

**The application of composting for phosphorous recovery from Alum and Ferric
precipitated sludges**

by

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ABSTRACT

In this study, the recovery of phosphorous (P) from sludge produced during phosphorous removal from secondary wastewater lagoons by using a controlled composting process was investigated. Two compost piles, one using Alum (Al) and the other Ferric (Fe) precipitated sludge, were established. Sludge was mixed with dry woodchips (1:3 ratio), manually turned weekly, and monitored for temperature, moisture, and pH, every two days. After an eight-week thermophilic phase and six-week maturity phase, compost met Category A criteria per CCME guidelines. The compost products were tested on switchgrass and canola to assess phosphorus availability, with control experiments using topsoil and Monoammonium Phosphate (MAP) fertilizer. Three cropping cycles, each lasting 50 days, were completed, and analysis of harvested biomass for total phosphorus content using the Inductively Coupled Plasma (ICP) method was conducted.

The analysis of the data showed that the phosphorus source with the greatest P uptake and biomass yield for switchgrass was Ferric Compost. Across different growth cycles, P uptake increased for all phosphorus sources, indicating a gradual release of P from composted chemical sludge over time through mineralization. In terms of canola, Fe compost was the most effective phosphorus source in promoting P uptake. P uptake increased steadily throughout growth cycles when cultivating canola with MAP. However, P uptake decreased with Al compost and Fe compost as growth cycles progressed. Regarding canola, among the three phosphorus sources, Al Compost resulted in the highest biomass yield for all phosphorus sources, while biomass yield decreased as growth cycles progressed. Overall, Fe compost proved most effective for P uptake and biomass yield in switchgrass, while Al compost showed better results for canola. Furthermore, the evaluation of phosphorus recovery efficiency (PRE %) underscored the fluctuating nature of phosphorus retention in both switchgrass and canola.

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Contribution of Authors

The thesis is organized as a "sandwich" or grouped-manuscript thesis with chapters 3 and 4 containing material from journal articles that is going to be submitted shortly and expecting for publication. Following are the titles of the prepared research articles, the authors' contributions, and relevant chapters of the thesis:

- 1- Chapter 3 includes the content submitted in the Sustainable Material and Technologies journal manuscript titled "Investigating the feasibility of using an enhanced composting process to recover nutrients from chemically precipitated phosphate sludge".

Author contributions:

Saba Vahedi (Thesis author): Conducting experiment. data collection, data analysis, methodology, writing original draft.

Arman Vahedi: Conceptualization, methodology, supervision, writing review & editing.

Qiuyan Yuan: Conceptualization, research funding acquisition, supervision, writing - review & editing.

- 2- Chapter 4 includes the content of the manuscript submitted in journal of Environmental Quality and titled "Bio availability Study of phosphorus from Composted Chemical Sludge Using Switchgrass and Canola".

Author contributions:

Saba Vahedi (Thesis author): Conducting experiment, data collection, data analysis, methodology, Writing original draft.

Arman Vahedi: Conceptualization, methodology, supervision, writing review & editing.

Elham Afzali: Data Analysis, graphs drawing and editing.

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Qiuyan Yuan: Conceptualization, research funding acquisition, supervision, writing - review & editing

CHAPTER 1 - GENERAL BACKGROUND

1.1 Background and Review of Relevant Prior Work

A vast majority of small municipalities and First Nations communities in Manitoba operate facultative or aerated lagoons for wastewater treatment. Most of them use Ferric Chloride (FeCl_3) or alum (usually in the form of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) as coagulant for phosphorous removal. The insoluble particles that form during the coagulation process result in a massive volume of sludge which is typically left in the lagoons. Therefore, phosphorous which is a valuable nutrient is lost in the process.

In this project, the recovery of phosphorous from the sludge produced during phosphorous removal from wastewater lagoons by using a controlled composting process is investigated. Since a vast majority of wastewater lagoons in Manitoba are treated by Aluminum Sulfate (Alum) and Ferric Chloride (Ferric), the focus of this project was to recover phosphorous from alum and ferric precipitated sludges.

Over the past year, InnoVantage Inc. (Winnipeg) and the Dr. Qiuyan Yuan's research group at the department of Civil Engineering in the University of Manitoba have been working on an innovative In-Line Phosphorous Removal and Recovery (IPRR) system. This system consists of a series of processes including an in-line alum and ferric dosing and coagulation, a flocculation process by using a specific polymer, a particle separation tank, and a sludge dewatering process by using geotextile bags. In the IPRR process, the alum and ferric precipitated particles that contain phosphorous are flocculated into large flocs and are contained in geotextile bags. In the IPRR process, the alum and ferric precipitated sludges are present which provide an opportunity for a complete recovery of phosphorous.

The recovery of phosphorous from wastewater has been attempted by using various biological, physical, or chemical methods (Desmidt et al., 2014; Tchobanoglous et al., 2003; Morse et al., 1998; Stratful et al., 1999). Depending on the phosphorous removal process that is used in the wastewater treatment, several phosphorous recovery processes have been developed. The chemical bond between phosphate and coagulants (alum and ferric) is strong, which is the primary reason that alum and ferric are used for phosphorous removal. Therefore, the recovery of phosphorous from alum and ferric precipitated sludges may present a challenge. In the IPRR process, alum (liquid aluminum sulfate; $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) and ferric are directly injected into the wastewater flow. They react with dissolved and particulate phosphorous which results in insoluble AlPO_4 and FePO_4 particles that are further flocculated and merge with other suspended solids and form a thick layer of flocs in a sludge form. The preliminary investigations have revealed that the produced sludge has a very high organic and high nutrient content. In the summer of 2020, InnoVantage Inc. in collaboration with the City of Selkirk and Triple Green Products (Morris, MB) conducted a feasibility study by using an in-vessel composting system for composting biosolids that are formed in the process of wastewater treatment with or without other organic materials. The preliminary results showed that sludge composting is feasible, and it is possible to combine organics with high carbon content and low moisture content (such as wood chips) with sludge and have a successful composting process.

The final compost products will be applied to two different plants to investigate the bioavailability of phosphorus in the compost products. The two types of plants will be selected based on their sensitivity, growth time, and their compatibility with the Manitoba climate. Switchgrass and canola are two candidates; however, research will be needed to determine the most suitable plants for the experimentations. For each plant, the mixing ratio of the compost with the topsoil will be

calculated to achieve the P application rates of 0, 4.8, 9.7, 19.4, 29.1 and 38.8 mg P kg⁻¹ dry soil, which corresponds to 0, 26, 52, 103, 155, and 206 kg ha⁻¹ P. The pots will be weighed and watered every day to replenish moisture lost by evapotranspiration. A control experiment will be also conducted by using topsoil soil and chemical fertilizers to achieve the same P application rates that is described above. The growth rates of plants will be compared with control samples. The size of plants, their overall health, and their growth rate will be monitored. And finally the concentration of total phosphorus in the biomass will be measured to compare three different parameters including phosphorus uptake, biomass yield, and phosphorus recovery efficiency, for both types of plants.

1.2 Research Objective

A) Investigating the potential for composting sludges generated from alum and ferric precipitation in the removal of phosphorus in wastewater lagoons, with the aim of creating compost that adheres to Class A standards outlined by the Canadian Council of Ministers of the Environment (CCME), within a laboratory environment.

B) Investigating the bioavailability phosphorous in the final compost product by applying the matured compost products as a fertilizer, to the selected plants (switchgrass and canola), in controlled environments.

Results from this work would provide some background understanding and give insights into the usage of chemical sludge and how it would reduce the socio-economic dependence on commercial phosphorus type fertilizer.

1.3 Thesis Outline

The general layout of this thesis follows the thesis guidelines of the Department of Civil Engineering, University of Manitoba. The individual research chapters (Chapters 3 and 4) were prepared in manuscript format and are as follows:

Chapter 1: General background

Chapter 2: Literature review

Chapter 3: Investigating the feasibility of using an enhanced composting process to recover nutrients from chemically precipitated phosphate sludge.

Chapter 4: Bio availability Study of phosphorus from Composted Chemical Sludge Using Switchgrass and Canola.

Chapter 5: General conclusions and recommendations.

2 CHAPTER 2 - LITERATURE REVIEW

2.1 Introduction

Phosphorus (P), a significant component in numerous fertilizers employed in agriculture, is an essential mineral, naturally present in many foods and is a component of human and animals' bones, teeth, DNA, and RNA (Singh et al. 2022). However, immoderate use of this element in farming practices and its excretion by humans into residential wastewater causes a high concentration of this element in receiving water bodies, therefore becoming a source of environmental concerns. The main environmental problem induced by the discharge of phosphorus-rich wastewater into the receiving surface water bodies is eutrophication, which can harm aquatic ecosystems, by depleting algae bloom and available oxygen (Cieślik and Konieczka 2017a)

Wastewater treatment plants without P removal mechanisms are one source of phosphorus pollution, as they often discharge treated water containing high levels of phosphates into water bodies. With the improvement of wastewater treatment plants due to the phosphorus discharge limitation over the years, the removal of P from wastewater prior to discharge has gained considerable attention. Such improvement of P removal from wastewater and the adoption of sustainable farming techniques have the potential to decrease the environmental effects of aquatic phosphorus contamination (Urdalen 2013). P removed from wastewaters is trapped in the sludge and further sludge management processes are required to recover the phosphorus. It is crucial to utilize sludge-P as fertilizer in order to optimize the utilization of the non-renewable nutrient P. Being an essential and irreplaceable component for organisms, P acts as a crucial nutrient in agriculture, as it greatly influences plant growth and serves as a limiting factor (Sattari et al. 2012).

Historically, urban wastewater treatment has employed various methods. However, the consistent challenge across these methods lies in effectively managing residual sludge, particularly in the context of filtration. This sludge, despite being heavily contaminated, contains a significant amount of water, posing significant challenges in its management. Conventional approaches like dewatering, landfilling, and spreading, struggle to effectively address this issue. In addition, conventional sludge management does not take into account the recovery of useful nutrients such as P in the sludge. On the other hand, composting is recognized as a promising remedy for this issue (Nemati, Samali, and Sanati 2019) and has both the advantage of sludge stabilization and nutrients recovery.

2.2 Phosphorus Background

2.2.1 Importance and scarcity of phosphorous as a critical nutrient

Phosphorus is a naturally existing element that is plentiful on the earth's surface. It exists partially in the phosphate form found in sedimentary and igneous rocks. Every form of life uses P in some way or another, making it an indispensable component. The reactivity of soluble phosphate released by weathering leads to its swift conversion into insoluble compounds (Smil 2000). P is one of the most important elements in living beings. It is a basic constituent in deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine triphosphate (ATP), bones, and teeth, and plays an important role in plant and fruit growth (Ashley et al., 2011; Cornel & Schaum, 2009). Modern agriculture relies on P as a main constituent for the production of fertilizer. Because P is a non-renewable resource, and industrial agriculture relies on P fertilizer to maintain its productivity, the reduced P fertilizer supply threatens the global agricultural industries (Dana Cordell, Drangert, and White 2009).

