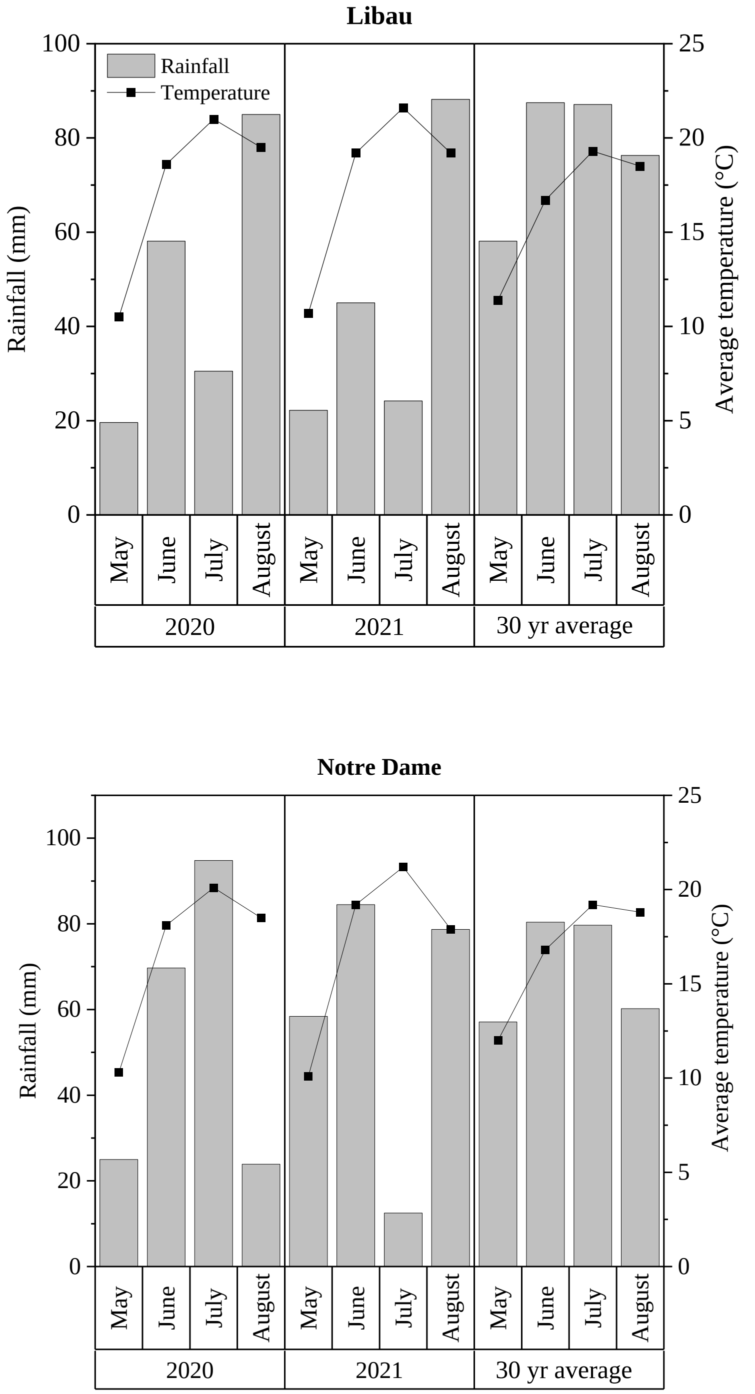

Figure 2.2 Monthly precipitation and air temperature during the growing season at the study sites obtained from the nearest provincially operated weather stations (Manitoba Agriculture 2023).

Table 2.2 Annual and seasonal (May through August) precipitation and air temperature during the study years at Libau and Notre-Dame.

Period	Total precipitation (mm)			Average temperature (°C)		
	2020	2021	30-yr average	2020	2021	30-yr average
Libau						
May-Aug.	193	180	309	17.4	17.7	16.5
Annual (Jan.–Dec.)	279	334	570	3.3	4.4	2.8
Notre-Dame						
May-Aug.	213	234	277	16.8	17.1	16.7
Annual (Jan.–Dec.)	312	387	530	3.5	4.3	3.3

Weather data for the Libau site was recorded at Selkirk, MB (8 km south of the site) and for Notre-Dame at Treherne, MB (8-10 km to the northeast) (Manitoba Agriculture 2023). 30-yr (1981-2010) averages were recorded for Libau at Beausejour, MB (within 30 km) and for Notre-Dame at Holland (within 10 km) (Environment and Climate Change Canada 2023)

2.4.2. Baseline soil properties

Initial soil test P (Olsen P) concentration was low at Libau (4 mg kg^{-1}) and high at Notre-Dame (17 mg kg^{-1}) (Table 2.2), based on the Manitoba Soil Fertility Guide (2007). The low STP at Libau reflects low P inputs, coupled with a long history of alfalfa-grass hay harvesting (one or two cuts per year) since 2006. A mix of molasses, fish and humic acid had been applied regularly to the cereal crops prior to establishment of the alfalfa-grass at the Notre Dame site. The general recommendation for P application for cereals under low soil P concentration in Manitoba is 20 kg ha^{-1} (Manitoba Soil Fertility Guide 2007).

Initial nitrate-N concentration in the 0-15 cm layer was medium at Libau and high at Notre-Dame, based on recommendations for spring wheat (Manitoba Soil Fertility Guide 2007). Extractable potassium concentration was very high at both sites while extractable S concentration was very high at Libau and moderate at Notre Dame. Therefore, all macronutrients, except P at Libau, were sufficient for field crops, including spring wheat.

Table 2.3 Baseline soil chemical properties prior to establishment of green manure crops in 2020

Soil property	**Libau**	**Notre Dame**
Nitrate-N (0-15 cm) (kg ha^{-1})	46	71
P (mg kg^{-1})	4	17
K (mg kg^{-1})	261	224
S (0-60 cm) (kg ha^{-1})	61	27
Organic carbon (g kg^{-1})	36	22
pH (0-15 cm)	8	8
pH (15-60 cm)	8.3	8.3

2.4.3. Wheat grain yield and grain phosphorus uptake

Wheat yield ranged 1057-2956 kg ha^{-1} at Libau and 2167-4806 kg ha^{-1} at Notre Dame. These yields were generally consistent with organic spring wheat yields reported in the region in previous field studies (Nicksy et al. 2022; Thiessen Martens et al. 2022; Vaisman et al. 2011) despite the drought in 2021. There were no main or interactive effects of the preceding GMC and P treatment on wheat yield and P uptake at Notre Dame (Table 2.5). At the Notre Dame site, GMC yield and P uptake in 2020 also did not vary among the GMC species and among the P treatments (Table 2.6). The relatively greater background STP concentration at this site likely precluded a yield response to P amendments.

At the Libau site, the main and interactive effects of green manure species and P treatment were not significant for wheat grain P concentration. The main effect of P treatment and the GMC × P interaction were significant for grain yield (Table 2.4; Fig. 2.3). One degree-of-freedom contrast analysis indicated that grain yield and P uptake were lower for struvite than MAP and lower for the no P treatment than the two P sources (Table 2.4). This corroborates results from earlier studies which tested the same P sources on neutral to alkaline soils and showed that crop response to struvite could be lower compared to soluble P fertilizer on alkaline soils (Ackerman et al. 2013; Hilt et al. 2016; Mehta et al. 2018). Based on one degree-of-freedom contrast analysis, the effect of a preceding buckwheat GMC on wheat yield response to struvite compared to the No-P treatment was significantly lower than that of a preceding faba bean or field pea GMC (Table 2.4). Regardless of the timing of application, struvite did not increase wheat yield following a buckwheat GMC compared to the no P treatment (Fig. 2.3). This suggests that buckwheat is less effective in increasing struvite P availability to a subsequent wheat crop compared to field pea and faba bean. The GMC × P interaction was significant for GMC yield and biomass P uptake in 2020 (Table 2.7) but by comparison to the wheat crop in the following year, yield and P uptake responses of buckwheat to struvite were greater than that the response to no P application (Fig. 2.5a and b). By comparison, faba bean and field pea did not respond to P application. This indicates that buckwheat responded to struvite application better than field pea and faba bean in the alkaline, low-P Libau soil. Nevertheless, this greater capacity of buckwheat to mobilize relatively unavailable struvite-P did not translate to a greater wheat yield in the following year. This is comprehensible since our results indicated a significant correlation of wheat grain yield with green manure P uptake ($r = 0.39$, $p = 0.002$) but not with green manure yield ($r = 0.24$, $p = 0.07$) in the previous year. In a pot study, Cavigelli and Thien (2003) observed that P uptake of a sorghum crop was inconsistently correlated with preceding green manure crop properties, including biomass yield and P uptake.

Our findings suggest that buckwheat is more efficient at mobilizing struvite P for its own use, but less efficient in P transfer to a subsequent wheat crop compared to field pea and faba bean. Arcand et al. (2010) suggest that, for a buckwheat crop to increase P availability to a succeeding crop, its tissue P concentration should be greater than 2.9 mg g^{-1}. In our study, buckwheat tissue P concentration was below 2.1 mg g^{-1} at Libau, indicating that tissue P concentration was insufficient to benefit the subsequent wheat crop. Struvite applied to field pea and faba bean might have increased subsequent wheat yield relative to buckwheat because, as explained by Hallama et al. (2019), crop response to preceding leguminous GMCs is often superior to preceding non-legume GMCs. The underlying mechanisms may include a relatively higher transfer of P to the main crop due to the abundance of legume biomass rich in P, an increase in arbuscular mycorrhizal fungi (AMF) abundance and phosphatase enzyme activity, or enhanced biological N fixation, which boosts N availability through the decomposition of legume residues. In addition, residual P benefit in subsequent grain crops from struvite application to legume green manure cover crops has previously been observed on an alkaline soil (Wollmann et al. 2018). Apart from enhancing yield and growth, P application to legumes offers additional benefits like increased nodulation and biological N_2 fixation (BNF). Olivera et al. (2004) observed that P application to common bean (*Phaseolus vulgaris* L.) increased both the number and the biomass of nodules, though they found no direct correlation between nodule biomass and BNF. Contrarily, Pereira and Bliss (1987) reported a positive correlation between nodule biomass and BNF. Moreover, research has shown P concentration in nodules to be correlated with BNF (Mitran et al. 2018). In our study, despite no increase in aboveground biomass yield or P uptake in the legume GMCs (likely due to weed pressure) following the application of either P source, we speculate that P application may have enhanced BNF. This potential improvement in BNF in faba bean and field pea following the application of struvite or MAP could have contributed to the observed increase in subsequent wheat yield compared to the untreated control. It is also important to note that faba bean and field pea are mycorrhizal crops whereas buckwheat is nonmycorrhizal. Symbiosis with arbuscular mycorrhizal fungi (AMF) is one of the mechanisms that enhance plant uptake of P. In a study using tomato plants, Di Tomassi et al. (2021) observed that a mycorrhizal genotype had higher P uptake when treated with struvite compared to a mutant with reduced mycorrhizal association. However, they found no evidence of an AMF effect on struvite dissolution. The authors attributed the observed benefit of AMF to P scavenging mechanisms by AMF rather than to a struvite-P dissolution by AMF. In a field study, Heydari et al. (2024) observed that the application of P fertilizers, including struvite, in conjunction with AMF bio-inoculation led to increased yield and P uptake in a barley crop. Conversely, Schwalb et al. (2021) reported that P uptake by rye (*Secale cereale* L.) was lower in treatments inoculated with AMF compared to the non-inoculated control treatments. Based on the findings of these previous studies, it can be anticipated that the observed increase in wheat yield following struvite application to a preceding faba bean or field pea crop compared to the no-P control may be facilitated by AMF symbiosis. However further investigation is needed to confirm such an effect of AMF on struvite-P mobilization.

Based on one degree-of-freedom contrasts analysis, averaged across P sources and preceding GMC species, P application to the preceding GMC resulted in higher grain yield and P accumulation in the grain compared with direct application of P to the current wheat crop (Table 2.4). However, pre-application of either struvite or MAP to the preceding GMC did not increase wheat grain yield regardless of GMC species (Fig. 2.3) and had no significant effect on wheat grain P uptake relative to application to the current wheat crop (Fig. 2.4). These findings do not support the hypothesis that struvite application to a previous green manure crop would increase its P release, hence P uptake by the subsequent crop. Past studies suggest residual P availability to later phases of crop rotations from previously applied struvite and MAP (Katanda et al. 2016; Thiessen Martens et al. 2022; Vogel et al. 2015; Wollman et al. 2018). The contradiction can be attributed to the relatively high P application rate (30 kg P ha^{-1}) in the present study compared to P application rates used in most of those previous studies (12 - 40 kg P ha^{-1}). The high rate of struvite application to the wheat crop in the current year might have supplied sufficient P to optimize wheat yield. Although, at 40 kg P ha^{-1} rate of struvite application to a wheat crop, Thiessen Martens et al. (2022) suggested residual P benefit to a subsequent crop might exist due to the presence of undissolved remnants of struvite granules after wheat harvest; however, they did not quantify that effect on a subsequent crop. Alternatively, the lack of response of GMCs to P application could have led to minimal P transfer to the subsequent wheat crop. It is important to note that weather at the study sites during the study period may have influenced crop response to P fertilizers. Both 2020 and 2021 experienced below-average precipitation compared to the 30-yr (1981-2010) average. Under typical precipitation levels, we would have anticipated a greater wheat yield response to struvite application to the preceding GMCs.

2.4.4. Grain protein concentration

Grain protein concentration at Libau was not significantly affected by the preceding GMC (Table 2.4). However, there was a significant main effect of P treatment on grain protein. The No-P control and struvite application to the wheat crop resulted in the greatest grain protein concentration. Struvite applied to the preceding GMC and MAP applied at either timing produced the lowest protein concentrations. Results from a previous study at the Libau site showed a negative correlation between grain yield and tissue N concentration as well as a P treatment effect on grain protein content (Nicksy et al. 2022). In that study, higher-yielding treatments, including MAP, resulted in relatively lower grain protein concentration compared to lower-yielding treatments such as struvite and the unfertilized control, suggesting a N dilution effect at greater yields.

Table 2.4 Wheat grain and biomass yields, P uptake indices, biomass N uptake, and residual Olsen P concentration after wheat harvest at Libau in 2021 as affected by phosphorus amendment (source × timing) and preceding green manure crop.

Effect	**Grain yield**	**DMY**[a]	**Grain P conc.**	**Biomass P conc.**	**Grain PU**	**Biomass PU**	**Grain protein**	**Biomass NU**	**Olsen P**
	kg ha^{-1}	**Mg ha^{-1}**	**mg g^{-1}**		**kg ha^{-1}**		**%**	**kg ha^{-1}**	**mg kg^{-1}**
Green manure crop (GMC)									
Buck wheat	1944	4.30	2.4	1.0a	4.20	4.28	16.8	66.3b	8.6
Field pea	2080	4.89	2.29	0.90ab	4.25	4.33	16.9	75.2a	8.6
Faba bean	2193	5.33	2.34	0.87b	4.57	4.66	17	78.5a	9.7
P treatment (source timing)[b]									
Str 1	2119bc[c]	4.61b	2.37	0.88	4.51bc	4.08b	16.7b	69.0bc	8.0b
MAP 1	2384a	5.07b	2.36	0.96	5.06a	4.85ab	16.2b	78.3ab	6.8b
Str 2	1952c	4.81b	2.35	0.93	4.10c	4.48b	17.4a	74.1ab	10.1ab
MAP 2	2258ab	6.11a	2.29	0.91	4.62ab	5.49a	16.7b	87.9a	16.2a
No P	1648d	3.60c	2.35	0.93	3.42d	3.21c	17.5a	57.4c	3.8b
Contrasts									
Struvite vs MAP	-285	-0.88	-	-	-0.54	-0.89	0.64	-11.52	-2.42
Struvite vs No P	388	1.11	-	-	0.88	1.07	-0.48	14.17	5.21
2020 vs 2021[d]	147	-0.62	-	-	0.43	-0.52	-0.56	-7.33	-5.75
Struvite vs No P for buckwheat	-279	-	-	-	-	-	-	-	-
					P value				
GMC	0.30	0.07	0.09	0.02	0.53	0.59	0.83	0.01	0.86
P treatment	< 0.0001	< 0.0001	0.76	0.82	< 0.0001	< 0.0001	< 0.0001	0.0001	0.001
GMC × P treatment	0.03	0.83	0.68	0.98	0.13	0.86	0.91	0.35	0.77
Contrasts									
Struvite vs MAP	< 0.0001	< 0.0001	-	-	< 0.0001	0.0001	0.0002	0.01	0.20
Struvite vs no-P	< 0.0001	< 0.0001	-	-	< 0.0001	0.0002	0.01	0.01	0.03
2020 vs 2021	0.002	0.0002	-	-	0.001	0.02	0.001	0.07	0.004

Struvite vs No P for buckwheat	0.03	-	-	-	-	-	-	-	-
Struvite vs No P for field pea	0.15	-	-	-	-	-	-	-	-
Struvite vs No P for faba bean	0.40	-	-	-	-	-	-	-	-
2020 vs 2021 for buckwheat	0.20	-	-	-	-	-	-	-	-
2020 vs 2021 field pea	0.50	-	-	-	-	-	-	-	-
2020 vs 2021 faba bean	0.52	-	-	-	-	-	-	-	-

[a] DMY, above-ground dry matter yield; PU, phosphorus uptake; NU, nitrogen uptake; Olsen P, soil residual Olsen P concentration (0-15 cm soil layer) after wheat harvest.

[b] Str 1, struvite applied to GMC; MAP 1, MAP applied to GMC; Str 2, Struvite applied to wheat; MAP 2, MAP applied to wheat; No P, unfertilized control.

[c] Means within the same column and factor followed by the same letter are not significantly different at α = 0.05 according to the Tukey multiple comparison procedure.

[d] 2020 vs 2021, P fertilizer application to the GMC in the previous year (2020) vs. P application to the wheat crop in the current year (2021).

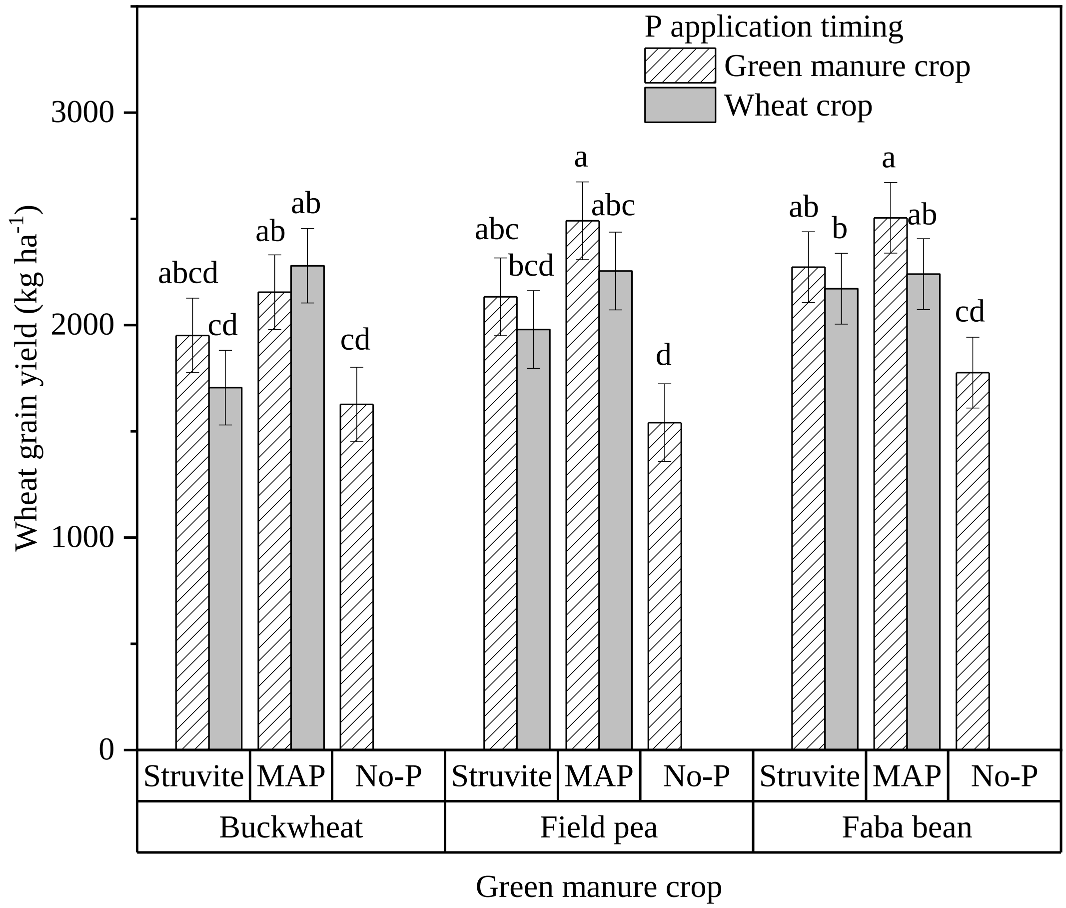

Figure 2.3 Effect of Green manure crop species × P treatment (source [MAP, struvite, No-P] × timing [P application to the green crop, P application to the wheat crop]) on wheat grain yield at Libau. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the means.

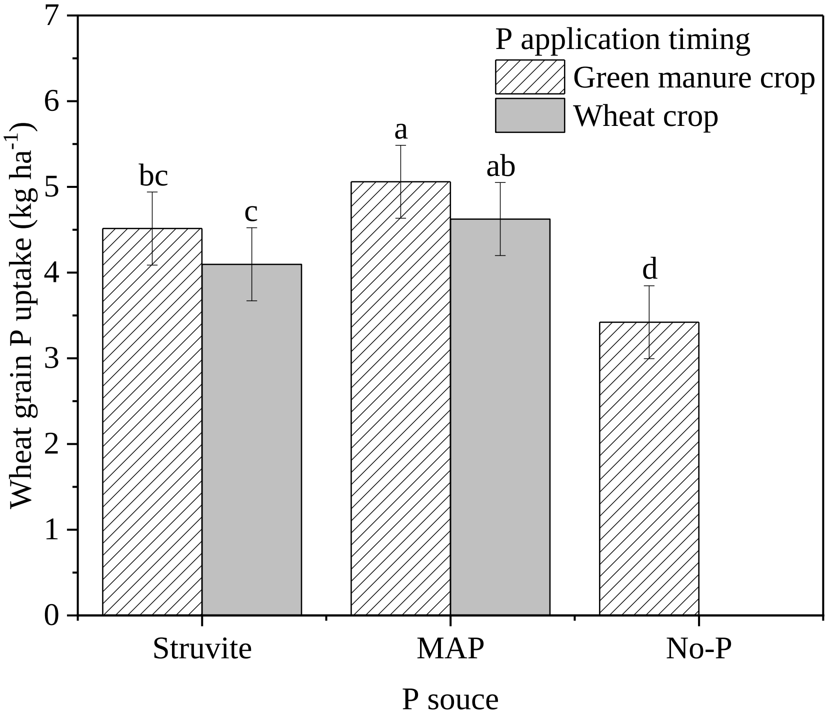

Figure 2.4 Effect of P treatment (source × timing) on wheat grain P uptake at Libau. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure (α = 0.05). Error bars indicate standard errors of the mean.

Table 2.5 Wheat grain and biomass yields, P uptake indices, biomass N uptake, and residual Olsen P concentration after wheat harvest at Notre Dame in 2021 as affected by phosphorus amendment (source × timing) and preceding green manure crop.

Effect	**Grain yield**	**DMY**[a]	**Grain P conc.**	**Biomass P conc.**	**Grain PU**	**Biomass PU**	**Grain protein**	**Biomass NU**	**Olsen P**
	kg ha^{-1}	**Mg ha^{-1}**	**mg g^{-1}**		**kg ha^{-1}**		**%**	**kg ha^{-1}**	**mg kg^{-1}**
Green manure crop (GMC)									
Buck wheat	2851	6.14	3.60	1.80	9.56	11.15	16.2	110	20.2
Field pea	3037	6.25	3.62	1.72	9.94	10.76	16.2	108	22.4
Faba bean	3326	6.35	3.99	2.16	12.0	13.72	16.3	117	22.7
P treatment (source × timing)[b]									
Str 1	3017	6.29	3.78	1.81	10.4	11.5	16.3ab[c]	110	22.1ab
MAP 1	3161	6.34	3.73	1.78	10.8	11.2	15.9b	104	22.8ab
Str 2	3098	6.19	3.73	2.15	10.7	13.4	16.3a	122	22.2ab
MAP 2	3102	6.25	3.67	1.78	10.5	11.2	16.4a	105	23.4a
No P	2979	6.15	3.78	1.95	10.2	12.2	16.2ab	116	18.3b
Contrast									
Struvite vs MAP	-	-	-	-	-	-	0.18	-	-1.0
Struvite vs No P	-	-	-	-	-	-	0.14	-	3.88
2020 vs 2021[d]	-	-	-	-	-	-	-0.26	-	-0.33
					P value				
GMC	0.07	0.92	1.0	0.11	0.05	0.14	0.87	0.61	0.58
P treatment	0.43	0.89	1.0	0.06	0.66	0.25	0.01	0.36	0.03
GMC P treatment	0.65	0.52	1.0	0.14	0.84	0.42	0.23	0.22	0.91
Contrasts									
Struvite vs MAP	-	-	-	-	-	-	0.07	-	0.39
Struvite vs No P	-	-	-	-	-	-	0.26	-	0.01
2020 vs 2021	-	-	-	-	-	-	0.01	-	0.77

[a] DMY, above-ground dry matter yield; PU, phosphorus uptake; NU, nitrogen uptake; Olsen P, soil residual Olsen P concentration (0-15 cm soil layer) after wheat harvest.

[b] Str 1, struvite applied to GMC; MAP 1, MAP applied to GMC; Str 2, Struvite applied to wheat; MAP 2, MAP applied to wheat; No P, unfertilized control.

[c] Means within the same column and factor followed by the same letter are not significantly different at $\alpha = 0.05$ according to the Tukey multiple comparison procedure.

[d] 2020 vs 2021, P fertilizer application to the GMC in the previous year (2020) vs P application to the wheat crop in the current year (2021).

Table 2.6 Effect of green manure crop species and P source on yield, biomass P concentration, and P uptake of green manure crops grown at Libau and Notre Dame, MB in 2020.