There is an uneven distribution of P rocks throughout the world. According to the literature, 71% of available rock reserves are found in Morocco and Western Sahara (Desmidt et al. 2015). It has been predicted that P reserves will be depleted within the next 100 years because of the tremendous increase in demand and usage over the last two centuries; despite this, there is a decline in the quality of extracted rocks as well as an increase in the cost of extraction and transportation of P rocks (Dana Cordell, Drangert, and White 2009). Such a situation poses an imminent threat to human survival and researchers are looking into ways of optimizing its use and recovering whenever possible.

2.2.2 Phosphorus in wastewater and Impact on Surface Waters

In recent years, rapid industrialization and population growth have intensified nutrient pollution (Ownby, Desrosiers, and Vaneeckhaute 2021). In addition to stormwater, erosion, and farmlands runoff, P pollution occurs from domestic and industrial activities. Generally, household wastewater is generated from activities such as bathing, washing, toileting, and cooking. Stormwater and agricultural wastewater are derived from rainwater runoff and farmland runoff, respectively. Industrial wastewater, on the other hand, is mainly generated by industrial activity. Human activities will always generate wastewater, but how it is managed will determine its environmental impact (Di Capua et al. 2022).

Depending on the loading of the system, the concentration of P in the influent wastewater varies. Studies have indicated that the P concentration in municipal wastewater commonly ranges between 4 to 11 mg/L, with many locations having an average concentration of 6 to 8 mg/L (Cornel and Schaum 2009). Nonetheless, regulations for treated wastewater often specify the highest permissible level of phosphorus below 1.0 mg/L or requires a removal rate of over 90% (D. Cordell

et al. 2011). Therefore, before wastewater is disposed of into the environment, it needs to undergo adequate treatment as excess phosphorus in surface water creates environmental imbalances. The treatment type, P composition, and the specific regional discharge limits determine the level of P removal from wastewater (Huber, Athanasiadis, and Helmreich 2020). When excess nutrients are loaded into surface water bodies, eutrophication becomes a major concern. When P, which is the major source of eutrophication, is discharged into the receiving waters, its concentration must be at a minimal level to prevent algae blooms. (Schindler et al. 2008).

A well-known example of the negative impact of P discharged into surface water is Lake Winnipeg in Manitoba. The lake has been eutrophicated by excess P discharged from farmlands and wastewater treatment plants. In southern Manitoba, the hog industry has recently grown and is geographically concentrated, which may contribute to high P levels in the Red River watershed. Due to the increase in farm size and proximity of farms, adjacent fields are being overspread with P. As excess P escapes into rivers, lakes, and oceans, it causes eutrophication (toxic blue green algae). The excess algae bloom reduces the dissolved oxygen in water, causing the death of aquatic life including fish (Schindler et al. 2008) and lowering the overall water quality. Recycling phosphorus back into the supply stream is essential for ensuring a viable agriculture industry in the future (Ackerman and Cicek 2013). Wastewater treatment is crucial for P recovery to support economic growth, preserve life on earth, and maintain environmental sustainability (Anders et al. 2021).

With an increase in population, food demand, advances in technology, scarcity of land and water, inefficient phosphorus use, and intensified agriculture have caused many environmental problems. As part of the solution, efficient fertilizer application mechanisms and sustainable P recovery methods need to be developed. Water treatment facilities have intensified efforts to separate and

recover phosphorus from wastewater due to its limited availability (Cornel and Schaum 2009). P in wastewater exists in different forms (orthophosphates, polyphosphates, and organic phosphates) and removal technologies date as far back as the 1950s. Chemical precipitation and enhanced biological phosphorus removal (EBPR), are well established methods for removing phosphorus (Morse et al. 1998). In addition, sustainability can be achieved with wastewater reuse along with P recovery (Schroder et al. 2011). A lot of studies (Ownby et al., 2021; Fernandes et al., 2012). have been conducted in the past to describe the removal and recovery of P from wastewater which contains phosphorus from erosion and surface run-off from agricultural farmlands, detergent usage, human waste, industrial waste, landfill, and fertilizers. With all human interferences on the P cycle, there is a major drive to close the gap between the modern societal P needs and the P cycle (Cornel & Schaum, 2009; Smil, 2000).

2.3 Phosphorus Removal

2.3.1 Chemical Precipitation of Phosphorus

To reduce the P load in wastewater, chemical precipitation dosing can be used at different stages of the treatment plant depending on the system's needs. A pre-precipitation process involves adding metal salts before or in the primary settling tank. Aluminum salts such as aluminum sulfate (alum) and polyaluminum chloride (PAC) as well as iron salts like ferric sulfate and ferric chloride are generally used for chemical treatment and removal of phosphorus (Kazadi Mbamba et al., 2015; Cheng et al., 2016). Metal salts are used as coagulants due to their ability to form insoluble compounds with phosphorus. When they are added and mixed with phosphorus rich wastewater, they form metal hydroxide precipitates which have a high affinity for phosphorus ions. The metal hydroxide precipitates can react with phosphate ions (PO_4^{3-}), a main form of phosphorus in

wastewater, and form insoluble metal phosphate compounds (aluminum phosphate or ferric phosphate), which are not soluble in water and settle as solid particles (Hasan et al. 2021).

The dosing of chemicals occurs after the primary settling tank, in the digestion tank, or before the secondary settling tank in co-precipitation. Post-precipitation metal dosing occurs after the secondary clarifier (Kazadi Mbamba et al. 2015). P can be recovered from chemical sludge after post-precipitation, making the effluent P concentration mostly within 1 mgL^{-1} . After the dosing operation is changed from pre-precipitation to post-precipitation, the amount of chemical sludge generated decreases (Cornel and Schaum 2009). The result of chemical precipitation is a discharge of low-phosphate effluent as well as the collection of metal phosphate precipitates in the sludge (Fernandes et al. 2012). Chemical dosing is usually done after anaerobic digestion, with over 90% of P precipitated into the sludge (Yuan, Q., 2011). pH, metal salt dosage, dosage point, initial phosphate concentration, and wastewater retention time are some factors that affect phosphate precipitation efficiency using these metal salts (Szabó et al. 2008).

The increasing volume of chemicals used, sludge produced, and sludge treatment and disposal are challenges related to the effective chemical precipitation of P (Elissen et al. 2006). The wastewater treatment lagoons, which act as a natural cleaner, has also been introduced with chemical precipitation. Small communities in Canada have employed this technology successfully despite difficulties with upgrades (Canadian Municipalities and Research Council 2004). The majority of wastewater treatment lagoons add metal salts to precipitate P in the lagoon in order to meet the P discharge standard of 1.0 mgL^{-1} (Hosetti and Frost 1995). The difficulty of sludge disposal increases as a result of the accumulation of sludge in these lagoons (Zhan, X. J, et al. 2015). In addition to achieving the discharge standards, the expense of dredging, trucking, and dumping sludge are other significant issues in the lagoon systems. Proper sludge management systems are

therefore required to prevent the loss of phosphorus in sludge which is a valuable and scarce product, and the reduction of the life span of the lagoon filled by sludge (Canadian Municipalities and Research Council 2004).

2.3.2 Enhanced Biological Phosphorus Removal

A more recent development in P removal is enhanced biological P removal (EBPR), which was found in 1959. This approach is widely accepted and used in numerous contexts across the world (Yuan, Q., 2011). Compared to the chemical removal of phosphorus, EBPR is a technology that offers more benefits in terms of phosphorus recovery. Because this process does not require the use of chemicals, EBPR systems result in lower costs for sludge management, as well as reduced metal content in the resulting sludge. Phosphorus recovered by this method is more beneficial for agricultural use because it is not attached to metals, making it more readily available to plants. Nonetheless, the effectiveness of the EBPR is heavily reliant on the specific features of the wastewater, and it is not as resilient or adaptable in comparison with chemical precipitation methods. Typically, the EBPR process requires more complex control and larger volumes of reactors. Generally, when conditions are favorable, approximately 90% of the P that enters can be conserved in the sludge (Petzet and Cornel 2013).

Under anaerobic conditions, microorganisms known as phosphate accumulating organisms (PAOs) are used to collect excess P. In this situation, when provided with volatile fatty acids (VFAs), microorganisms consume their reserved polyphosphates as a source of energy and discharge orthophosphates into the solution. The collected poly-hydroxybutyrate (PHB) is later decomposed in the aerobic area to promote the development and absorption of all the orthophosphates available in the solution (Stratful et al., 1999; Morse et al., 1998). The carbon

reserves in the aerobic zone can be oxidized, enabling the absorption of orthophosphate to compensate for the energy consumed in the anaerobic zone. Because more energy is discharged when carbon reserves are oxidized than when it is stored in the anaerobic zone, this leads to higher absorption of orthophosphate than what is released in the anaerobic zone. While a portion of the P can be reused in the anaerobic zone to support the continued development of PAOs in the system, the P can also be recovered as wasted activated sludge (WAS) (Ong et al. 2014). With effective effluent filtering and a combination of chemical dosing and EBPR, it is possible to obtain an effluent P content as low as 0.1 mgL^{-1} (Kazadi Mbamba et al. 2015).

2.4 Wastewater Sludge

The treatment of wastewater induces the generation of sludge, generally defined as primary sludge and secondary sludge. Primary sludge is the result of sedimentation, chemical precipitation, or other primary processes, while secondary sludge is waste biomass resulted from biological treatment processes. In many wastewater treatment systems, and particularly in rural municipal wastewater lagoons phosphorus management, different chemicals are used to coagulate and settle the phosphorus content of the lagoon water before discharge.

2.4.1 Phosphorus Rich Chemical sludge from Wastewater Lagoon Treatment Plants

To meet phosphorus discharge regulation, many wastewater lagoons rely on chemical phosphorus treatment. In Manitoba, Canada, smaller communities commonly employ chemical precipitation for wastewater treatment. This is primarily due to the ample availability of aluminum and ferric salts, making it a convenient and dependable method for conventional wastewater treatment (Desmidt et al. 2015). By using this method, concerns related to the initial investment cost and the instability of microorganisms in biological wastewater treatment are effectively avoided (Stratful

et al., 1999; Morse et al., 1998). However, chemical treatment generates high volume sludge that needs further management. Alum or ferric sludge refers to the residue produced during water purification and wastewater treatment operations that involve addition of ferric chloride (FeCl_3) or alum (usually in the form of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) as part of the coagulation procedure (Dassanayake et al. 2015). Approximately 5% of the total volume of processed water is comprised of wet sludge, which presents challenges in terms of treatment due to its high cost and complexity. Sludge production rises with chemical precipitation, primarily as a result of the process's increased chemical requirements. This treatment process generates sludge, which needs to be disposed of properly to minimize contamination and pollution. The appropriate handling of sludge is essential for protecting water resources and enhancing environmental quality (Hassan Basri et al. 2019). The expense of treatment, transportation, and disposal are some of the concerns in sludge disposal (Bunce et al. 2018). Chemical sludge is frequently dumped in landfills, causing a large loss in P, due to the insufficient number of reuse options (Kyncl et al., 2012; Hassan Basri et al., 2019). The average cost of disposal, the scarcity of dump sites, and the landfill prohibition in some countries are barriers to this (Keeley, Jarvis, and Judd 2012).

2.4.2 Sludge Management

Due to the continuous enforcement of strict wastewater effluent guidelines, more treatment will be implemented and as a result, additional sludge (increased sludge volumes) will be generated to ensure that these limits are satisfied (Parsons and Doyle 2002). The development of proper sludge treatment and management methods is therefore crucial. The treatment methods for sludge may vary depending on its composition and quality. The existing literature contains a wealth of research studies focusing on the utilization of sewage sludge. Nevertheless, there is a limited number of review articles available on the utilization of chemical sludge. Conventional waste management

approaches encompass employing alum sludge to eliminate pollutants such as heavy metals, utilizing it in environmental contexts such as wastewater treatment as a coagulant, and exploring its potential applications in the agricultural or forestry industries (Dassanayake et al. 2015). Typically, chemical sludge is commonly disposed of in landfills due to the limited availability of viable reuse options. Landfilling is regarded as an emergency measure rather than a favorable choice, as it lacks benefits. As a part of its strategic plan, the City of Winnipeg is considering the application of sludge on land due to economic incentives and the advantageous utilization of nutrients (City of Winnipeg 2014). Therefore, it is necessary to explore possible solutions for recycling and reusing alum sludge in order to evaluate the potential cost savings and advantages offered by alternative approaches. While there have been some studies conducted on the potential industrial reuse and recycling of alum sludge, research regarding its agricultural applications is currently limited. (Dassanayake et al. 2015).

2.5 Phosphorous recovery

2.5.1 Importance and Constraints of phosphorus recovery from Chemical Sludge

Phosphorus recovery from sludge is of significant importance because of its positive environmental impact. The recovery of this scarce resource will therefore create a circular economy and lead to resource sustainability. Chemical sludge from lagoon plants has the potential to act as a valuable phosphorus source. Due to their nutrient content and as a means of recycling nature's gift, P recovery from sludge and sludge streams is considered essential regardless of the wastewater treatment method. P recovery assures sustainability, mining P rocks are mitigated, and renewable P resources are created (Mayer et al. 2016).

On the other hand, the strong link that exists between P and the metals makes the recovery of P from the chemical sludge of Alum or Ferric difficult (Wilfert et al. 2020). However, consideration must be given to P recovery from sludge in order to ensure environmental sustainability and satisfy the expanding population's P needs (D. Cordell et al. 2011). In that contest, considerable progress has been made, particularly in the recovery of P from ferric phosphate sludge (Oleszkiewicz et al. 2015). Several industries can benefit from consideration and assessment of P recovery from chemical sludge (Wu and Williams 2013).

The use of chemical sludge is still recognized as a risk to the environment today. Because of the sludge's high organic content, acceptable amounts of chemical sludge application would lower the price of inorganic fertilizer, sustain the progress in enhancing the quality of groundwater, and improve soil qualities. Because chemical sludge contains beneficial nutrients and has organic content that can be applied in a controlled manner, the original landfilling of the sludge needs to be reduced. One idea for reusing chemical sludge is to utilize it to grow and produce bioenergy crops that are supposed to be used in the manufacturing of biofuels. This might reduce the already-existing fertilizer competition with food crops, help achieve net-zero emissions, and more. The evaluation of chemical sludge with various crops to assess availability would increase groundwater quality, preserve the environment, cut down on waste, and also lower greenhouse gas emissions (Maghsoodi et al., 2020; Kering et al., 2012).

2.5.2 Phosphorus Recovery Techniques from Sludge

It has been considered over the years that P can be recovered in the sludge stream and the sewage sludge ash, as well as in the liquid stream, with technologies such as crystallization (struvite, hydroxyapatite), wet oxidation and thermochemical (incineration with chemical extraction)

methods. The best results can also be achieved by combining these technologies (Peng et al., 2018; Stemann et al., 2015).

Some of the most successful recoveries are recorded in the form of struvite (Magnesium ammonium phosphate) and hydroxyapatite (calcium phosphate). With P recovery as struvite, the enriched P side stream is most targeted. Magnesium, phosphorus, ammonium, and potassium are abundant in the digested solution from the anaerobic zone (Yuan et al., 2012). Struvite is a slow-release fertilizer that competes well with conventional fertilizers when magnesium, phosphate, and ammonium are mixed in a 1:1:1 ratio (Ackerman and Cicek 2013). A solution's pH and magnesium concentration affect the precipitation of struvite (Parsons and Doyle 2002). In a high pH environment, ammonium leaves the system as ammonia and magnesium is no longer available as $Mg(OH)_2$ is formed (Ackerman and Cicek 2013). At pH levels greater than 8, struvite can reduce P to as little as 10 mg/l in sludge streams or ash and it's quite comparable to commercial fertilizer. On the other hand, hydroxyapatite reduces P under 10 mg/l, but it has limited effectiveness in alkaline soils (Yuan, Q, 2011).

To recover struvite (magnesium ammonium phosphate) from the side stream, the phosphorus-rich solution is mixed with an ammonium stream to facilitate its formation. In the case of the digested stream, which contains a high concentration of phosphorus and ammonium, struvite can be precipitated by making certain pH adjustments (Ackerman & Cicek, 2013; Monea et al., 2020). On the contrary, hydroxyapatite ($Ca_5(PO_4)_3OH$) can be formed by introducing lime into the phosphorus-rich side stream, and its precipitation is influenced by factors such as pH, phosphorus concentration, and other ions present in the solution. Countries such as Canada, USA, Japan, Germany, among others, have utilized both struvite and hydroxyapatite in various recognized

processes like Phosphrip, Phosnix, Ostara, Prisca, Pearl, Kurita, and more (Yuan, Q. 2011; Karunanithi et al., 2015; Monea et al., 2020).

In a study on recovering P from hog manure using batch reactors in 2012, Ackerman compared the struvite produced from precipitated dung to pure struvite and other commercial fertilizers (Ackerman and Cicek 2013). A fluidized bed reactor was also used by Bowers and Westerman (2005) to recover struvite from swine lagoon liquor. Struvite precipitation depends on pH and Mg:NH₄:PO₄ molar ratios (Bowers and Westerman 2005). It is also possible to recover P by chemical leaching, in which activated or/and chemical sludge is contacted with an acid or alkaline. As a result of chemical leaching, organic pollutants and metals may be released into the solution, affecting struvite precipitation quality (Monea et al. 2020).

P can also be recovered from solid sludge by thermal pre-treatment and thermochemical treatment. Thermochemical techniques provide high temperature sludge treatment via pyrolysis and incineration, where dry sewage sludge is converted to ash and subsequently washed in acids for maximum P recovery. Sludge can also be processed for P recovery by wet pyrolysis and gasification, followed by acid dissolution. Nano nucleation, membrane-assisted recovery, adsorption, and ion exchange are additional methods that are regarded as techniques for effectively capturing phosphorus and maximizing its recovery. In general, the combination of various technologies can lead to the development of a cost-efficient phosphorus recovery process (Karunanithi et al. 2015).

2.6 Sludge Composting

2.6.1 Definition and Principles of Sludge Composting

Composting is a controlled, microbial process that creates a stable product like manure by converting biodegradable organic materials. It is an effective way to manage waste biomass generated during numerous production processes (Cesaro, Belgiorno, and Guida 2015).

Composting is an exothermic process that can kill pathogens under appropriate temperature and time conditions (Alvarenga et al. 2015). As a result, a wide variety of thermophilic microorganisms (bacteria, actinomycetes, and fungi) which grow at relatively high temperatures (Greater than 55 °C), carry out most of the work. The decomposition of organic matter or sludge in manure leads to oxidized end products, mostly carbon dioxide (CO₂) and water (Sweeten and Auvermann 2008).

Composting is an aerobic, complex process that requires optimum conditions to encourage microbiological activity and the stabilization of organic matter (Białobrzewski et al. 2015). Aerobic composting employs aerobic bacteria and oxygen to regulate the temperature of sludge fermentation. This method proves both economical and efficient for city sludge disposal, facilitating the complete decomposition of harmful organic substances such as pathogens, heavy metals, and organic chemicals. Moreover, its short composting cycle is easy to manage and offers numerous additional advantages (Chen 2012).

Three stages are usually involved in composting: the mesophilic stage (Stage 1), the high-temperature phase (Stage 2), and the maturity phase (Stage 3). The composting process is divided into pretreatment, fermentation, post-treatment, storage, etc. Due to the high water content, low organic matter content, low porosity and high viscosity of sludge from sewage treatment plants, it is well composted with the addition of leaves, sawdust, wood, straw, or garbage (Chen 2012)

known as bulking agents. The use of appropriate bulking agents during a composting process can improve the sludge treatment and result to a mature compost (Lu et al. 2020).

2.6.2 Importance of composting chemical sludge

One of the most economical ways to manage and dispose of sludge is through composting and land application among these technologies (Wong et al. 2011). As a result of population growth and urbanization, wastewater production has increased in recent years. A higher level of wastewater treatment is required to meet the current environmental standards and regulations. As a result, large volumes of sludge are produced, containing mostly organic material and dead bacteria (Naidoo and Olaniran 2013). Wastewater treatment plants face a serious challenge in treating and disposing of sewage sludge (Li et al. 2014). Despite substantial investment in human and material resources for sewage management, the control and effectiveness of sewage treatment sludge, a byproduct of the process, remains inadequate. This greatly diminishes the environmental significance of sewage treatment efforts. The issue of sludge disposal has emerged as a pressing environmental problem in need of urgent resolution (Chen 2012). There have been different approaches to reducing sewage sludge production in WWTPs, including physical, chemical, and biological methods. The treatment of sewage sludge using biological methods has received significant interest as an environmentally friendly and viable approach.

Normally, municipal sludge must be treated before it can be reused or disposed of, in order to remove infectious organisms, viruses, and organic pollutants (Dong et al., 2014). A variety of technologies have therefore been developed, such as dewatering, anaerobic digestion, and aerobic composting (Dong et al., 2014). In composting, sludge is converted into fertilizer by biochemical and microbial processes (Abbasi, Mokhtari, and Jalili 2019; Sadeh, Poulsen, and Bester 2014).

When sewage sludge is treated properly to destroy or reduce pathogenic microorganisms, it can be used as a fertilizer or soil improver. It contains high organic content and nutrients including nitrogen, phosphorous, potassium, and various trace elements (Elissen et al. 2006).

2.6.3 Advantages and challenges of chemical sludge composting

Chemical sludge is high in water content and causes anaerobic conditions (Richard et al. 2002). For the sludge composting process, a pre-composting mixture should include a bulking agent, amendment, and recycled materials. Adding this combination to dewatered sludge will modify sludge properties, such as static and porosity conditions, and will optimize moisture content and carbon to nitrogen (C/N) ratio (Białobrzewski et al., 2015; Doublet et al. 2011)..