Effect	DMY[a]		Biomass P concentration		Biomass P uptake	
	Mg ha^{-1}		mg g^{-1}		kg ha^{-1}	
	Libau	**Notre Dame**	**Libau**	**Notre Dame**	**Libau**	**Notre Dame**
Green manure crop (GMC)						
Buck wheat	3.23a[b]	3.42	1.33b	3.27	4.61a	11.1
Field pea	2.53a	3.48	1.27b	3.24	3.31ab	11.0
Faba bean	1.27b	2.46	1.98a	3.42	2.56b	8.25
P source						
Struvite	2.36b	2.91	1.48b	3.32	3.22b	9.44
MAP	2.94a	3.16	1.88a	3.38	5.27a	10.5
No P	1.74c	3.29	1.21c	3.23	1.99c	10.4
	P value					
GMC	0.01	0.23	0.001	0.73	0.03	0.22
P source	< 0.0001	0.32	< 0.0001	0.3	< 0.0001	0.35
GMC × P source	0.0002	0.41	0.001	0.5	0.001	0.58

[a] DMY, aboveground dry matter yield

[b] Means within the same column and factor followed by the same letter are not significantly different at $\alpha = 0.05$ according to the Tukey multiple comparison procedure.

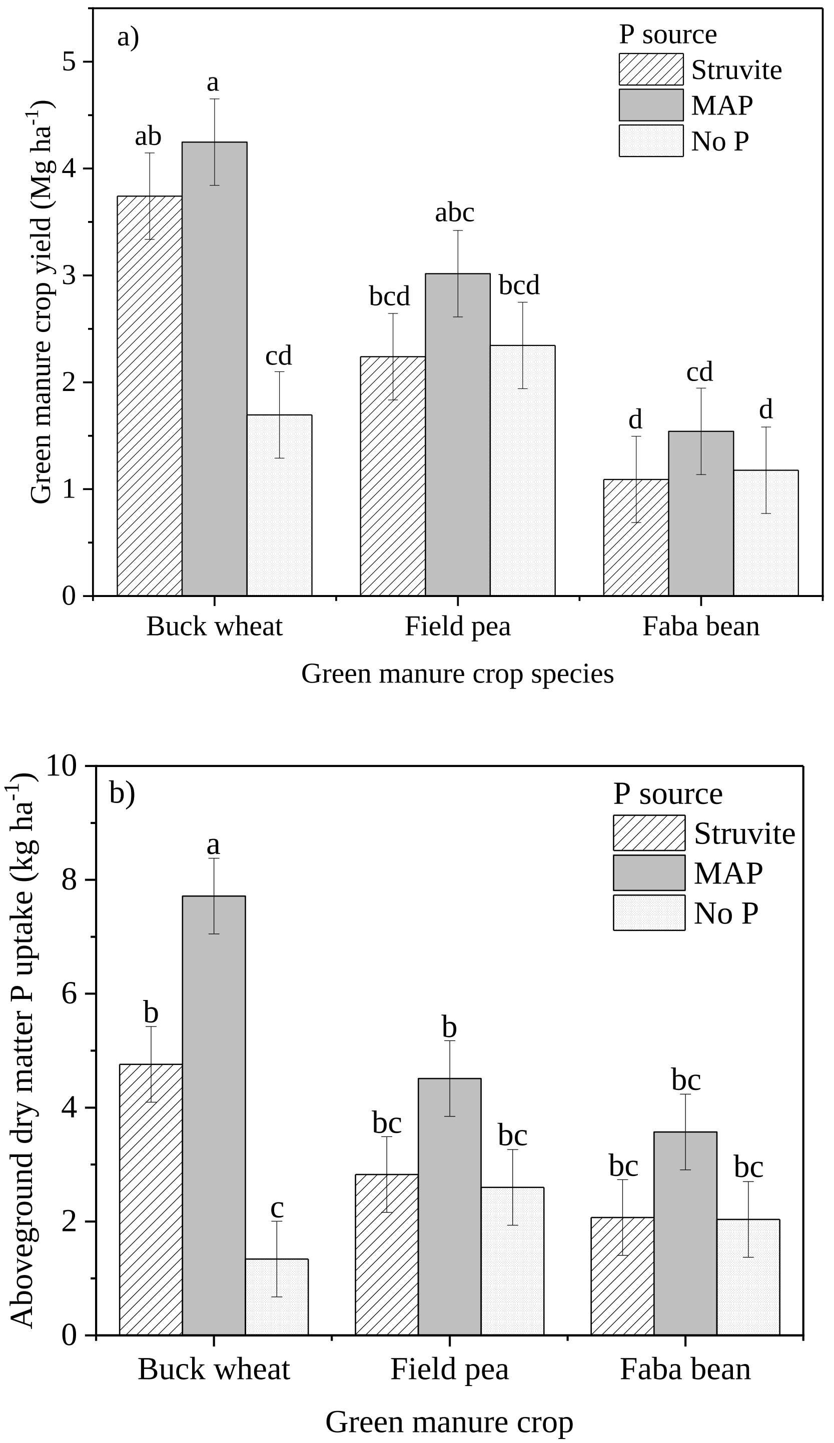

Figure 2.5 Effect of the green manure crop species × P source interaction on (a) yield and (b) aboveground dry matter P uptake of green manure crops at Libau. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the mean.

2.4.5. Wheat aboveground biomass yield and P accumulation

Above-ground biomass yield and P accumulation by wheat at Notre Dame showed no response to the preceding GMC species and to the P treatments (Table 2.5), perhaps reflecting the high soil test P concentration at the Notre Dame site. At Libau, the P treatment effect on DMY and biomass P uptake was significant (Fig 2.6a and b; Table 2.4). Averaged across the P application timings, DMY and biomass P uptake from struvite application were greater than those from the control but lower than those from MAP (Table 2.4). In contrast, results from a previous study at the Libau site with spring wheat showed no yield or P accumulation response to struvite relative to the no-P control (Nicksy et al. 2022). The authors attributed the lack of response to the broadcast application of P fertilizer in that experiment. Therefore, band application of P in the present study appeared to have benefitted wheat yield. Grant and Flaten (2019) explain that seed banding of P fertilizer is effective under the cold spring weather, which is common in the Northern Great Plains region. Further, a growth room experiment using two alkaline soils from Manitoba showed similar wheat DMY for struvite and MAP (Katanda et al. 2016). The contrasting results versus the present study can be attributed to the struvite granule size. Katanda et al. (2016) used uniform sized hog-manure recovered struvite granules similar in size to commercially available MAP, whereas we used approximately 3 mm-sized struvite granules, which were larger in size than MAP granules. Dissolution of struvite is faster for smaller particle sizes compared to larger particle sizes due to the increased surface contact with soil (Degryse et al. 2017). Katanda et al. (2016) found no significant increase in spring wheat PU relative to the unamended control following P application. They observed a response only from a high MAP application rate in the sandy soil. They attributed the poor PU response of wheat to applied fertilizer to arbuscular mycorrhizal fungi colonization in wheat that was facilitating P uptake in low P soils.

In contrast to the response of grain yield and P uptake, P application in the wheat phase produced greater wheat DMY at Libau relative to application to the preceding GMC, indicating that P transfer through green manure crops did not improve wheat dry matter production in the following year (Table 2.4). Contrary to our observation of no wheat DMY or biomass P uptake benefit from struvite application to the preceding GMC (Fig. 2.6a and b), results from a previous pot experiment showed that a red clover green manure crop treated with recycled P fertilizers, including struvite, mobilized P for its own use and for the use of a subsequent maize crop, leading to the conclusion that P bioavailability from the recycled fertilizers increased in a crop sequence that included legumes (Wollmann et al. 2018). Overall, 2021 was an extremely dry year at our study sites. Aboveground biomass production of green manure in 2020 and wheat in 2021 might have responded more to precipitation patterns than to fertilizer or GMC treatments. In organic field experiments in the same region as our study, Cicek et al. (2014, 2015) and Nicksy et al. (2022) observed that above-ground biomass yields of green manure crops and wheat varied with precipitation patterns, with greater biomass yields under normal wet conditions compared to dry weather. Relatively higher precipitation in 2020 might have favored dry matter accumulation in GMCs and resulted in a dilution effect on tissue P concentration, hence lower P transfer to the subsequent wheat crop through decomposition. Even though the actual physiology is uncertain, a dilution of applied nutrients occurs as the rate of dry matter accumulation exceeds the rate of nutrient accumulation (Jarrell and Beverly 1981). Moreover, data from 2020 indicate greater weed competitiveness relative to the succeeding wheat crop (Table S.1), which should be a result of relatively higher rainfall in 2020. This greater weed competitiveness might have negatively impacted GMC growth and P uptake. However, wheat DMY and P uptake from plots receiving P application to the preceding GMC did not differ significantly between struvite and MAP (Fig. 2.6a and b), indicating similar residual benefits of previously applied struvite and MAP to biomass production of the subsequent wheat crop.

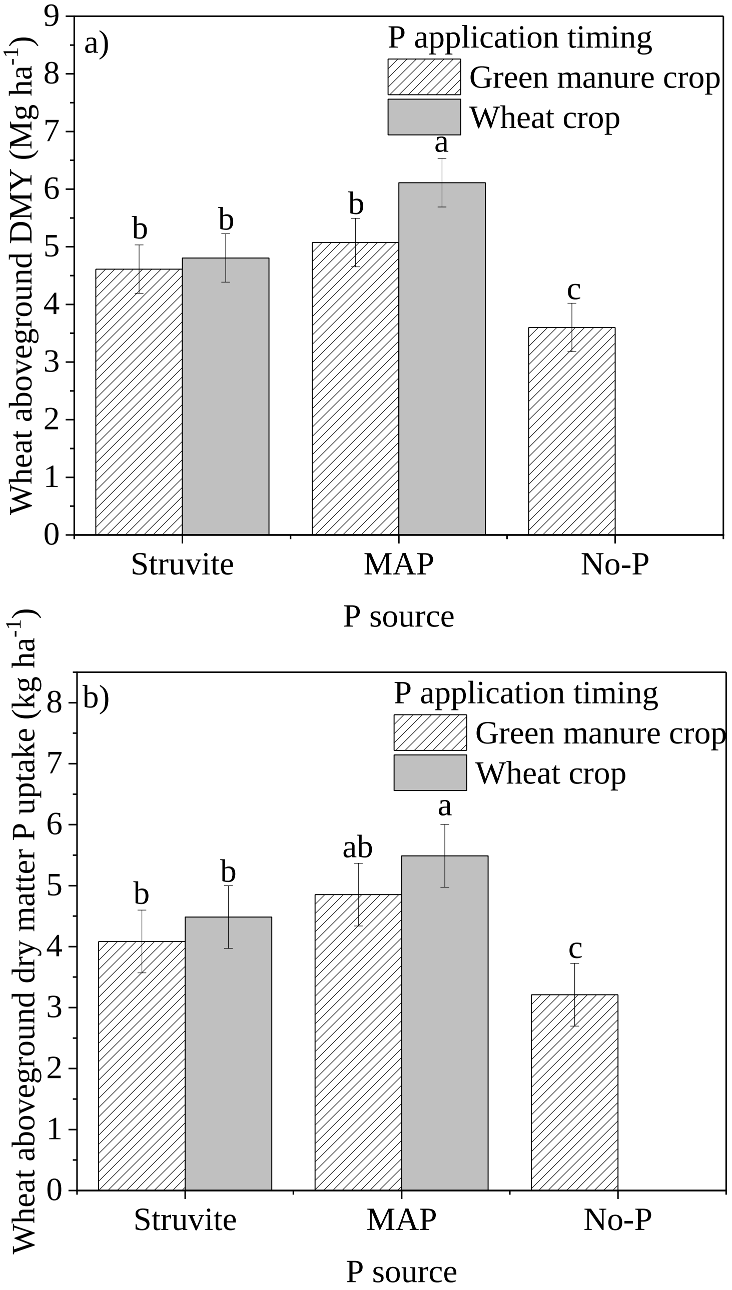

Figure 2.6 Effect of P treatment (source × timing) on wheat above-ground dry matter: (a) yield and (b) P uptake at Libau. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the means.

2.4.6. P use efficiency of wheat at Libau

The results from Notre Dame were excluded due to the presence of negative values, which could be attributed to the relatively high background soil P. Therefore only the results from Libau are discussed. Phosphorus treatment had a significant effect on both P recovery efficiency (PRE) and agronomic P use efficiency (AE) of wheat aboveground biomass (Table 2.7; Fig. 2.7). Averaged across the preceding GMCs and the timings of P application, PRE and AE were lower for struvite than MAP (Table 2.7). Similar to wheat DMY and P uptake responses, P application to the wheat crop in the current year resulted in greater PRE and AE than P application to the GMC in the previous year (Table 2.7). Accordingly, struvite previously applied to the GMC did not increase PRE or AE of the subsequent wheat crop (Fig. 2.7a and b). In general, PRE of wheat aboveground biomass for both struvite and MAP treatments in the present study were slightly lower than those observed in similar research in the same region (4.24% for struvite and 7.59% for MAP application to the wheat crop in 2021 (Table 2.7)). Thiessen Martens et al. (2022) reported 5.4% PRE in wheat grain for struvite application at 30 kg P ha^{-1} and anticipated a slightly higher PRE if wheat straw was included. Nicksy et al. (2022) reported mean PRE in wheat grain of 5% and 15% for struvite and MAP, respectively, applied at 20 kg P ha^{-1}. The relatively low aboveground biomass PRE in our study for P application to the wheat crop in 2021 compared to results from similar research in the region might be a result of the relatively low precipitation during the growing season in 2021. Moisture stress can slow down P diffusion in soil and subsequently reduce plant P availability. Averaged across the preceding GMCs, MAP application to the wheat crop resulted in greater wheat AE compared to other P treatments (Fig. 2.7b). Phosphorus utilization efficiency (UE) in wheat was not significantly affected by main or interactive effects of the preceding GMC species and P treatment. This indicates that, despite the low struvite P recovery efficiency of struvite than MAP in this study, biomass production from struvite-P was similar to that from MAP-P. Conversely, in a pot study using a sandy loam soil with moderate soil test P concentration, Ackerman et al. (2013) reported comparable P uptake by a canola crop for struvite and MAP but relatively low struvite-P conversion to biomass. This is conceivable because response of different crops to struvite vs. MAP is highly variable (Hertzberger et al., 2020).

Table 2.7 Effect of green manure species and the application of struvite and monoammonium phosphate (MAP) on P efficiency indices of wheat at Libau

Effect	**PRE**[a]	**AE**	**UE**
	%	**g DM mg^{-1} P**	
Green manure species			
Buck wheat	4.65	0.04	1.15
Field pea	5.15	0.06	2.52
Faba bean	5.36	0.06	1.07
P treatment (source × timing)			
Str 1[b]	2.91b[c]	0.03b	1.12
MAP 1	5.47ab	0.05b	1.04
Str 2	4.24ab	0.04b	2.72
MAP 2	7.59a	0.08a	1.45
Contrast			
Struvite vs MAP	-2.96	-0.03	-
2020 vs 2021[d]	-1.73	-0.02	-
		P value	
Green manure species	0.89	0.26	0.48
P treatment	0.01	< 0.0001	0.54
GMC × P treatment	0.43	0.93	0.52
Contrast			
Struvite vs MAP	0.0004	< 0.0001	-
2020 vs 2021	0.02	0.001	-

[a] PRE, P recovery efficiency; AE, Agronomic P use efficiency; UE, P utilization efficiency

[b] Str 1, struvite applied to GMC; MAP 1, MAP applied to GMC; Str 2, Struvite applied to wheat; MAP 2, MAP applied to wheat.

[c] Means within the same column and factor followed by the same letter are not significantly different at α = 0.05 according to the Tukey multiple comparison procedure.

[d] 2020 vs 2021, P fertilizer application to the GMC in the previous year (2020) vs P application to the wheat crop in the current year (2021).

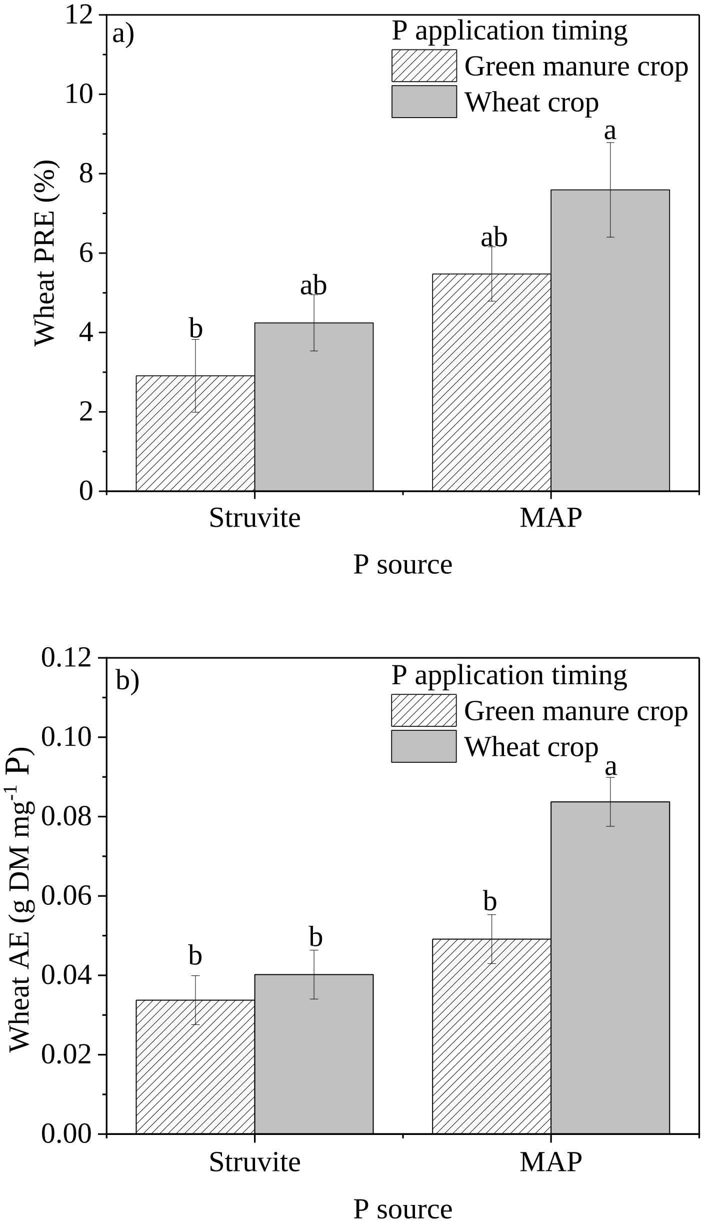

Figure 2.7 Effect of P treatment (source × timing) on wheat (a) P recovery efficiency (PRE) and (b) agronomic P use efficiency (AE). Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the means.

2.4.7. Residual soil Olsen P concentration

Residual Olsen P concentration in the soil after wheat harvest was of interest to determine if there was a potential residual benefit from struvite for a subsequent (third) crop in the rotation. The results from Libau show that both struvite and MAP applied either to the GMC or to the wheat crop resulted in significantly greater residual Olsen P concentration compared to the control treatment (Fig. 2.8a). Thus, available P supply from the P applied to the green manure crop in the first year of the rotation was likely to be still available for plant uptake in the third year following initial application. This resonates with previous research that provided evidence of residual P effects of struvite in subsequent crops in later years after application (Katanda et al. 2016b; Talboys et al. 2016; Thiessen Martens et al. 2022; Vogel et al. 2015; Wollmann et al. 2018). Although a significant P treatment effect was detected at Notre Dame for residual soil Olsen P concentration after wheat harvest, P treatments were comparable to the no P treatment except MAP application to the current wheat crop (Fig. 2.8b). Interestingly, at the Libau site there was no notable difference in Olsen P concentration between struvite and MAP treatments applied to the preceding GMC. This may be an over-estimation of Olsen P concentration for the struvite treatment, which could be due to partially dissolved struvite granules still remaining in the soil samples. Despite attempts to remove any remaining struvite granules from the samples, some grains might still be present, possibly because they were too small and not easily visible.

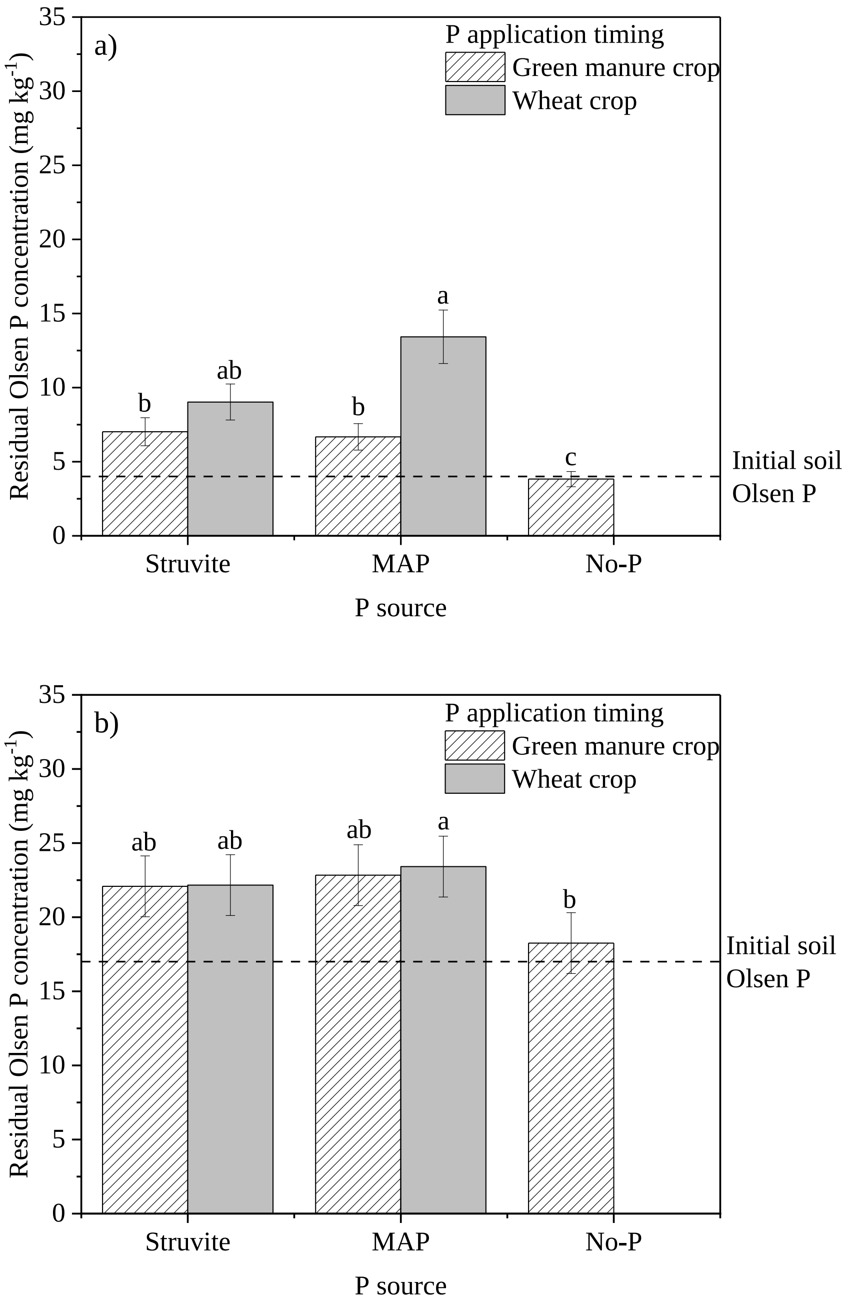

Figure 2.8 Effect of P treatment (source× timing) on residual soil Olsen P concentration at (a) Libau and (b) Notre Dame after wheat harvest in 2021. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the means.

2.5. Conclusion

Differential effects of green manure species on improving grain yield of an ensuing wheat crop suggest that crop-specific strategies of P mobilization can be implemented to increase P use efficiency in organic crop rotations. Overall, struvite application increased wheat grain and biomass yields and P uptake relative to the unfertilized control treatment. However, struvite P supply was inferior to MAP. In the alkaline, low-P Libau soil, buckwheat showed greater potential to mobilize struvite-P compared to field pea and faba bean but resulted in relatively low yield benefit to the subsequent wheat crop. Struvite applied to faba bean or field pea increased subsequent wheat yield relative to the no P control. Therefore, applying struvite to a preceding legume GMC appears to be an effective strategy for enhancing crop response to struvite in organic rotations in Manitoba. Overall, P application timing did influence grain and biomass yield of the wheat crop. Grain yield and P uptake were greater for P application to the GMC whereas P application to the wheat crop produced greater wheat biomass yield. However, struvite application to preceding GMCs irrespective of the GMC species did not increase P availability to the succeeding wheat crop relative to application to the wheat crop itself.

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3. STRUVITE APPLICATION TIMING EFFECTS ON PHOSPHORUS AVAILABILITY AND RECOVERY BY BUCKWHEAT IN CHERNOZEMIC SOILS

3.1. Abstract

Organic anions have been shown to enhance the dissolution of struvite ($MgNH_4PO_4.6H_2O$), which may be used as an alternative phosphorus (P) fertilizer and is known to have slow-release properties. Therefore, green manure species, such as buckwheat, that exude abundant organic acids may increase the plant availability of P from struvite. The mechanism is still not clear since there is evidence of increased struvite P availability even in the absence of crops. This growth room bioassay examined the impact of P source [struvite, monoammonium phosphate (MAP), and a no P control] and timing of application (28 d prior to seeding (pre-seeding application, PSA) vs. P application at seeding (at-seeding application, ASA) on P availability as affected by the presence of a buckwheat crop. Phosphorus supply rate in in the soil was determined using plant root simulator (PRS) probes. Overall, P uptake by buckwheat from struvite was greater than that from the no P control, but lower than that from MAP. Cumulative P release from struvite, as indicated by PRS probe measurements, was lower than that from MAP, indicating the low solubility of struvite. Phosphorus fertilizer application 28 d prior to seeding did not affect the cumulative uptake of struvite-P by buckwheat but reduced the cumulative uptake of P from MAP. The presence of buckwheat had no significant impact on residual soil Olsen P concentration at the end of the bioassay. Overall, our results indicate that struvite has the potential to serve as an effective source of P for organic crop production in chernozemic soils, but neither application to a previous buckwheat nor the presence of buckwheat are likely to improve struvite P availability.

Key words: monoammonium phosphate, soil phosphorus, green manure crop, soil incubation

3.2. Introduction

Phosphorus (P) deficiency is a major constraint to crop production globally, particularly in regions where P fertilizers are not readily accessible. Conventional P fertilizers are manufactured from phosphate rock (PR), which is a non-renewable resource of limited availability. It is projected that global reserves of PR will be exhausted within the next several decades at the present extraction rate (Cordell et al. 2009; Vaccari et al. 2019). Therefore, using alternative sources of P derived from waste streams, such as struvite, will be crucial to meeting future P demand in agriculture (Jupp et al. 2021; Schneider et al. 2019; Withers et al. 2014).