The following reasons make the composting of sewage sludge difficult: 1- The carbon-to-nitrogen (C/N) ratio of sewage sludge is undesirable, 2- The substrate has low porosity, which makes aeration difficult, and 3- Prior to being used as fertilizer, sewage sludge must be sanitized (Neugebauer et al. 2017). The impact of the carbon-to-nitrogen ratio on the composting process has been explained by (Kumar, Ou, and Lin 2010), and (Ekinci, Keener, and Akbolat 2006) has contributed to the discussion regarding the influence of the aeration rate on composting. Adding bulking agents that improve the porosity of composted substrate, can increase the rate of aeration, especially in natural aeration systems (F. Yang et al., 2013). When the temperature inside the composted prism exceeds 60°C for at least 3 days, the substrate is effectively sanitized (Raj and Antil 2011). Municipal sludge can hardly be composted by itself due to its compacted structure, high water content, and low C/N ratio. It is therefore beneficial to co-compost municipal sludge with other wastes such as sawdust, food industry waste, and municipal solid waste, due to their complementary characteristics. Garden waste typically has a loose structure, low water content,

and high carbon to nitrogen ratio, which makes it ideal for co-composting with sludge (Zhao et al. 2015).

Some advantages of sludge composting are as follows: 1- The end product has low odor, good physical properties, and does not attract flies, 2- Storage, transportation, disposal, and use of material are considerably reduced, and 3- Taking measurements on-site is an easy, reliable, and flexible method without the need for extensive equipment (Sweeten and Auvermann 2008).

Sludge composting is also associated with some drawbacks. The expenses associated with equipment and labor are high, which could pose a significant barrier. The demand for compost in the market may not be long-lasting and may be challenging to maintain. During the initial stages of composting, obnoxious odors may be produced, and a permit is necessary in certain states of USA when constructing composting facilities (Sweeten and Auvermann 2008). The heavy metal content of sludge compost is an important indicator of its safety. Compost can transfer heavy metals to soil and groundwater, where they can accumulate in plants, animals, and finally humans (Lu et al. 2020).

2.6.4 Constraints Associated with the Application of Composted Chemical Sludge

While reports indicate that the recovery of phosphorus (P) from chemical sludge (such as alum and ferric phosphate) is challenging due to existing bonds and high costs, phosphorus remains available in chemical sludge (Oleszkiewicz et al. 2015). The type of chemical employed in wastewater treatment to precipitate phosphorus has a significant impact on P availability, and the method and rate of P release in chemical sludge vary depending on the properties of the soil (Sorption, pH). Conflicting reports have suggested that excess metal hydroxide in chemical sludge may cause available P to precipitate in the soil and that P would be unavailable to plants (Vogel,

Nelles, and Eichler-Löbermann 2015). Older investigations also demonstrated that the excess metal hydroxide did not restrict the availability of P in the soil and that the chemical nature of the sludge did not affect the availability of P there (Kirchmann et al. 2017). According to some studies, the addition of chemical sludge can reduce the rapid availability of P, however, the addition will accelerate the synthesis of metal oxalates, increase soil P sorption capacity and, over time, P availability (Bøen, Haraldsen, and Krogstad 2013). Despite the fact that chemical sludge's organic P content might vary, the amount of organic materials in the sludge is said to cause most of the P availability to come from the breakdown of organic P. Inorganic P would build up and be released on the soil surface below 30 cm of soil depth as a result of the mineralization of biological P (Kyle and McClintock 1995).

Ferric salts are said to be economical and extremely effective at removing P from wastewater, but the precipitated ferric phosphate sludge needs to be disposed of correctly (Zhang et al. 2010). According to experimental research done in 1978 by Soon and associates, when used as fertilizer, ferric phosphate sludge is a very slow-release P source because it is highly insoluble. As ferric phosphate sludge has very limited reuse options, it is disposed of in landfills. Groundwater can be contaminated by ferric over time. It is for this reason that ferric phosphate sludge disposal is not only costly, but also has environmental consequences in the long run (Kato et al. 2006). It was also reported in a study that the growth of the plant can be adversely impacted by the occurrence of Al toxicity, which can be influenced by the level of aluminum in the sludge and, in particular, the pH of the soil in which it is applied (M. Yang et al. 2015; Kluczka et al., 2017). In pot experiments with varying concentrations of aluminum (0.5, 2.0, and 5.0 mM), it was observed that as the Al concentration in the soil increased, both plant growth and phosphorus uptake declined. However,

the impact of aluminum on plant growth was less pronounced at higher levels of phosphorus compared to lower concentrations of phosphorus (Poaceae et al., 1989).

Tolofari et al. 2021 conducted a study to examine the bioavailability of phosphorus in alum sludge by cultivating Switchgrasses. Four different rates of alum sludge and a chemical fertilizer, monoammonium phosphate (MAP), were applied to Switchgrasses. Potted soil units, both with amendments and without (control), were planted with pre-germinated switchgrass seeds and subsequently harvested three times, with each harvest taking place at 50-day intervals. Throughout the three growth cycles, the phosphorus from alum-P sludge gradually became available, with the maximum P recovery efficiency of 28%. The findings indicate that alum-P sludge serves as a productive source of accessible phosphorus for cultivating switchgrass in soils with high pH and low Olsen-P levels (Tolofari et al. 2021). To ensure the optimal utilization of phosphorus (P) and safeguard the quality of surface water, amendments are applied based on the P content (Shock, Pratt, and Station 2003).

2.6.5 Factors influencing composting of Metal Salts-precipitated sludge

According to previous studies aerobic composting of sewage sludge is influenced by several factors. Composting rates are influenced primarily by moisture content, physical structure, carbon-to-nitrogen ratio, aeration, nutrient balance, pH, and temperature (Sweeten and Auvermann 2008). The moisture content of composting sludge must be between 50% to 60%. The range of pH for optimal microbial activity of sludge composting is 5 – 9. The carbon to nitrogen ratio for composting sludge must be 25 - 35:1. In addition, the organic matter content of composting sludge needs to be 20 - 80%. (“Biosolids Composting Strengthens Its Base” 1994). Oxygen concentrations suitable for composting are 15-20%, with a minimum of 8% (Augenstein et al. 1996).

2.6.6 Carbon, Nitrogen and Other Nutrients

Carbon to nitrogen ratio (C/N) refers to the ratio of carbon element content in organic matter to its nitrogen element content. The C/N ratio is a significant factor affecting composting and compost quality (Gao et al. 2010). A high C/N ratio in wood chips helps improve the low C/N value of composting materials to some extent, as well as significant water sorption in them, which reduces sludge moisture content (Ingelmo et al. 2012). It is seen that the best C/N ratio is 20-30 atoms of carbon for each atom of nitrogen (20-30 carbon atoms to 1 nitrogen atom). When the C/N ratio is high or low, it will negatively affect the digestion of the material (-Priya .V, Lokesh .M, Kesavan .D, Komathi .G 2017).

In a study conducted by Neugebauer et al. (2017), the objective was to investigate the relationship between the C/N ratio and its impact on the rate of composting. To minimize heat loss, closed bioreactors were insulated. Compost was created from sewage sludge mixed with straw and sawdust at different ratios. All bioreactors were composted for 25 days. Aeration was performed in all bioreactors. Four different ratios of C/N were used in this research including 9.2, 12.1, 17, 26.4. Neugebauer et al. (2017) reported that elevating the C/N ratio is linked to higher temperature accumulation, extended composting duration, and an enhanced rate of composting.

During the decomposition of organic residues, microorganisms require nitrogen and other nutrients for metabolism and reproduction. C/N ratios of wastes have a significant effect on the rate of decomposition, but the amount of nitrogen per unit of organic matter depends on the type of microorganism involved. Microorganisms use carbon for building cells and supplying energy. The carbon is converted into carbon dioxide, which is lost to the atmosphere. Decomposition of organic material results in a significant loss of carbon, but a relatively smaller loss of nitrogen. While most

nitrogen is immobilized and stored in the bodies of microorganisms during composting, some nitrogen is lost as ammonia or nitrogen gas. Therefore, during the composting process, the C/N ratio decreases. When composting most manures and sludges, the C/N ratio should be between 20:1 and 30:1. Composting organic waste also requires an appropriate amount of phosphorus (P) and potassium (K). The osmotic pressure within bacterial cells is regulated by phosphorus and potassium present in microbial protoplasm. Ideally, the phosphorus content should be about 20 percent of the nitrogen content. As a result, composting common types of organic waste requires a C/N/P/K ratio of 25:1:0.2:0.08 (Sweeten and Auvermann 2008).

2.6.7 Aeration

To support aerobic microbial activity, a compost pile must be aerated. In addition to reducing microbial activity, aeration also removes moisture released from the soil and excess heat. In the composting process, oxygen levels should range from 5 to 15 percent. Aeration can be done in two ways. The first method involves turning the compost pile mechanically with front-end loaders or compost turners. Initially, the pile should be turned several times per week, and less frequently later. There is also a second aeration method known as forced air, which either draws or blows air through the compost. As composting progresses, the aeration rate can be reduced. After composting, the material should be aged in a pile for about 2 months to complete its stabilization (Sweeten and Auvermann 2008).

2.6.8 Composting system

Preparation of the materials and biological stabilization are the two basic steps for successful composting. Preparation involves making necessary adjustments to moisture content, structure, or chemical content. If high-moisture manure or sludge is blended with finished compost or bulking

agents (wood chips, cotton gin trash, cornstalks, straw, etc.), it can be dried to below 60 percent moisture. By adding water to dry manure or sludge, the moisture content may be raised to 40 to 60 percent. Composting can be performed in windrows, static piles, or aerated containers. Each method involves varying levels and types of mechanization, affecting the time, cost, and amount of space, labor and management needed to complete the process. Windrow composting involves stacking organic wastes into long windrows and turning them periodically. Managing temperature and moisture is all that is required for windrow composting. The height of windrows should be between 3 and 5 feet, and the width of the base should be between 10 and 15 feet. As internal heating occurs, air should move through the porous composting material from bottom to top, like a chimney. It is a good idea to turn windrows often at first and then less frequently. To ensure that composting restarts effectively after turning, water may be added during the turning process if the moisture content falls below 35 percent during the first five weeks. Turning should be determined by the temperature of the compost pile (Sweeten and Auvermann 2008).

2.6.9 pH

pH values have a major impact on microbial growth and activity (He et al. 2013). Le et al (2020), reported that during the entire composting process, the pH remained between 6.5 and 8.8, which is a good range for microbial activity. There are many reactions that take place during composting that cause increased NH_3 production, which lead to a decrease in pH due to the formation of organic acids and possible nitrification (Yu et al. 2010). However, the pH becomes more stable due to biological stabilization (Yu et al. 2010).

For the best composting results, pH should initially range from 6.5 to 7.2. The pH of the composted manure or sludge can drop to below 6.0 in the early stages as organic acids are formed. Acids like

these have strong odors, and they prevent the growth of thermophilic aerobic bacteria. If a pH is less than 6.0, little heating will occur because bacteria don't digest as efficiently until near-neutral conditions are reestablished. It may be beneficial to add a buffering agent or lime during the initial stage of composting. Compost will have a pH of 7.5 to 8.5 or greater when finished. In the initial stage of composting, the pH level increases (8.7 on the eighth day and 9.3 on the sixth day) likely because of the presence of proteolytic bacteria that release ammonia when organic matter is decomposed. In the final days of the process, due to ammonia oxidation and nitrate production by nitrobacteria, the ammonia content decreases, and the pH value drops to around 7 (Sweeten and Auvermann 2008).