The slow dissolution of struvite compared to soluble P fertilizers, such as monoammonium phosphate (MAP), offers several benefits, including the reduced risk of P surface runoff, lower seedling toxicity to susceptible crops (Katanda et al. 2016), and facilitation of mycorrhizal root colonization (Thiessen Martens et al. 2023). Although the agronomic potential of struvite is well-established for low pH soils, crop response to struvite on alkaline soils is often inferior to soluble P fertilizers (Hertzberger et al. 2020).

Despite its low water solubility, the citrate-solubility of struvite is similar to the solubility of ammonium phosphates in water and in neutral (pH 7.0) ammonium citrate plus water, which suggests that an interaction with plants has the potential to enhance struvite dissolution via root exudation of organic acids (Hertzberger et al. 2020). There is evidence from previous research of increased struvite P bioavailability in the presence of certain crops, which has been attributed to rhizosphere processes (Talboys et al. 2016). Wollmann et al. (2018) observed that a clover cover crop mobilized P from recycled sources, including struvite, and suggested fertilizer P mobilization through root activity as a possible underlying mechanism. Other alternative scenarios they put forward were: mobilized P recycling through crop residues, augmentation of root colonization by beneficial plant growth promoting rhizobacteria and acceleration of soil mineral P dissolution by organic acids generated during residue decomposition. However, incubation studies have also demonstrated an increase in soil test P (STP) following struvite application in the absence of plants (Anderson et al. 2020; Duboc et al. 2017; Nongqwenga et al. 2017).

Available inorganic P concentration is generally low in organically managed soils on the Canadian Prairies (Entz et al., 2001) and across Canada (Martin et al. 2007; Roberts et al. 2008). Therefore, it is important to implement strategies for expanding labile soil P pools for sustainable crop production on the prairies. A field survey on organic crops in the eastern Canadian Prairies and in North Dakota showed that buckwheat was the second most common cover crop for establishing forage sweet clover (Entz et al. 2001). In the literature, buckwheat has been observed to have P-mobilizing abilities. For example, Zhu et al. (2022) observed greater P use efficiency of buckwheat on calcareous soils. The ability of buckwheat to scavenge P efficiently is thought to be associated with rhizosphere soil acidification via the excretion of organic anions (acetate, oxalate, malate, and citrate) (Talboys et al. 2016; Zhu et al. 2002). Buckwheat also shows root morphological adaptations that increase P acquisition, including its large root surface area, high root surface area to shoot weight ratio, and rapid root growth (Amann and Amberger 1989). Moreover, buckwheat shows promise on calcareous soils as it is capable of extracting Ca-bound P effectively (Boglaienko et al. 2014).

Soil characteristics should be considered when evaluating the reactivity and P bioavailability of struvite. Soil pH is among the most important soil characteristics governing the dissolution of struvite (Degryse et al. 2017). Further, struvite dissolution is enhanced by higher P sorption capacity of soils, likely because P sorption sites become a sink for dissolved P, thereby increasing P dissolution (Degryse et al. 2017). Therefore, it is expected that the slow, yet sustained release of P from struvite, will be favorable in soils with high P sorption capacity where sustained P supply from soluble P sources is limited due to P fixation.

It is evident from the above literature review that gaps exist in our understanding of the long-term dissolution dynamics of struvite in calcareous soils and also in the implications for struvite-P availability to plants in crop rotations. Examining how struvite interacts with soil, both in the presence and absence of plants, can contribute to a better comprehension of the mechanisms that drive the residual phosphorus effect from struvite (whether an effect of the first crop on struvite or an effect of struvite application timing). Therefore, the objective of this study was to determine if buckwheat could enhance struvite P mobilization in calcareous soils. We hypothesized that (1) pre-incubation of soil with struvite enhances P bioavailability and P uptake by buckwheat; (2) the response of soil Olsen P concentration to P application in the presence of buckwheat differs between struvite and MAP; (3) pre-seeding application (PSA) of struvite increases Olsen P concentration relative to at-seeding application (ASA); (4) struvite PSA enhances cumulative P supply in the amended soil relative to ASA; and (5) cumulative P supply will be greater in soil treated with MAP than that treated with struvite.

3.3. Materials and Methods

3.3.1. Soils

Two soils with contrasting textures and low to moderate Olsen P concentrations were collected (0-15 cm layer) from Libau (50°14'34.4"N 96°43'51.9"W) and Treherne (49°32'00.9"N 98°44'57.6"W) in southern Manitoba, Canada. The soil from Libau was a Gleyed Rego Black Chernozem (Udic Boroll; Dencross series) with a clay texture and that from Treherne was an Orthic Dark Gray Chernozem (Typic Hapludoll) with a loam texture. The field from which the soil was sourced at Libau had been under alfalfa hay production for many years and was later converted to annual crops (wheat, flax). The Treherne site had been under alfalfa hay production for at least 10 years prior to soil collection.

3.3.2. Experimental Setup

The growth room bioassay was laid out in a completely randomized design with a four-way factorial treatment structure and three replicates per treatment. The factors were soil type (clay and loam), P application timing (pre-seeding application (PSA) and at-seeding application (ASA)), crop (buckwheat and no crop), and P source (struvite, MAP and no P). Of the 72 experimental units (pots) in the experiment, 36 received the respective P fertilizer 28 d prior to seeding. Each pot (23.3 cm long x 23.3 cm wide x 18 cm ht.) was filled with 6 kg of soil (oven-dry basis) and watered with reverse osmosis water to attain 70% water filled pore space (WFPS) (details described below). All pots, including controls, received a P-free nutrient solution containing (kg^{-1} soil) 100 mg N (accounting for N from struvite and MAP), 20 mg S, 4 mg Zn, 0.4 mg Mo, 1 mg B, and 1 mg Cu (Zvomuya et al. 2006).

The units were placed in a walk-in growth room that was maintained at 22 °C during the 16-h photoperiod and 15 °C during the 8-h dark period. Light intensity in the growth room was 270 $\mu mol\ m^{-2}\ s^{-1}$ during the photoperiod, while relative humidity was set at 65% at all times. Pots were weighed every two days and watered as needed with RO water to maintain soil moisture content at 70% WFPS. Pots designated for pre-seeding treatment received struvite or MAP at a rate corresponding to 68.7 kg P_2O_5 ha^{-1} in a 2.5 cm wide band in the seed row on Day 1, that is, 28 d prior to seeding. The remaining pots designated for P treatment were fertilized on Day 28 just before seeding following the same procedure as described above. Pots designated for cropping were seeded (2.5 cm deep) with 16 buckwheat seeds per pot on Day 28. Two plant rows were established 12 cm apart in the middle of the pot. Seedlings were then thinned to 4 plants per row, corresponding to the recommended plant density of 140-183 plants m^{-2} (Manitoba Agriculture, n.d.).

Plant root simulator (PRS) probes (Western Ag Innovations, Saskatoon, SK, Canada) were installed in pots with clay soil and no plant treatments to measure P supply rate. Two pre-treated anion exchange resin probes were installed per pot. The probes were installed (0-2.5 cm layer) at an angle of ~ 45° in each fertilizer band (one probe per row). The PRS probes were retrieved from the pots once every two weeks throughout the pre-seeding period and then once a week after seeding (Day 28) until Day 70 (two weeks after buckwheat was terminated). One PRS sample consisted of a pair of anion probes from one pot. The PRS probes were replaced with another pre-treated probe at the same slot until the last measurement was taken. The probes were shipped to Western Ag Laboratory for P analysis. Prior to analysis, the probes were eluted in 0.5 M HCl (17.5 ml per probe) for one hour. The eluant was analyzed for P concentration using inductively coupled plasma optical emission spectrometry (ICP-OES) using a SpectroGreen analyzer (SPECTRO Analytical Instruments Inc., USA). The data were reported as the total amount of P adsorbed per unit area of membrane over the burial period (2-wk during the pre-seeding period and 1-wk thereafter).

3.3.3. Harvesting and tissue processing

Aboveground biomass was harvested at late flowering (Day 57, i.e., 28 d after planting) by cutting the plants in each pot at the soil surface using clippers. All intact roots (belowground biomass) were collected separately from each pot by lifting gently from the soil, shaking off excess soil, and washing with RO water on a 2 mm sieve. Shoot samples were oven-dried to constant weight at 70°C and weighed for aboveground biomass yield determination. Plant tissue samples were ground into a fine powder using a coffee grinder prior to laboratory analysis.

3.3.4. Soil Sampling

At the end of the 28-d pre-seeding period, four soil core samples per pot (2 cores adjacent to each seed/fertilizer row) were taken from the 0- to 2.5-cm layer using the 2-cm diameter head of a soil probe. At biomass harvesting, another soil sample was taken from each pot using the same procedure. Samples were submitted to Agvise Laboratories for determination of Olsen P concentration (Olsen et al. 1954).

3.3.5. Laboratory Analysis

3.3.5.1. Soil and Plant Tissue Samples

Air-dried soil was sieved through a 6-mm screen and homogenized. Representative samples of each soil type were analyzed for initial properties at a commercial laboratory (AGVISE Laboratories, Northwood, ND). Electrical conductivity and soil pH were measured in a 1:1 (mass/volume) soil to deionized water suspension using an EC meter (ICM Meters, 7510) and a pH meter (SI Analytics, G-P Combo w/RJ). Total organic matter (OM) content was determined using the loss on ignition method (Combs and Nathan, 2015). Soil organic carbon (SOC) was obtained by dividing OM concentration by 1.72 (Combs and Nathan, 2015). For NO_3-N determination, 7.65 g of soil was extracted in 19.15 mL of 0.12 M KCl and measured using the Cd reduction method with a flow-injection analyzer (FIA Lab, FIAlyzer-1000) (Gelderman and Beegle, 2015). Bicarbonate-extractable P (Olsen P) was determined by spectrophotometry using a flow-injection analyzer (FIA Lab, FIAlyzer-1000) following extraction of 1 g of soil with 20 mL of 0.5 M $NaHCO_3$ at pH 8.5 (Frank et al. 2015). Concentrations of potassium (K), calcium (Ca), magnesium (Mg), and sodium (Na) were measured in 1.0 M NH_4OAc at pH 7.0 with an inductively-coupled plasma atomic emission spectrometer (ICP-AES) (PerkinElmer, Avio 550 Max) (Warncke and Brown 2015). Sulphate sulfur (SO_4-S) was extracted with 0.12 M KCl and its concentration was measured turbidimetrically using a flow-injection analyzer (FIA Lab, FIAlyzer-

1000) (Franzen 2015). Zinc (Zn), iron (Fe), manganese (Mn) and copper (Cu) concentrations were measured with an ICP-AES (PerkinElmer, Avio 550 Max) in an extracting solution of 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M TEA, at pH 7.3 (Whitney 2015). Cation exchange capacity (CEC) was calculated by summing exchangeable bases and exchangeable acidity.

Tissue P concentration was measured by ICP-OES (Perkin Elmer, Avio 550 Max) following the digestion of finely-ground tissue samples with HNO_3 and H_2O_2 at 150 °C (Havlin & Soltanpour, 1980).

Soil water holding capacity was estimated using container capacity. Container capacity was determined by adding different quantities of water to air-dried soil columns packed inside transparent cylinders to attain a range of moisture contents. The moisture content at which an entire soil column was wetted without draining excess water was selected as the container capacity for each soil. The selected values were converted to water-filled pore space (WFPS) as:

$$\text{WFPS} = \frac{\text{Soil moisture content cm}^3/\text{cm}^3}{\text{Soil porosity }(\Theta)\ \text{cm}^3/\text{cm}^3} \qquad [1]$$

where

$$\Theta = 1 - \frac{\text{Bulk density}}{\text{Particle density}} \qquad [2]$$

where particle density = 2.65 g cm^{-3}. The WFPS of Libau and Treherne soils were 67% and 68%, respectively.