2.6.10 Temperature

Temperatures of 45°C are considered to be the start of aerobic, thermophilic composting. Afterward, the temperature rises rapidly due to the release of heat by the breakdown of complex molecules and organic matter into simpler compounds. Temperatures may exceed 65°C during the peak period. Temperatures of 85 °C or more could indicate a dangerous conversion to chemical oxidation, which can result in spontaneous composting. The high temperature and frequent turns during composting increase the evaporation of water (Lu et al. 2020). When pile temperatures approach 71 °C, the pile should be mechanically turned or aerated. For windrows, 55 °C must be maintained for at least 15 days in vessels, bins, or aerated static piles. It is recommended by most western countries that windrow composting be carried out at a temperature greater than 55°C for at least 15 days to kill pathogens in sludge (CCME, 2005). At 65°C degrees to 71 °C, weed seeds are mostly inactivated (Sweeten and Auvermann 2008). In general, a long-stemmed thermometer with a length of three to four feet is the best tool for measuring the temperature in the compost system.

2.6.11 Moisture content

Adequate moisture is required for aerobic and thermophilic composting. Initial moisture content should be between 40 and 60 percent (by mass). Decomposition will be much slower if the moisture content is lower than 35%. Therefore, water should be added to dry manure to initiate composting. If compost material is too moist, water removes air from the pore spaces and prevents gas exchange, creating anaerobic conditions. Composting material with a moisture content greater than 65 percent can accumulate and restrict airflow in mechanical systems. A bulking agent or dry material should be added to wet organic materials such as sludge prior to composting to reduce their moisture content. Suitable bulking agents include cotton burrs, sawdust, peanut hulls, corncobs, wood chips, rice hulls, and brush trimmings. In addition to providing carbon, these materials help microorganisms break down organic matter. The moisture content of finished compost is usually between 20 and 30 percent (Sweeten and Auvermann 2008).

2.6.12 Composting additives and amendments (e.g., bulking agents, microbial inoculants)

To promote aeration, composting materials must have sufficient porosity so that air can freely flow through them. To increase the porosity of fine-textured materials and absorb extra moisture, bulking agents are usually needed. Depending on particle size and initial moisture content, the amount of bulking agent can range from less than 1:1 (volume to volume ratio) to more than 5:1 (Sweeten and Auvermann 2008).

Lu et al. (2020), conducted research using wood chips, ceramsite, and plant ash as bulking agents during the 44 days of composting of sewage sludge at a pilot scale during the winter months. Wood chips were effective in bulking up sewage sludge composting while ceramic failed to do so. In the

pretreated wood chips, tree branch pieces were 3 mm thick and 2–3 cm in diameter. (Lu et al. 2020).

In research conducted by Lu et al. (2020), four different wood chips to sludge ratios based on wet weight, were well mixed. Subsequently, windrows of 1.8 m width and 1 m height were set up. Composting continued for 44 days. The mixed waste was turned daily at the beginning, then every three to four days at the end of composting. The results indicated that the best composting ratio was 3:1 (woodchips to sludge). Temperature, moisture content, and pH were measured every day during the first fermentation stage (0-30 days). After that, they were monitored every two days until the compost reached maturity. Temperatures were measured 5, 20, and 40 cm beneath the surface using a long probe thermometer. By drying the samples at 105°C until their weight was stable, the moisture content was determined. During the initial phase of composting, the temperature rose due to the degradation of organic matter. The temperature evolution using wood chips as a bulking agent (3:1) rose in only two days from ambient temperature of 13°C to the highest value of 67°C (Lu et al. 2020).

Rihani et al. (2010) conducted research for in-vessel aerobic composting of urban primary sludge by mixing them with some agricultural waste including sugar beet leaves and straw. The physicochemical properties, levels of heavy metals, and microbiological parameters of the final compost product were observed. The end compost displayed minimal levels of heavy metals, comparatively elevated nutrient content, and a substantial decrease in pathogens. These findings indicate that urban primary sludge can be effectively utilized for agricultural purposes. (Rihani et al. 2010).

3 CHAPTER 3 - Investigating the feasibility of using an enhanced composting process to recover nutrients from chemically precipitated phosphate sludge

3.1 Abstract

An increased burden to nation-wide municipalities and the environment is usually sludge from chemically treated lagoons. This study investigated the feasibility of composting alum and ferric phosphate sludges that is produced in the process of phosphorous removal at wastewater lagoons. The dewatered alum and ferric precipitated sludges were well mixed with woodchips as the bulking agent, with ratio of 3:1 (woodchips to sludge), in two compost piles at a controlled laboratory scale. Several parameters including moisture content, temperature, and pH of the compost mixtures were monitored throughout the process of composting. Both compost piles maintained the temperature of 55°C or higher for a minimum period of 15 days. The final compost products were analyzed for different parameters including maturity, foreign matter, pathogenic organisms, organic matter, moisture content, and pH. The results demonstrated that both alum and ferric composts meet the criteria for category A compost Canadian Council of Ministers of the Environment (CCME) standards.

3.2 Introduction

3.2.1 The issue of excess phosphorous and phosphorous removal in lagoons

A major environmental issue in many watersheds is the excess discharge of phosphorous and nitrogen into rivers and streams which may result in the eutrophication of water resources. Lake Winnipeg in the Province of Manitoba in Canada is an interesting example of such water resources. The runoff of agricultural farms and wastewater from scattered communities in an area of over one million square kilometers spanning over four Canadian provinces and two American states end up

in Lake Winnipeg resulting in significant algae growth in the lake (Manitoba Agriculture and Resource Development 2020).

Regulations for treated wastewater often specify the highest permissible level of phosphorus is less than 1.0 mg/L or requires a removal rate of over 90% (D. Cordell et al. 2011). According to the Manitoba Water Quality Standards, Objectives, and Guidelines, as of January 1, 2016, all wastewater treatment facilities discharging greater than 820 kg TP per year (or communities with a population more than 2,000/equivalent due to industrial contributions) are required to meet 1 mg/L TP discharge limit if their effluents discharge to surface waters. This includes wastewater lagoons that are broadly used by numerous communities and municipalities across Manitoba. Most wastewater lagoons cannot naturally meet the provincial limits of 1 mg/L under cold climate conditions in Manitoba (Vahedi et al, 2022). A vast majority of these lagoons use aluminum sulfate (alum) or ferric chloride to remove phosphorous in a chemical coagulation process to reduce the phosphorous level. The process is either accomplished by simply pouring chemicals in the lagoons (in-situ) or dosing the wastewater in a separate process (ex-situ) and in both approaches, phosphorous is removed in the formed of sludge.

3.2.2 The importance and challenges of phosphorous recovery

Being an essential and irreplaceable component for organisms, phosphorous acts as a crucial nutrient in agriculture, as it greatly influences plant growth and serves as a limiting factor (Sattari et al. 2012). A number of researchers argue that at a certain point (maybe as early as 2040) the rate of extraction of phosphate rocks – the primary source of phosphorous – will decline, due to the decrease of phosphate reserves (Dana Cordell, Drangert, and White 2009). Given that a significantly large portion of the world's population suffers from the lack of proper nutrition, the mandatory decline of phosphate production may threaten the agricultural industry and the future

global economy growth. Recycling phosphorus back into the supply stream is essential for ensuring a viable agriculture industry in the future (Ackerman & Cicek, 2013; Huber et al., 2020). Typically, the phosphorous recovery technologies are complex and require a large capital investment, perfect environmental conditions, high level of maintenance, and a significant amount of energy (Sengupta et al., 2015; Cieřlik & Konieczka, 2017; Uzkurt Kaljunen et al., 2022). In particular, the known processes of phosphorous recovery from chemically precipitated sludge can be significantly challenging due to the strong bond between phosphate molecules and metals which is the main reason for using a coagulation process to remove phosphorous in the first place.

As discussed earlier, chemical coagulation in lagoons can be accomplished either in-situ or ex-situ. The in-situ precipitation is simple; however, this method is very inefficient as the technicians do not have any control over the mixing conditions. Poor mixing may result in excessive use of chemicals. In addition, the sedimentation of formed particles typically results in a large volume of sludge which accumulates at the bottom of lagoons and reduces the hydraulic capacity and lifespan of lagoons. Since phosphorous stays in the water system in the form of sludge, phosphorous recovery and reuse is almost impossible (Brown and Shilton 2014). Ex-situ chemical precipitation is more complex and involves pumping and treatment of wastewater in a separate process, however, it guarantees the complete removal of phosphorous and provides the opportunity to contain the sludge for further phosphorous recovery.

3.2.3 Sludge Formation in Chemical Coagulation & Sludge Treatment

Phosphorous in wastewater exists in different forms (orthophosphates, polyphosphates, and organic phosphates) and removal technologies date as far back as the 1950s due to eutrophication issues in surface water. Chemical precipitation and enhanced biological phosphorus removal (EBPR), are the established methods for removing phosphorus (Morse et al. 1998).

Most wastewater lagoons in Manitoba use a variation of chemical precipitation for phosphorous removal. Chemical precipitation is a process of binding soluble phosphate molecules with a positively charged metal (e.g., Al^{3+} , Fe^{3+} , Ca^{2+}) to form non-soluble precipitates that can be removed by sedimentation (Metcalf & Eddy Inc et al. 2013). In mechanical wastewater treatment plants, the dosing of chemicals may occur after the primary settling tank, in the digestion tank, before the secondary settling tank in co-precipitation, or even after the secondary clarifier (Kazadi Mbamba et al. 2015). In municipal wastewater lagoons, the dosing of coagulants can be done in-situ by simply pouring the coagulating chemicals (typically Ferric Chloride (FeCl_3) or Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)) into the lagoon or ex-situ by dosing the wastewater in a separate plant and separating the formed sludge. A number of parameters including pH, metal salt dosage, dosage point, initial phosphate concentration, and wastewater retention time may affect phosphate precipitation efficiency using these metal salts (Szabó et al. 2008).

In both cases, the coagulation process results in a significant volume of phosphorus-rich sludge with a very high moisture content (typically 95-99%). The accumulated sludge at lagoons during in-situ coagulation or the produced sludge in ex-situ coagulation processes usually must go through a series of stabilization, dewatering, and volume reduction processes before being disposed in landfills as solid waste (Kyncl et al., 2012; Dassanayake et al., 2015). The increasing costs of handling, dewatering, hauling, and disposal is a barrier for phosphorous removal in chemical precipitation processes (Elissen et al. 2006). As a result, municipalities are encouraged to find alternative applications for chemically precipitated sludge to avoid the disposal and environmental costs.

In addition to high water content, wastewater sludge contains infectious organisms, viruses, and organic pollutants. A range of treatment processes including incineration, dewatering, anaerobic

digestion, and aerobic composting have been developed for treating wastewater sludge (Dong et al., 2014).

3.2.4 Composting as an alternative sludge treatment process

The formed sludge in the chemical precipitation processes is nutrient-rich and typically contains organic materials. Therefore, theoretically, it is possible to be used in composting processes. In fact, composting is often regarded as an effective way to manage waste biomass generated during numerous wastewater processes and is considered as one of the most economical ways to manage sludge (Wong et al., 2011; Cesaro et al., 2015; Nemati et al., 2019). The composting process is essentially a method for phosphorous recovery that can potentially make the phosphorous bioavailable in the form of fertilizer.

Aerobic composting of sewage sludge is influenced by several factors including moisture content, physical structure, carbon-to-nitrogen ratio (C:N ratio), aeration rate, nutrient balance, pH, and temperature (Ekinici et al., 2006; Kumar et al., 2010; Yang et al., 2013; Sweeten & Auvermann, 2008). Typically, the moisture content of 50%-60%, pH between 5 to 9, C:N ratio of 25-35, and the organic matter content of 20 - 80%, oxygen concentrations of 15-20%, with a minimum of 8% are desirable for a successful aerobic composting process (*Biosolids Composting Strengthens Its Base*, 1994; Augenstein et al., 1996).

The composting process of wastewater sludge may be challenging due to several limiting factors. Firstly, the C:N ratio of sewage sludge is typically below 10 and is significantly lower than the desired range of 25-35 for aerobic composting. Second, the formed sludge usually has very low porosity, making the aeration difficult or impossible. Third, the sludge may contain harmful or toxic substances and heavy metals which may interfere with biological activities during the composting process. The final product often needs to be stabilized and/or neutralized prior to being

used as fertilizer (Ekinici et al., 2006; Kumar et al., 2010; Neugebauer et al., 2017). In addition, the heavy metal content of sludge compost can be a limiting factor as the metals can transfer heavy metals to soil and groundwater, where they can accumulate in plants, animals, and finally humans (Lu et al. 2020). Therefore, it is important to check the concentration of heavy metals in the final product before using it as fertilizer.

To increase the C:N ratio and to improve the porosity of composted substrate, bulking agents such as leaves, sawdust, wood chips, straw, or municipal organic wastes can be added to the compost piles (Chen, 2012; Lu et al., 2020). Adding bulking agents that improve the porosity of composted substrate, can increase the rate of aeration, especially in natural aeration systems (F. Yang et al. 2013). In addition to improved aeration, the bulking agents improve the C:N ratio as well as the moisture content by absorbing the excess moisture (Gao et al., 2010; Doublet et al., 2011; Ingelmo et al., 2012). Depending on particle size and initial moisture content, the amount of bulking agent can range from less than 1:1 (volume to volume ratio) to more than 5:1 (Sweeten and Auvermann 2008). Lu et al. (2020) conducted research using wood chips, ceramsite, and plant ash as bulking agents during the 44 days of composting of sewage sludge at a pilot scale during winter months. Wood chips were effective in bulking up sewage sludge composting while ceramic failed to do so. In the pretreated wood chips, tree branch pieces were 3 mm thick and 2–3 cm in diameter. In another study, Zhao et al. (2015) analyzed the different woodchips to sludge ratios of 3:1, 4:1, and 5:1 and concluded that the 3:1 ratio resulted in the most successful composting process.

3.3 Objectives

The objective of this study is to investigate the potential for composting sludges generated from alum and ferric precipitation in the removal of phosphorus in wastewater lagoons, with the aim of

creating compost that adheres to Class A standards outlined by the Canadian Council of Ministers of the Environment (CCME), within a laboratory environment..

3.4 Materials and Methods

3.4.1 Compost Feedstock

In this research, the chemically precipitated sludge was recovered from a pilot-scale ex-situ phosphorous removal process configured by Innovantage Inc. (a company located Winnipeg, Canada). Two different types of chemically precipitated sludge formed by injecting alum and ferric chloride solutions into the wastewater stream were used in this study.

The alum precipitated sludge was recovered and dewatered from the phosphorous removal process at a secondary wastewater lagoon cell located in the Rural Municipality of Taché (Manitoba, Canada). Ferric precipitated sludge was collected and dewatered from a similar process at a primary wastewater lagoon cell located in Town of Altona (Manitoba, Canada). Approximately, 10m³ of sludge was produced every week in the pilot phosphorous removal system. The produced sludge was dewatered in geotextile bags with a moisture content between 80%-95%.

Physicochemical properties of both sludge samples, including moisture content, pH, Carbon per Nitrogen ratio, total Phosphorus (TP), total Aluminum or Ferric (TAI, TFE), total Carbon (TC), total Nitrogen (TN), and metal composition were determined prior the experiments (Table 3.1). In this study, woodchips were used as a bulking agent and carbon amendment for both sludge types. The woodchips were fragmented tree branches, and collected from Brady Road Resource Management Facility (Manitoba, Canada) and were approximately 3-4 mm thick and 2–3 cm in diameter after pretreatment and screening. The collected woodchips had a moisture content of 33% and a C:N ratio of 45:1, as reported by the City of Winnipeg. Woodchips typically have a high

potential of water sorption, which can decrease the moisture content of sludge. In addition, woodchips have a high C:N ratio, which helps to improve the low C:N ratio of sludge (Ingelmo et al. 2012).

Table 3-1 Physicochemical properties of dewatered sludge

Parameter	Alum Sludge	Ferric Chloride
Moisture Content (%)	90.9	87.7
pH	7.92	7.13
C: N Ratio	9.2:1	8.56:1
Phosphorus (P) (mg/kg)	27,400	26,600
Aluminum (Al) (mg/kg)	134,000	975
Iron (Fe) (mg/kg)	4,400	170,000
Total Carbon (mg/kg)	115,000	284,000
Total Nitrogen (mg/kg)	12,700	33,100
Potassium (K) (mg/kg)	990	8710
Magnesium (Mg) (mg/kg)	5560	8110
Cadmium (Cd) (mg/kg)	4.7×10^{-2}	0.139
Cobalt (Co) (mg/kg)	9.80	4.38
Chromium (Cr) (mg/kg)	6.35	9.34
Copper (Cu) (mg/kg)	8.26	70.6
Nickel (Ni) (mg/kg)	10.5	10.9
Lead (Pb) (mg/kg)	1.60	2.05
Zinc (Zn) (mg/kg)	19.6	69.6

3.4.2 Experimental Design and Statistical Analysis

Controlled laboratory scale compost piles were tested at the environmental engineering laboratory of University of Manitoba. The compost piles were formed in a walk-in environmental chamber with the capability of controlling temperature at 25°C. After several trials and testing different configurations of woodchip to sludge ratio ranging from 1:1.5 to 4:1, eventually two compost piles were designed for two types of sludge with woodchip to sludge ratio of 3:1. The details of woodchips and sludge volumes are shown in Table 3.2. The first compost pile consisted of alum

sludge, characterized by a C:N ratio of 9.2:1, combined with woodchips, which had a C:N ratio of 45:1. By employing a ratio of three parts woodchips to one part sludge, the compost mixture attained a C:N ratio of 36.05:1. Additionally, the second compost bin comprised ferric sludge with a C:N ratio of 8.56:1, along with woodchips at a ratio of 45:1. A combination of three parts woodchips to one part sludge yielded a resulting C:N ratio of 35.89:1.

Table 3-2 Compost piles bulking agent and sludge ratios

Compost Feedstock	Volume (L)	C: N Ratio
Alum Sludge	80	9.2:1
Ferric Sludge	80	8.56:1
Woodchips	240	45:1
Alum sludge composting mixture	320	36.05:1
Ferric sludge composting mixture	320	35.89:1

The bulking agents (woodchips) and sludge samples were mixed in two laboratory-scale 0.3115 m³ (311 L) composting bins. A schematic of the composting setup can be seen in the following figure (Figure 3.1)

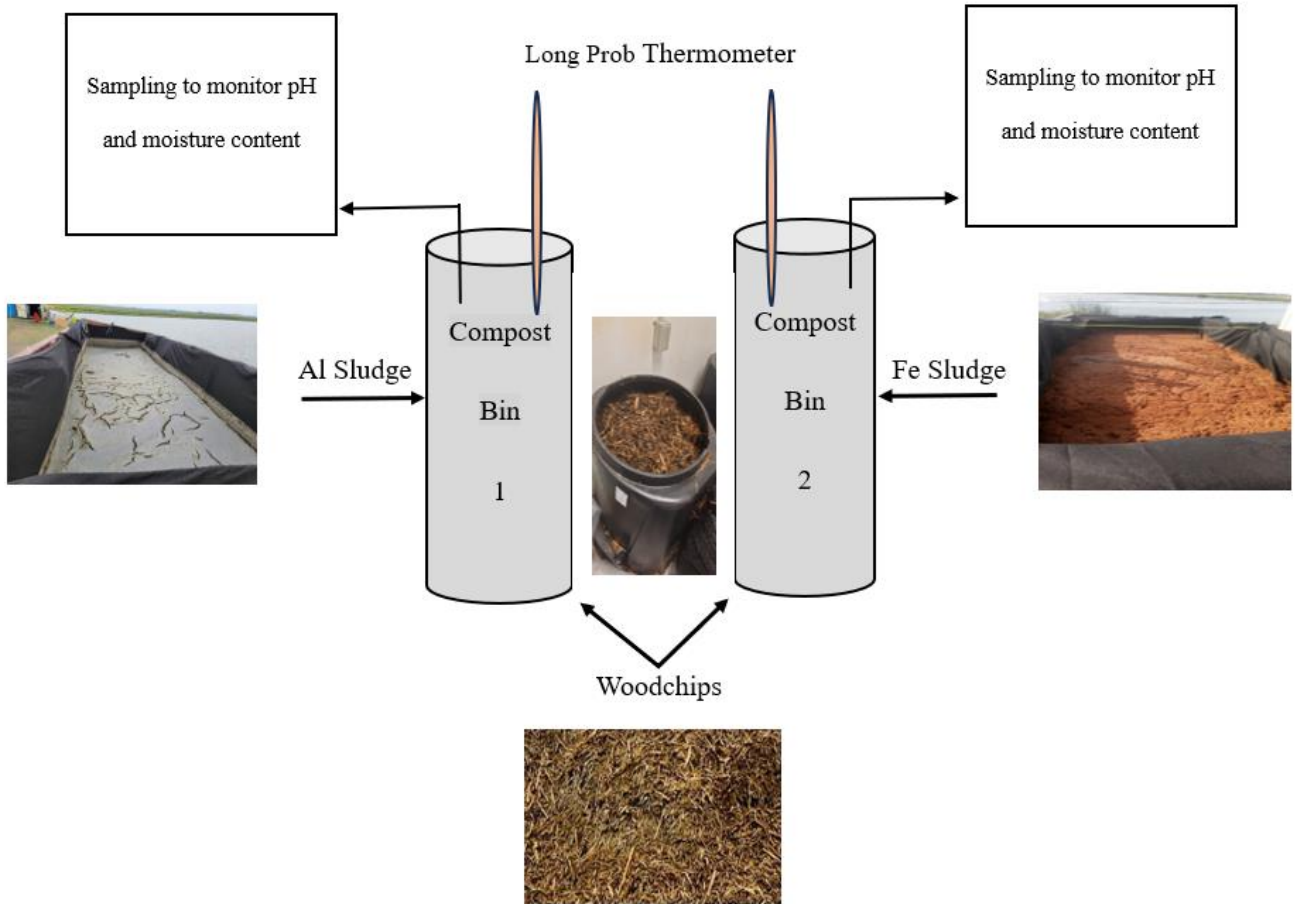


Figure 3-1 Schematic of the composting setup

In composting process, it is essential to maintain an aerobic decomposition environment which is typically accomplished by periodic turning. Turning the compost pile and large particle size of woodchips lead to promote air circulation and to decrease moisture content. As a consequence of the heat loss due to turning, the temperature dropped, which was normal. The initial turning of the windrows typically occurs when the temperature reaches 60°C. The growth of microbes during the early stages of composting was greatly affected by the low temperatures (Strom 1985). In this study, at the beginning of composting process, for the first two weeks, the compost mix piles were turned manually once a week and after two weeks, the piles were turned over every two weeks.