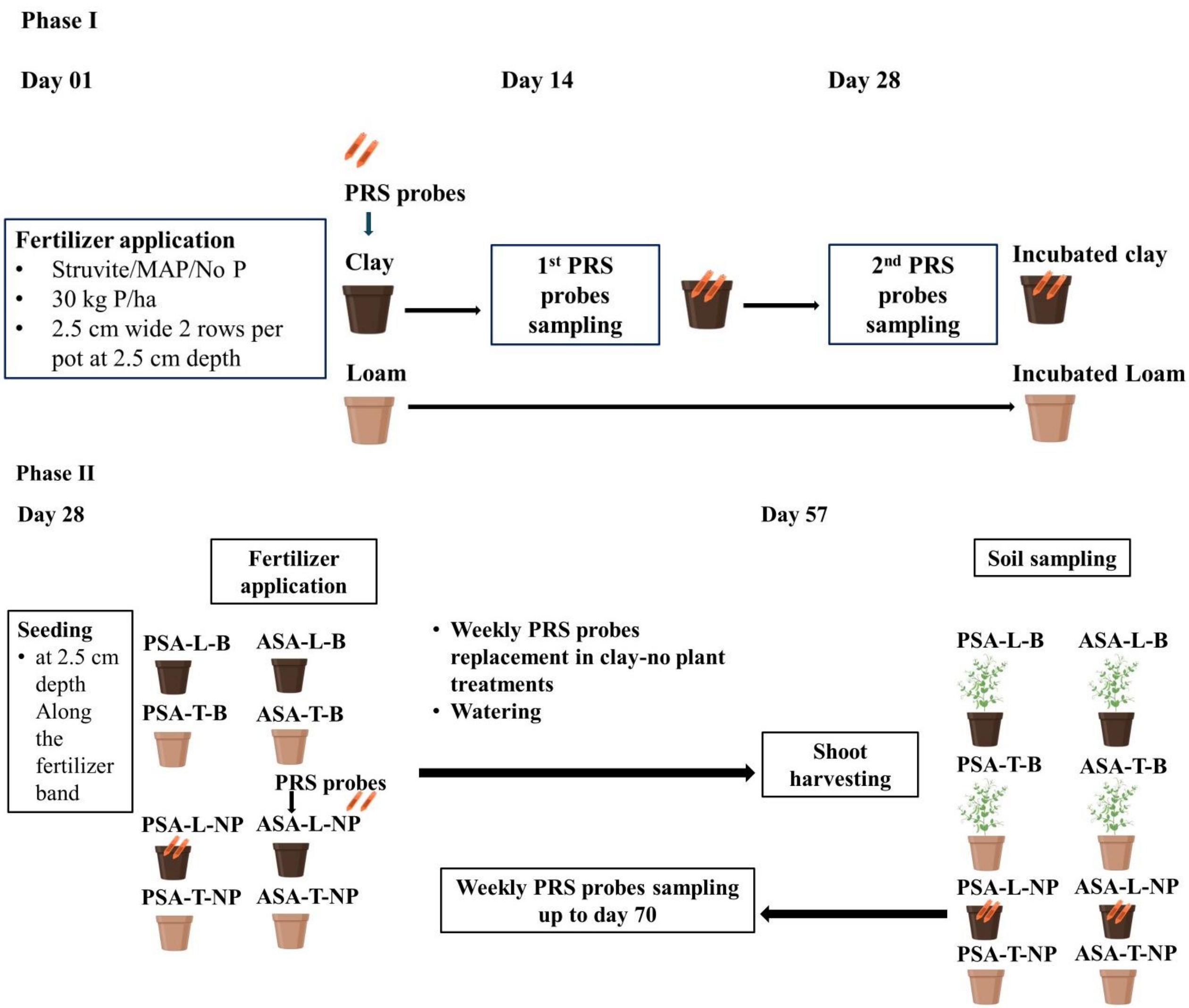
3.3.6. Calculations and Statistical Analysis

Cumulative soil P supply was calculated as the sum of P adsorbed by the PRS probes during all sampling intervals. Plant uptake of fertilizer P by the buckwheat crop (PU, mg P pot^{-1}) was calculated as:

$$\text{PU} = \text{DMY} \times \text{P}_{\text{conc}} \qquad [3]$$

where DMY is the aboveground biomass dry matter yield (g pot^{-1}) and P_{conc} is the respective tissue P concentration (g kg^{-1}).

Analysis of variance was conducted using PROC GLIMMIX of SAS® software (version 9.4, SAS OnDemand for Academics; SAS Institute, Cary, NC) to determine treatment main and interaction effects on cumulative soil P supply, P supply rate, buckwheat aboveground (shoot) dry matter yield, tissue P concentration, tissue P uptake and residual soil Olsen P concentration. Plant P uptake data were normally distributed (Shapiro-Wilk's W-statistic > 0.9). Soil P supply rate data were gamma-distributed while cumulative soil P supply data and residual Olsen P concentration followed a lognormal distribution. The effects of soil type, preincubation treatment, the presence of buckwheat, and P source were modelled as fixed effects. Sampling time was modeled as a repeated measures factor for soil P supply rate. To accommodate unequally-spaced sampling dates, compound symmetry (CS), heterogeneous compound symmetry (CSH), first order autoregressive (AR1), heterogeneous first order autoregressive (ARH1), first order antedependence [ANTE(1)], and spatial power (sppow) covariance structures were compared using the Generalized Chi-Square/DF stastic for their fit to the repeated measures data. The CS structure provided the best fit as it had the lowest Generalized Chi-Square/DF statistic. To account for unequal variances, the RANDOM_residual_/Group statement along with ddfm = Satterthwaite was specified in the GLIMMIX procedure for aboveground DMY, tissue P concentration, P uptake, soil residual Olsen P concentration, P supply rate and cumulative P supply of soil. Treatment means were compared using the Tukey multiple comparison procedure at $\alpha = 0.05$.



PSA-L-B: PSA-Libau-BW **PSA-T-B:** PSA-Treherne-BW **PSA-L-NP:** PSA-Libau-No Plant
PSA-T-B: PSA-Treherne-BW **ASA-L-B:** ASA-Libau-BW **ASA-T-B:** ASA-Treherne-BW
ASA-L-NP: ASA-Libau-No Plant **ASA-T-B:** ASA-Treherne-No Plant

Figure 3.1 Phases of the study.

3.4. Results and Discussion

3.4.1. Initial Soil Properties

The Libau soil had a clay texture, alkaline pH and a low soil test P (STP) concentration, whereas the Treherne soil had a loam texture, a neutral soil pH and a moderate STP (Manitoba Soil Fertility Guide 2007) (Table 3.1).

Table 3.1 Extractable nutrients, CEC, organic matter content, pH, and texture of soils (0–15 cm) used in the experiment.

Soil property	Libau	Treherne
Nitrate-N (mg kg^{-1})	14.5	17.5
Olsen P (mg kg^{-1})	5.0	11.0
K (mg kg^{-1})	290	454
Ca (mg kg^{-1})	6173	2398
Mg (mg kg^{-1})	770	481
Na (mg kg^{-1})	17	50
Sulphate-S (mg kg^{-1})	2.0	2.0
Zn (mg kg^{-1})	0.54	0.47
Fe (mg kg^{-1})	81	18.9
Mn (mg kg^{-1})	13.56	3.42
Cu (mg kg^{-1})	1.03	1.25
B (mg kg^{-1})	0.6	1.2
Cl (mg kg^{-1})	1.0	2.0
CEC (cmol$_c$ kg^{-1})	38.1	17.4
EC (dS m^{-1})	0.59	0.39
Soil organic carbon (g kg^{-1})	27	26
pH	7.7	6.9
Texture	Clay	Loam
Sand (%)	26	41
Silt (%)	28	36
Clay (%)	46	23

3.4.2. Aboveground Dry Matter Yield

There was a significant P source × soil interaction for buckwheat aboveground dry matter yield (DMY) (Table 3.2; Figure 3.2). In the Libau soil, MAP application increased DMY relative to the unfertilized control, whereas DMY showed no significant response to struvite application. By comparison, neither MAP nor struvite elicited a response in aboveground DMY in the Treherne soil, which can be attributed to relatively high initial P concentration in the Treherne soil. On the other hand, the lack of response to struvite in the Libau soil suggests that the rate of application of struvite P (68.7 kg P_2O_5 ha^{-1}), although above the recommended P application rate of 45.8 kg P_2O_5 ha^{-1} (Manitoba Soil Fertility Guide 2007), was not sufficient to produce a positive response in aboveground DMY in the low-P Libau soil. Baseline soil Olsen P concentration was relatively high in the Treherne soil. Alternatively, buckwheat, a known P-efficient crop, might have effectively mobilized soil P from the low-P Libau soil even in the unamended treatment.

3.4.3. Tissue P Concentration and P Uptake

The P source × P application timing effect was significant for P accumulation in the aboveground biomass and this effect was consistent across the two soils (Table 3.2; Figure 3.3 b). Phosphorus uptake from struvite did not differ significantly between pre-seeding application and at-seeding application of P. However, plant uptake of P from MAP was significantly greater when applied at seeding than when pre-applied 28 d before seeding. Because of the higher solubility of MAP and its rapid initial release of P, the propensity for P sorption in highly P sorbing soils following MAP application is expected to be high (Dobermann et al. 2002; Lombi et al. 2004). This may have caused lower availability of P and subsequently lower plant P uptake from MAP applied pre-seeding. Periodic addition of small amounts of P to soil can reduce the susceptibility to P fixation and ensure sustained P uptake by plants (Nyborg et al. 1998), a phenomenon often expected of slow-release P fertilizers such as struvite (Everaert et al. 2017). Regardless of P application timing, plant P uptake in the present study increased with fertilizer P application in both soils (Figure 3.3a), relative to the unfertilized soil, but the response was significantly lower for struvite than for MAP. However, the effect of struvite on P uptake was significant in the Libau soil but not in the Treherne soil (Fig. 3.3a). The lack of a P uptake response to struvite in the Treherne soil can be attributed to the relatively high initial soil P concentration. Nongqwenga et al. (2017) observed that dissolution of struvite and subsequent plant P uptake is restricted where background soil P concentration is high. By comparison, Talboys et al. (2016) reported similar P uptake responses to struvite and MAP applied to a low-P acidic soil in a 30-d pot experiment with buckwheat. The difference between their and our results likely reflects the difference in soil properties as Hallama et al. (2019) noted that the effect of a cover crop in a rotation strongly depends on site specific conditions and management practices. Unlike the low pH of the soil used by Talboys et al. (2016), the soils in our study were neutral to alkaline. In alkaline soils, crop response to struvite has been shown to be lower than that observed with soluble P fertilizer (Ackerman et al. 2013). Although struvite underperformed MAP in both soils, the difference in the Libau soil was much larger (Fig. 3.3a). In a field experiment on the same Libau soil, response of a wheat crop to the application of struvite continued to increase even at an application rate of 40 kg P ha^{-1} (Thiessen Martens et al. 2022). Therefore, the 30 kg P ha^{-1} rate of struvite application in the present study presumably did not maximize P uptake by buckwheat in the Libau soil.

Averaged across P sources, the effect of P application timing on P uptake by buckwheat varied with soil type, as indicated by the significant soil × timing effect (Table 3.2; Figure 3.3c). While timing had no significant effect on P uptake in the Libau soil, significantly more P was taken up by buckwheat from the Treherne soil when P fertilizer was applied at seeding compared with pre-seeding application. This difference was likely related to the difference in P sorption capacity between the two soils. Adsorption/desorption and dissolution/precipitation reactions are among the major interrelated processes that determine soil and fertilizer P availability to plants (Horst et al. 2001). High P sorption capacity results in low inorganic P concentrations in soil solution (Nair & Reddy, 2015). In an incubation experiment, Everaert et al. (2017) noted faster diffusion of P in a neutral soil compared to both acidic and alkaline soils. Ige et al. (2005) further elucidated that clay content contributes significantly, accounting for 40% of the P sorption capacity in Canadian Prairie soils. Therefore, it could be anticipated that P retention would be comparatively higher in the Libau soil, which was an alkaline clay, than in the Treherne soil, which was a neutral loam. This enhanced retention in the Libau soil could have led to reduced P availability for buckwheat regardless of the timing of P application. Conversely, in Treherne soil, continued P diffusion and fixation reactions might have caused low P availability for buckwheat when P was applied pre-seeding only. In an incubation study using alkaline-calcareous soils from Manitoba, Duminda et al. (2016) observed no significant increase in solution P concentration in a soil that had the highest clay content and P sorption following application of MAP relative to no P application, irrespective of P application timing. In contrast, in the soil with the highest sand content and the lowest P sorption capacity, MAP increased solution P concentration for up to 4 wk, after which the P concentration declined. In our study, even though the soil × timing interaction among the struvite, MAP and no P treatments, the observed P uptake values shown in Fig. 3.3c might have largely been due to MAP.

Table 3.2 Selected crop and soil attributes as affected by P source, soil type, presence of buckwheat crop, and P application timing.

Effect	**Aboveground DMY**[a]	**Shoot P concentration**	**Shoot P uptake**	**Residual Olsen P**
	g pot^{-1}	**g kg^{-1}**	**mg pot^{-1}**	**mg kg^{-1}**
P source				
MAP	25.6a[c]	2.79a	70.7a	9.08a
Struvite	19.5b	2.34b	46.6b	7.63b
No P	15.3b	2.0c	31.4c	6.67b
Soil				
Libau	17.1b	2.01b	36.1a	3.88b
Treherne	23.1a	2.75a	63.0b	11.6a

P application timing				
PSA[b]	17.6b	2.39	42.5a	6.69b
ASA	22.6a	2.36	56.7b	6.51a
Crop				
Present	NA[d]	NA	NA	6.20b
Absent	NA	NA	NA	7.02a
	P value			
P source	< 0.0001	< 0.0001	< 0.0001	0.001
Soil	0.0003	< 0.0001	< 0.0001	< 0.0001
Timing	0.002	0.75	< 0.0001	0.55
Crop	NA	NA	NA	0.01
P source × soil	0.001	0.66	0.001	0.36
P source × timing	0.76	0.30	0.02	0.01
P source × crop	NA	NA	NA	0.12
Soil × timing	0.06	0.99	0.001	0.16
Soil × crop	NA	NA	NA	0.97
Timing × crop	NA	NA	NA	0.18
P source × soil × timing	0.81	0.45	0.91	0.31
P source × soil × crop	NA	NA	NA	0.98
P source × timing × crop	NA	NA	NA	0.51
Soil × timing × crop	NA	NA	NA	0.18
P source × soil × timing × crop	NA	NA	NA	0.20

[a] DMY, dry matter yield

[b] PSA, pre-seeding application of P fertilizer; ASA, at-seeding application of P fertilizer

[c] Means within the same column and factor followed by the same letter are not significantly different at $\alpha = 0.05$ according to the Tukey multiple comparison procedure

[d] NA, not applicable

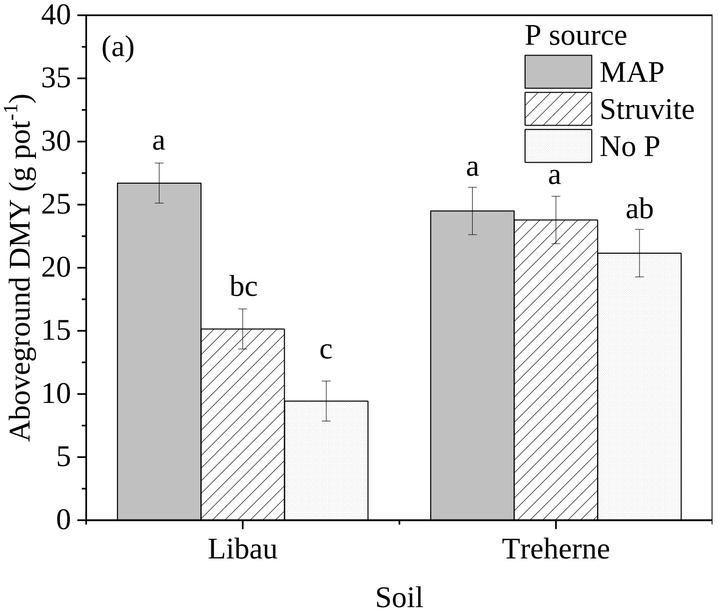


Figure 3.2 Effect of P source [monoammonium phosphate (MAP), struvite and No-P] × soil (Libau and Treherne) on buckwheat aboveground dry matter yield. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the means.

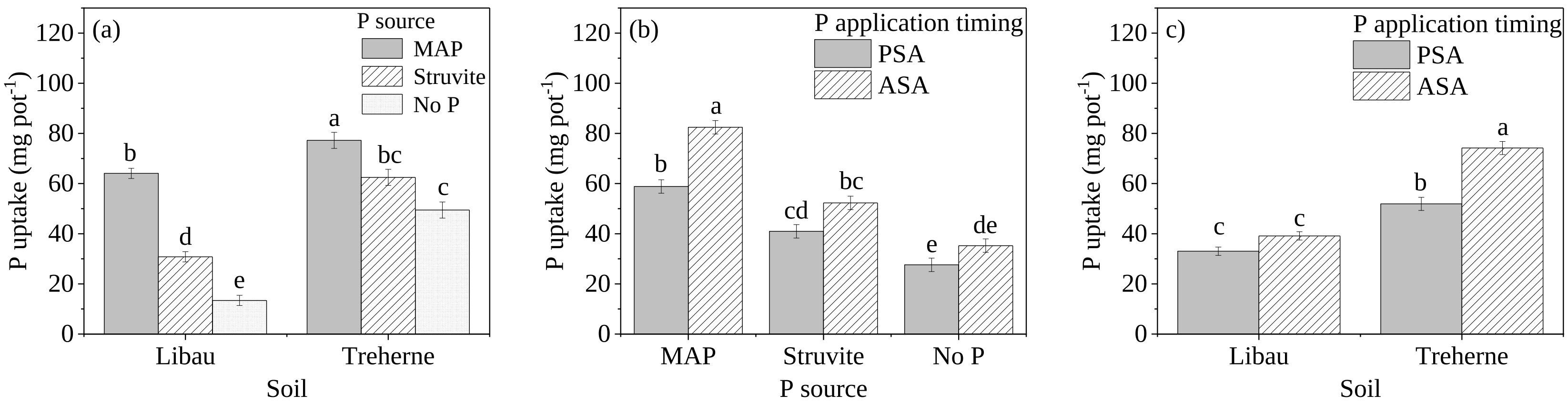


Figure 3.3 Effect of (a) P source [monoammonium phosphate (MAP), struvite and No P] × soil (Libau and Treherne), (b) P source × P application timing (PSA, pre-seeding application and ASA, at-seeding application) and (c) soil × P application timing interaction on P uptake by buckwheat. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure ($\alpha = 0.05$). Error bars indicate standard errors of the means.

3.4.4. Residual Olsen P Concentration

The P source × timing interaction was significant for soil Olsen P concentration at harvest (Table 3.2; Figure 3.4). While pre-seeding application of either struvite or MAP did not significantly alter Olsen P concentration at harvest relative to at-seeding application, PSA resulted in significantly lower residual Olsen P concentration for struvite compared with MAP. This indicates that solubility of struvite in the soils used in this study was low relative to that of MAP. Similarly, incubation studies such as Everaert et al. (2017) and Thiessen Martens et al. (2023) identified partial dissolution and limited diffusion of P in granular struvite in soil because of the presence of undissolved granules at the end of incubation whereas MAP dissolved completely. By comparison, ASA in the present study produced statistically similar residual Olsen P concentrations for the two P sources. This can be attributed to P uptake by buckwheat. Similar residual Olsen P availability following at-seeding application of MAP and struvite might be due to the significantly greater plant P uptake for MAP compared to struvite when applied at seeding. We expected a difference in residual Olsen P concentration between the two P fertilizers and that difference to decrease in the presence of buckwheat. However, the results contradict this because the P source × crop interaction was not significant for Olsen P concentration at the end of the bioassay. Therefore, the results suggest no impact of the buckwheat crop on the release of struvite P, hence accumulation of Olsen P. In contrast, previous studies have demonstrated a sustained residual P availability from struvite beyond the first crop phase under varying soil conditions and a range of preceding crops. For example, Wollmann et al. (2018) reported positive residual P effects in a subsequent maize crop following red clover treated with struvite. Thiessen Martens et al. (2022) observed an increase in yield and P accumulation by an alfalfa-grass forage fertilized with struvite in later years of a multi-year field experiment (where struvite was applied at the trial onset in a one-time application).

Katanda et al. (2016) reported residual effects of struvite P in a subsequent canola crop following a wheat crop, but there was no increase in residual Olsen P in the first crop phase regardless of the crop species when P application rate was increased from 1.1 to 2.2 g P m^{-2}. Arcand et al. (2010) observed a statistically significant, but agronomically insignificant increase in P availability in the spring following phosphate rock application. They attributed the increase to phosphate rock application residues from a preceding buckwheat green manure crop but found no evidence of buckwheat enhancement of P availability from phosphate rock, which also has low solubility in high-pH soils.

Although previous studies have shown that buckwheat is a high exuder of organic anions (Talboys et al. 2016), overall, our results show that it might not improve residual P availability from struvite. Similarly, in a field study under organic management, Possinger et al. (2013) observed no significant increase in extractable soil P concentration during the growth or at the time of soil incorporation of buckwheat and suggested that an increase in soil test P could be expected upon decomposition of the crop residues. The presence of buckwheat resulted in significantly lower soil residual Olsen P at harvest (Table 3.2), likely due to plant P uptake. Olsen P concentration at harvest was significantly greater in the Treherne soil than in the Libau soil (Table 3.2), reflecting the relatively higher initial soil test P concentration in the Treherne soil.

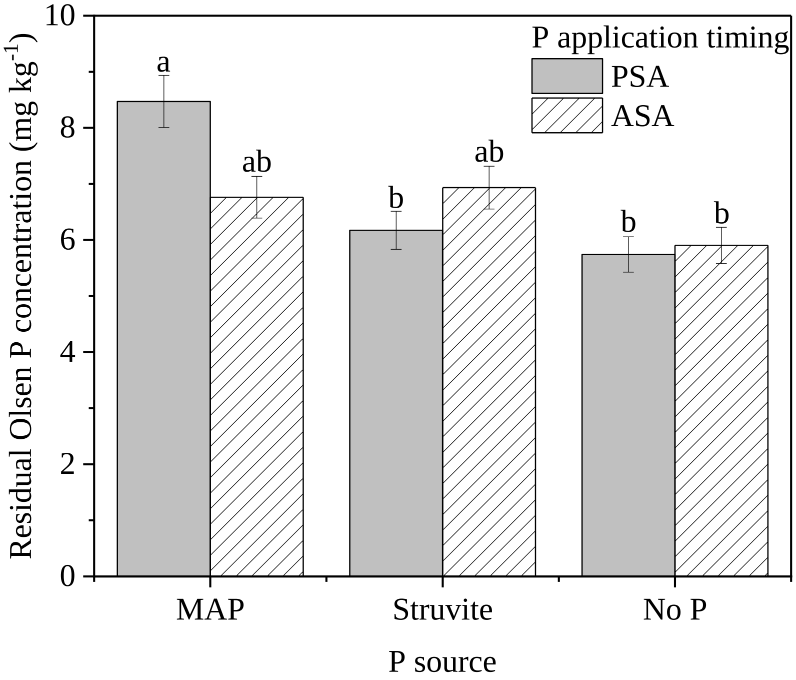


Figure 3.4 Soil residual Olsen P concentration as affected by P source [monoammonium phosphate (MAP), struvite and No P] and timing of application (PSA, pre-seeding application; ASA, at-seeding application). Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure (α = 0.05). Error bars indicate standard errors of the means.

3.4.5. Soil P Supply Rate and Cumulative Soil P Supply

P source and timing had a significant interaction effect on cumulative soil P supply from the Libau soil (Table 3.3; Fig. 3.5). Cumulative P supply at buckwheat harvest from soil treated with MAP was significantly greater than that from soil treated with struvite for both P application timings. Cumulative P supply at buckwheat harvest did not vary between PSA and ASA for both MAP and struvite. Therefore, the results do not support the hypothesis that application of struvite 28 d prior to seeding would enhance P supply from the sparingly soluble fertilizer over time. Temporal changes in available P supply rates from bare (i.e., no crop) soil were analyzed separately for the two P application timings (Figure 3.6). The interactive effect of P source and sampling day on P supply rate was significant (Table 3.3). No notable differences between successive sampling days were observed in struvite P supply rate regardless of application timing. By comparison, a significant decline in P supply rate was detected for MAP after the first sampling period under ASA, after which the P supply rate continued to decrease during the next two successive sampling dates. Jeke and Zvomuya (2018) attributed the lack of distinct trends and significant differences between successive PRS probe sampling times to the reduced statistical power resulting from the inherently large variability in the measurements. Most of the soil P supply rate data for struvite were below the method detection limit (MDL) of 0.2 μg cm^{-2}, reflecting the low solubility of struvite. By comparison, there was a rapid P release in soil treated with MAP one week after application, captured by measurements in the ASA treatment (Figure 3.6b). Soluble sources of P result in immediate release of P into the soil after application. Using a visualization technique in an incubation experiment, Everaert et al. (2017) observed a rapid release of P from MAP in acidic, neutral as well as calcareous soils and a slow release of struvite P. Over the course of 100 d, they identified a gradual and more sustained P release from struvite granules and a peak P release from MAP in the calcareous soil approximately 14 d after application, followed by a rapid decline, similar to our observations. They also observed that at 7 d after application P supply from MAP was substantially greater than that from struvite. The rapid decline in P supply rate after peaking might be related to soil chemical properties, including P sorption capacity. The Libau soil tested with PRS probes had a clay texture.

Table 3.3 Soil P supply rates and cumulative P supply as affected by P source, P application timing and sampling day

Effect	**Soil P supply rate for PSA**[a]	**Soil P supply rate for ASA**	**Cumulative soil P supply**
	µg cm^{-2} Burial period^{-1}	**µg cm^{-2} Burial period^{-1}**	**µg cm^{-2}**
P source			
MAP	0.10a	0.06a	1.04a
Struvite	0.01b	0.03b	0.08b
No P	0.02c	0.01c	0.04c
P application timing			
PSA	NA[c]	NA	0.16
ASA	NA	NA	0.13
Sampling day			
14	0.05ab	NA	NA
28	0.05abc	NA	NA
35	0.07a	0.10a	0.10b
42	0.03abc	0.04b	0.14ab
49	0.02bcd	0.02bc	0.17ab
56	0.01d	0.01c	0.19a
63	0.03bcd	0.03bc	NA
70	0.02dc	0.02bc	NA
		P value	
P source	< 0.0001	< 0.0001	< 0.0001
Timing	NA	NA	0.21
Sampling day	< 0.0001	< 0.0001	0.04
P source × timing	NA	NA	< 0.0001
P source × sampling day	< 0.0001	< 0.0001	0.60
Sampling day × timing	NA	NA	0.79
P source× timing × sampling day	NA	NA	0.86

[a] Soil P supply rate for PSA, soil P supply rate for pre-seeding application of P fertilizer; Soil P supply rate for ASA, soil P supply rate for at-seeding application of P fertilizer

[b] Means within the same column and factor followed by the same letter are not significantly different at α = 0.05 according to the Tukey multiple comparison procedure

[c] NA, not applicable

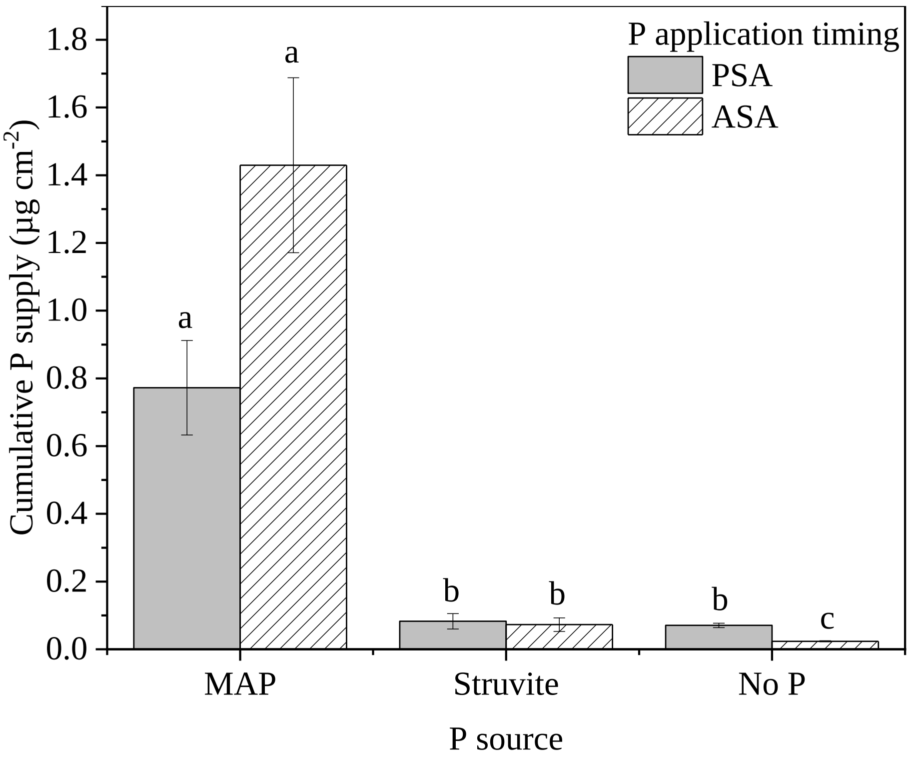


Figure 3.5 Cumulative P supply in soil up to buckwheat harvest as affected by the P source [monoammonium phosphate (MAP), struvite and No P] × timing (PSA, pre-seeding application; ASA, at-seeding application) interaction. Vertical bars are standard errors of the mean. Columns with the same letter are not significantly different according to the Tukey multiple comparison procedure (α = 0.05).