The composting process continued for a period of 55 days and the compost products were kept in the lab for another 40 days to be matured. Critical parameters including moisture content, pH, and temperature were monitored throughout the process. At the end of the composting process, the final products were analyzed to determine the characteristics of the product and the success of the process.

3.4.3 Physicochemical analysis

During the composting process, temperature was monitored using a long probe thermometer at 5cm, 15cm, 30cm, and 45cm depth in composting piles. The temperature was recorded daily for the first 30 days and every two days thereafter. The pH values were also measured using a glass pH electrode by sampling from different depths of composting piles and diluting in deionized water. pH measurements were conducted daily initially and then shifted to a bi-daily frequency after reaching day 30. In order to measure the pH, 20 grams of compost were dissolved in 100 mL of distilled water while stirring constantly.

For the moisture content, samples of compost piles were weighed and dried for a minimum of 24 hours at 105°C. Then samples were placed inside a desiccator and cooled, then weighed to determine the moisture content of the composting mix. The moisture content was measured every day for the first 30 days and every two days after 30 days.

The final products after maturity phase were sent to the A&L Canada Laboratories Inc. located in the City of London (Ontario, Canada). The final compost products were analyzed for a number of parameters including total organic matter, C:N ratio, moisture content, pH and other elements (see Table 3.3).

3.5 Results and Discussion

3.5.1 Temperature evolution

Temperature plays a crucial role in the composting process and is considered one of the most important factors. At the beginning of the composting process, the breakdown of organic materials leads to a rise in temperature. This thermophilic stage typically persists for a few days and the elevated temperatures enhances the breakdown of organic matter (Lu et al. 2020). It is recommended by most guidelines to carry out the composting at a temperature above 55°C for at least 15 days in order to kill pathogens in sludge (CCME, 2005). As shown in Figure 3.2, the temperature rose in 15 days from ambient temperature of 21°C to the highest values of 60°C for alum sludge bin. Similarly, the temperature rose from 22°C to 63°C in just 7 days for ferric sludge bin. After reaching the peak temperature, the temperatures in compost piles began to decrease starting from day 35 and day 25 for alum and ferric sludges respectively. The corresponding temperature readings were approximately 28°C and 23°C, which was observed by the end of the 55-day period.

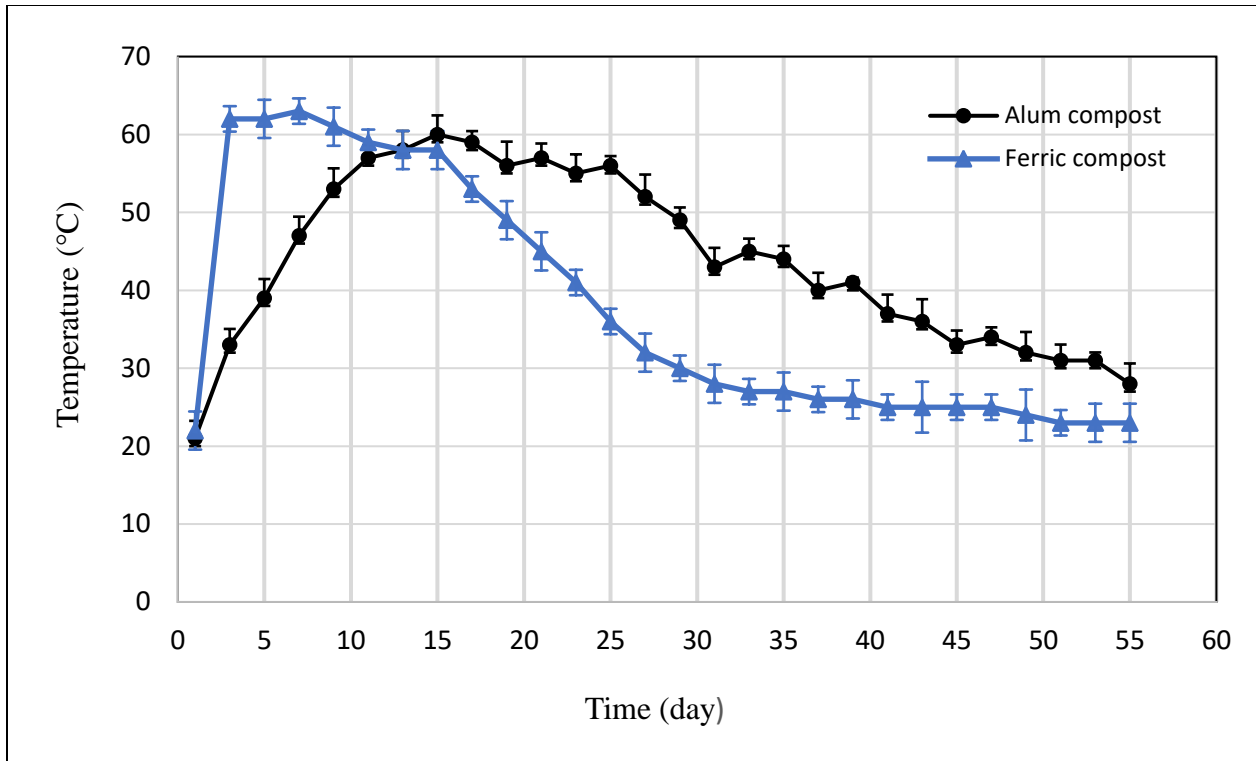


Figure 3-2 Temperature evolution during chemical sludge composting

3.5.2 Moisture Content Evolution

As previously stated, sludge from the phosphorous removal process contained very high moisture content and even after dewatering, the moisture content was in the range of 75%-80%. Throughout the composting process, the combination of high temperatures and regular turning accelerates the evaporation of water. Moisture is required for aerobic and thermophilic composting and the initial moisture content for an optimum composting process should be between 40 and 60 percent (by mass). In fact, the decomposition tends to be much slower if the moisture content is lower than 35%. The moisture content of finished compost is usually between 20 and 30 percent (Sweeten and Auvermann 2008).

Figure 3.3. shows the evolution of the moisture content for alum and ferric bins during the composting process. It indicates that the moisture content in the alum compost pile experienced a reduction from 78% on the first day to 55% on day 35. On the other hand, composting with the ferric precipitated sludge resulted in a moisture loss from 80% on the first day to 56% on the 25th day, which could mainly be attributed to physical turning and heat. For the Ferric precipitated sludge composting pile, as the moisture content decreased to 39% on the day 19, water was added to the pile to prevent decreasing water content below 35%.

After the completion of the thermophilic phase, which lasted for 30 days, the moisture content of both composting piles gradually reached a stable state. Specifically, the moisture content stabilized at 47%, and 42% in each respective pile.

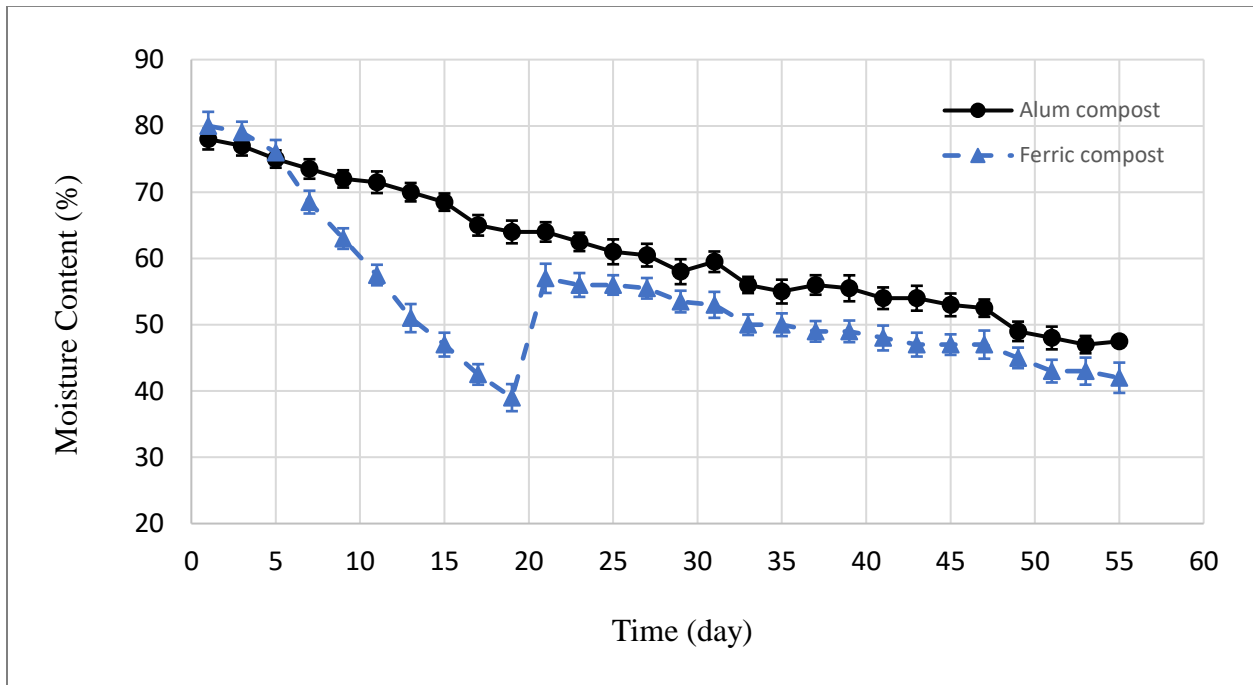


Figure 3-3 Moisture content evolution during chemical sludge composting

3.5.3 The variation of pH

The pH of compost piles has a major impact on microbial growth and activity (He et al. 2013). Le et al (2020) reported that during the entire composting process, the pH range of 6.5 to 8.8 is a good range for the aerobic microbial activities in the composting process. There are many reactions that take place during composting that cause increased NH_3 production, which leads to a decrease in pH due to the formation of organic acids and possible nitrification. Finally, the pH becomes more stable due to biological stabilization (Yu et al. 2010).

As shown in Figure 3.4, pH values during the entire composting period remained within a range of 7-8 for both alum and ferric piles.