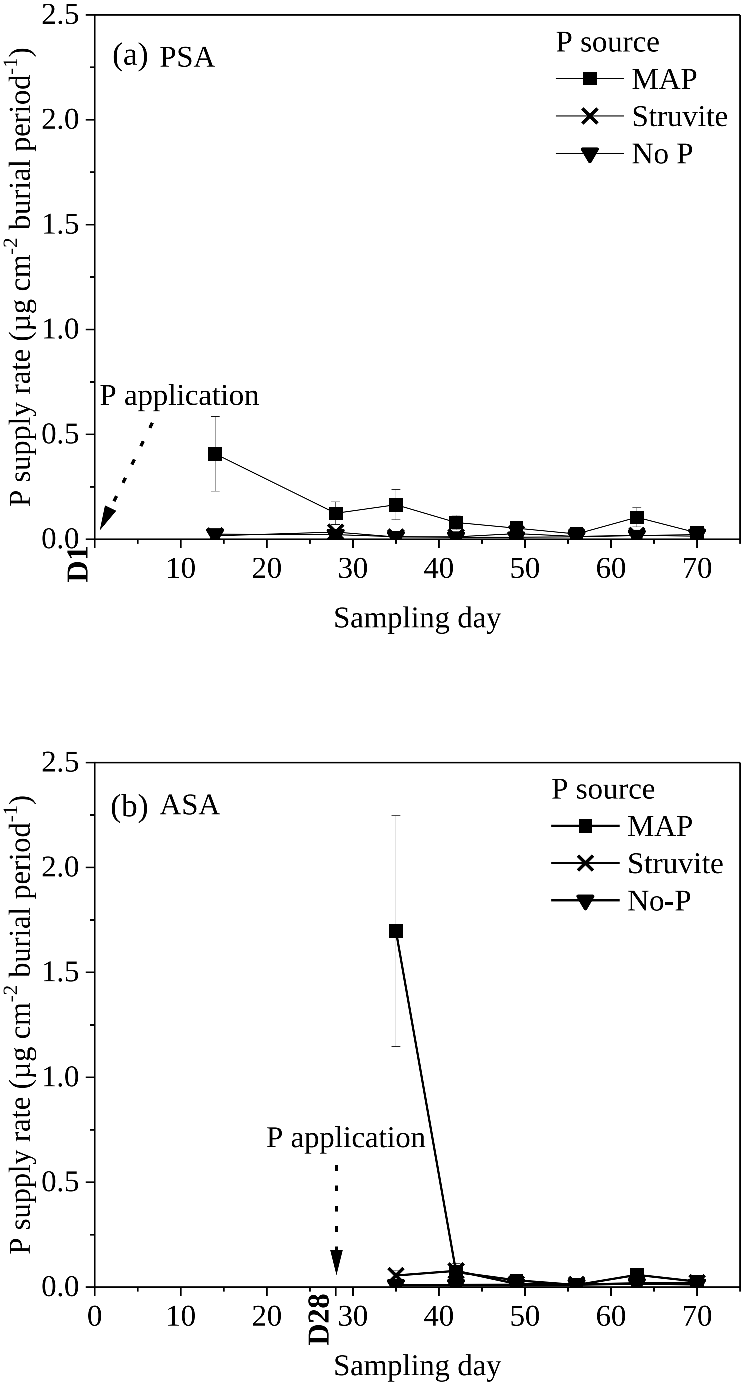


Figure 3.6 Temporal changes in soil P supply rate as affected by the P source [monoammonium phosphate (MAP), struvite and No P] × sampling day interaction: (a) pre-seeding application (PSA); (b) at-seeding application (ASA). Vertical bars denote standard errors of the mean.

3.5. Conclusion

Our results showed no evidence that the application of struvite 28 d prior to seeding would improve the availability of P to the buckwheat crop. This was also evident in the aboveground DMY and crop P uptake, for which pre-seeding application of struvite showed no benefit relative to application at seeding. By comparison, pre-seeding application of MAP reduced P uptake relative to application at seeding, although this did not translate to a significant reduction in DMY. Further, while struvite application increased P uptake by buckwheat relative to the control (No P) in the low-P Libau soil, P uptake from struvite was significantly lower than that from MAP in both soils. Despite the relatively low uptake of struvite P by the crop, there was no evidence of a buildup in residual Olsen P in the soil fertilized with struvite at harvest, suggesting that struvite granules dissolved slowly in the alkaline soils used in this study. Overall, the results showed no significant enhancement of P availability and uptake by either the presence of a buckwheat crop or the pre-seeding application of struvite. However, it is conceivable that mechanisms associated with residue decomposition would result in residual P effects of struvite in low P alkaline soils. Further research is needed to test this hypothesis.

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4.OVERALL SYNTHESIS

4.1. Summary of Findings and Contribution to Knowledge

Phosphorus management in agricultural soils is becoming increasingly intricate due to a wide range of interconnected challenges, including soil P deficiency, excessive use of P fertilizers resulting in losses and pollution of surface water bodies, and the depletion of the finite phosphate rock (PR) resource. The challenge is accentuated in organic crop production as P amendment options are limited and PR is not effective in some soils. Therefore, promoting a circular economy for P through recycling and reusing P from organic wastes is gaining global significance. The use of recycled P also has implications for sustainable organic crop production in the Canadian Prairies. Soil test P (STP) concentrations are generally low in organic fields in the prairies. Furthermore, regional P surpluses collectively due to livestock intensification, expanding human settlements, and increased use of chemical fertilizers in the Red River Valley, alongside the increased occurrence and severity of spring floods, has led to the rapid eutrophication of Lake Winnipeg in Manitoba (Schindler et al., 2012). Various recycled P fertilizers have been recently tested on prairie organic crops, with struvite standing out as a promising option. Although struvite is known to be a slow-release P fertilizer, crop response to struvite appears comparable to soluble fertilizers. However, this is not always the case, as struvite P availability depends on the properties of struvite and the soil, and the crop-specific potential for struvite P mobilization. Therefore, there is a need to elucidate the behavior of struvite in soil, and its agronomic potential within the context of a soil-struvite-plant continuum. Green manure cover crops favor the transformation of sparingly soluble soil and fertilizer P into plant-available forms. Nevertheless, the processes that different green manure species adopt to access relatively unavailable P pools can be unique.

This research explored approaches to optimize the use of green manure cover crops and struvite to enhance crop response in typical organic crop rotations on alkaline, low soil test P soils in Manitoba. Chapter 2 examined the ability of certain green manure cover crop species, each with different P acquisition mechanisms, to increase P mobilization from struvite applied in different phases of the crop rotation. Chapter 3 explored the mechanisms (either root activity from an actively growing crop or the pre-application of struvite) leading to the increased P availability of struvite that was observed in previous research on organic crop sequences under soil conditions similar to those in Manitoba.

In Chapter 2, we identified a superior crop response of buckwheat to struvite compared to the legumes, faba bean and field pea. Despite the greater potential demonstrated by buckwheat to access struvite-P relative to the other two green manure crop species, there was no significant benefit to the subsequent wheat crop yield from struvite being applied to a preceding buckwheat crop. Unlike buckwheat, the application of struvite to either of the two legume GMCs led to an increase in the yield of a subsequent wheat crop relative to the no-P treatment. This suggests a potential benefit from enhanced biological N fixation. These results suggest crop-specific responses of green manure crops to struvite. Struvite or MAP application to the green manure crop, irrespective of species, did not increase the yield of the subsequent wheat crop compared to the application directly to the wheat crop. Therefore, there was no indication of enhanced struvite-P availability through optimizing the timing of application (Chapter 2). Similar to the findings from similar research on calcareous soils (Ackerman et al., 2013), wheat crop response to struvite at Libau was lower than that of MAP, but greater than that of the no P control treatment. Residual P availability to a third crop in the rotation from both struvite and MAP applied to the green manure crops or the wheat crop was evident in the Libau soil.

In Chapter 3, we noted varying responses of buckwheat to P application, depending on the background STP concentration. We compared buckwheat crop response and soil P dynamics in a loam soil with moderate STP (Treherne) and a clay soil with low STP (Libau). In the Libau soil, struvite increased tissue P concentration relative to no P application, but to a lesser extent than MAP. Even though we used a P application rate above the recommendation for the region, there was evidence that even higher struvite application rates might be needed to maximize dry matter yield in the Libau soil. Surprisingly, the interaction between the buckwheat crop and the P source was not significant for soil residual Olsen P concentration at the time of harvesting, thus leading to the conclusion that root exudation by buckwheat did not enhance the plant availability of struvite P. One of the key findings in this chapter was that with the application of struvite 28 d prior to seeding did not increase either buckwheat tissue P uptake or cumulative soil P supply in the clay soil. In contrast, a pre-seeding application of MAP appeared to result in a reduction in buckwheat tissue P uptake. This suggests a gradual and more sustained supply of plant available P from struvite in low P soils compared to soluble P fertilizers.

Overall, while struvite performed comparably to MAP on moderate to high P soils, the response of wheat and green manure crops to struvite application was inferior to the response to MAP in the low P soil, regardless of application timing (Chapters 2 and 3). Therefore, in general, both Chapters highlight that the timing of struvite availability to plants in the soil does not affect the agronomic effectiveness of struvite in the low P Manitoba soil. However, struvite P appears to be less susceptible to P fixation processes in highly P-sorbing soils than MAP and thus may supply plant-available P sustainably for a longer period. Our findings do not definitively suggest that struvite application can be optimized in such a way as to completely replace soluble P fertilizer application in low P, calcareous soils in Manitoba. However, the relatively greater crop response to struvite compared to unfertilized soil that we observed in this research highlights the potential of struvite as an efficient P source with low risk to the environment in Prairie organic crop production, where conventional P fertilizers are not allowed. Importantly, in this study, we applied P fertilizer in the seed row. Previous field experiments on the same soils provide no evidence of improvement in crop response to broadcast-applied struvite relative to no P application (Nicksy et al. 2022). Therefore, our results suggest that in-soil banding of struvite could be more beneficial than broadcast application in these Manitoba soils. Although the results suggested that buckwheat likely mobilizes struvite-P effectively, there was no sufficient evidence of increased struvite P availability to a subsequent crop.

The field study reported in Chapter 2 was conducted from 2020 through 2021, which were drought years. Manitoba Agriculture (n.d.) reports that the drought in 2021 was reminiscent of some significant historical droughts in Manitoba and across western Canada. Extremely high temperatures and low precipitation might have compromised wheat yields in 2021.

4.2. Recommendations

In this study, we used a P application rate which is slightly greater than the provincial recommendation for field crops. The relatively lower crop response to struvite in the low-P Libau soil suggests that future studies that further investigate struvite's agronomic potential in this type of soil should examine higher application rates than those tested in our study. Phosphorus runoff loss is often associated with high application rates of soluble P fertilizers. Therefore, measuring the water-soluble P fraction in struvite-amended soils and the increase in soil test P in future studies will provide insight into the maximum safe rates of struvite application in Manitoba soils.After harvesting buckwheat in the growth room study, crop residue incorporation into the soil and examination of the potential transfer of P from residue decomposition to a subsequent crop will be informative.

4.3. References

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APPENDICES

Appendix A: Supplementary tables

Table S.1 Weed weight and percent weed content at Libau in 2020 as affected by the green manure crop species and P source

Effect	Weed biomass	Weed composition
	kg ha^{-1}	% of DMY
Green manure species		
Buck wheat	207.7b	3.2b
Field pea	377.6ab	10.4ab
Faba bean	872.3a	38a
P treatment (source × timing)		
Struvite	431.2ab	10.8
MAP	633a	10
No P	393.3b	15
	P value	
Green manure species	0.01	0.04
P treatment	0.02	0.07
GMC × P treatment	0.0002	<0.0001