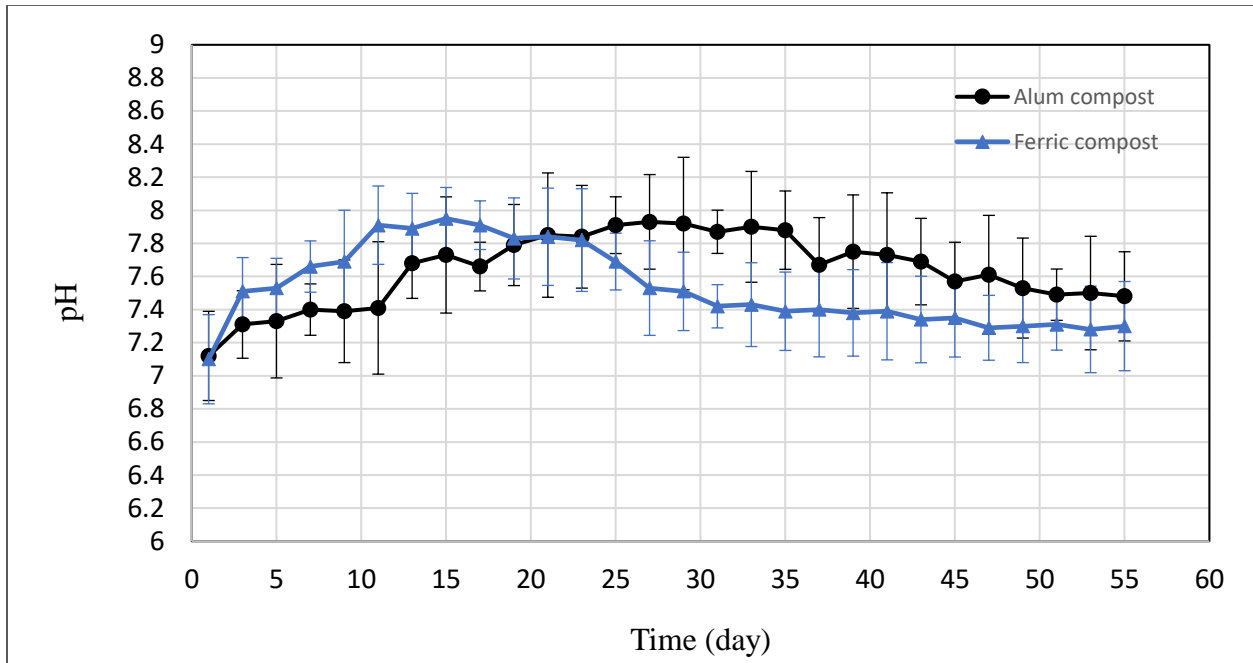


Figure 3-4 pH evolution during chemical sludge composting

3.5.4 Final Product Characteristics

Back in 1996, CCME created guidelines for compost products, during a period when the composting industry was still relatively new. Since then, numerous industries and municipalities have adopted extensive composting operations. Because of the various regulatory approaches in Canada, these guidelines primarily focus on ensuring the quality of compost rather than regulating the actual composting process. The CCME standard categorizes compost into two types: A, and B, arranged in descending order of quality. The global recognition of these compost types is determined by their level of quality and safety, rather than their intended usage. The classification is primarily determined by the amount of foreign matter, maturity, and pathogens in the compost. The remaining criteria remain consistent across all two classes of compost (CCME, 2005).

To demonstrate that the final compost products meet the criteria for Class A compost in Canada, various parameters were analyzed and compared to the guidelines set by the Canadian Council of Ministers of the Environment (CCME). The results of analysis of the final products of alum and ferric sludge composting (by A&L Laboratories) are provided Table 3.3. Comparing the results with CCME guidelines, showed that both compost products meet the criteria for category A compost CCME standards. The characteristics of final compost products will be discussed at the following sections.

Table 3-3 Characteristics of final compost products for alum and ferric sludges

Parameter	Results		
	Alum Sludge Compost	Ferric Sludge Compost	CCME Guidelines – Class A compost
Bulk Density (kg/m ³)	478	464	-
Total Nitrogen (%)	1.9	1.5	-
Total Phosphorus (%)	0.80	1.43	-
Total Potassium (%)	0.59	0.83	-
Calcium (%)	5.02	3.19	-

Magnesium (%)	1.41	0.81	-
Sodium (%)	0.36	0.24	-
Organic Matter (%)	68.64	71.08	More than 50 %
Moisture (%)	59.36	58.57	Less than 60 %
C: N Ratio	12:1	17:1	Less than 25
Total Organic Carbon (%)	38.13	39.49	More than 30 – 40 %
pH	7.26	8.04	6 - 8
Total Solids (%)	40.64	41.43	-

3.5.5 Analysis of maturity of compost products

Assessing the quality of compost requires careful consideration of its maturity, as the utilization of immature compost can negatively impact plant growth. The maturity of compost plays a crucial role in determining its quality and suitability for use. The CCME recommends employing the subsequent tests to determine the maturity of compost products:

- The C:N ratio of the final compost must be lower than 25.
- After the thermophilic phase concludes, it is necessary to allow compost to undergo a maturation period of a minimum of 21 days.

In the absence of any other means of assessing maturity, the compost should undergo a curing period of six months. During this time, the compost pile should maintain conditions that support aerobic biological activity. The curing stage commences once the process of pathogen reduction is finished, and the compost no longer undergoes reheating to thermophilic temperatures (CCME, 2005).

As shown in Table 3.3, the C:N ratio of the final product of alum sludge and ferric sludge compost products are 12:1 and 17:1, respectively. In addition, both compost products were maintained in aerobic conditions to mature for six weeks after finishing the compost period. Therefore, both compost products meet the criteria for category A compost CCME standards.

3.5.6 Analysis of foreign matter in final products

During the formulation of an industry-wide standard for compost quality, it is crucial to account for the presence of foreign matter in compost. As outlined in the CCME guidelines, mineral soils, sand, rocks, and wood are not classified as foreign matter. Both Category A and Category B compost must have minimal presence of foreign matter that could potentially cause inconvenience, harm, or injury to humans, plants, or animals during or after its intended use. Specifically, the compost should not contain any sharp foreign objects measuring more than 3 mm in any direction, nor any foreign matter larger than 25 mm in any dimension. The final products in this study were screened and they contained no foreign matter according to CCME guidelines.

3.5.7 Pathogenic organisms in compost products

Since pathogenic organisms can be found in the initial compost feedstock, the final compost product may potentially contain these pathogens, leading to potential health risks. In order to effectively minimize these health hazards, the guidelines recommend that the compost must adhere to the specified criteria as follows:

- When employing the in-vessel composting technique, it is necessary to sustain the compost at operational conditions of 55°C or higher for a duration of three days.
- When utilizing the windrow composting approach, the compost should reach a temperature of 55°C or higher for a minimum of 15 days throughout the composting period.
- By employing the aerated static pile composting technique, the compost will be kept under operational conditions of 55°C or higher for a period of three days.

Figure 3.1 indicates that the alum compost maintained the temperature of 55±3°C or higher for 15 days and ferric compost maintained the temperature of 55±3°C or higher for 16 days.

3.5.8 Other characteristics

When addressing safety and health concerns related to compost utilization, the guidelines consider three key categories of criteria: foreign matter, maturity, and pathogenic organisms. However, the compost product, being primarily an organic soil amendment, possesses additional characteristics that can be used to assess its agricultural value. Parameters such as organic matter, moisture content, and pH are often used for determining the quality of compost products.

The organic matter content in compost plays a vital role in determining its quality. According to CCME guidelines, compost categories A and B have minimum requirements of 50% and 30% organic matter, respectively. As shown in Table 3.3, the organic matter of alum and ferric composts were 68.64% and 71.08%, respectively. It can be concluded that the final compost products follow the requirements of category A of the CCME standards.

Compost categories A and B should not exceed a maximum allowable water content of 60% of the compost's wet mass, expressed as a percentage. Table 3.3 shows the moisture content of 59.36% and 58.57% for alum and ferric composts, respectively, indicating that both products meet the criteria for category A of CCME standards.

Compost serves as an organic soil conditioner and should be utilized with this purpose in mind. It is not recommended to use pure compost alone. Consequently, although pH analysis of compost offers valuable insights, it cannot be regarded as an absolute quality criterion when establishing a compost standard. The standardization committee deemed it irrelevant to include this criterion in the standard (CCME, 2005).

3.6 Conclusions

In this study, the feasibility of composting of chemically precipitated sludge derived from a phosphorous removal process was investigated. Two distinct types of sludge (alum-phosphate and ferric-phosphate) were well mixed with woodchips in a controlled laboratory condition, maintaining a woodchip to sludge ratio of 3:1. Key parameters such as temperature, moisture content, and pH were monitored throughout the composting process. The evolution of these parameters provided valuable insights into the progress of the composting process for both alum and ferric sludge.

Temperature profiles showed that both compost piles could maintain a temperature greater than 55°C for at least 15 days. Moisture content, a critical factor for effective composting, exhibited a steady reduction, aligning with the requirements for optimal decomposition. The pH levels remained within the favorable range for aerobic microbial activities, promoting efficient composting. The final compost products were subjected to a comprehensive analysis, including assessments of maturity, foreign matter, and the presence of pathogenic organisms. Both alum and ferric sludge composts met the criteria for category A compost as per CCME standards, showcasing their suitability for various applications.

Overall, this study demonstrates the efficacy of composting chemically precipitated sludge, offering a sustainable solution for the management of wastewater byproducts. The successful conversion of these sludges into nutrient-rich compost products underscores the potential for large-scale implementation, contributing to both environmental sustainability and resource recovery efforts.

4 CHAPTER 4 - Bio availability Study of phosphorus from Composted Chemical Sludge Using Switchgrass and Canola

4.1 Abstract

The study investigated the biomass yield, phosphorus uptake (PU), and Phosphorus Recovery Efficiency (PRE %) of canola and switchgrass grown in a soil with a low amount of available phosphorus amended with composted chemical sludge (alum-P compost and ferric-P compost) and a conventional fertilizer (monoammonium phosphate (MAP)), at rates of 0, 4.8, 9.7, 19.4, 29.1 and 38.8 mg P kg⁻¹ dry soil. The experiment involved planting pre-germinated canola and switchgrass seeds in units of potted soil, both amended and control, and harvesting them in three growth cycles at 50-day intervals. The total phosphorus of harvested biomass was measured by Inductively Coupled Plasma (ICP) method. The analysed data showed that, there was a statistically significant difference in phosphorus uptake, biomass yield, and PRE % among different Phosphorus sources. Ferric (Fe) compost emerged as the most effective phosphorus source, which resulted in both higher Biomass Yield and Phosphorus Uptake compared to Alum (Al) compost and MAP, for switchgrass. The choice of phosphorus source significantly affected P uptake and biomass yield in canola. While Fe Compost is the most effective for P uptake, Al Compost surprisingly leads to the highest biomass yield. MAP is the least effective source in terms of Canola in this study.

4.2 Introduction

Phosphorus (P) is a crucial element found in various agricultural fertilizers. It is a vital mineral naturally occurring in a wide range of foods and forms an integral part of the bones, teeth, DNA, and RNA in both humans and animals (Singh et al. 2022). Because P is a non-renewable resource, and industrial agriculture relies on P fertilizer to maintain its productivity, the reduced P fertilizer supply threatens the global agricultural industries (Dana Cordell, Drangert, and White 2009).

In recent years, rapid industrialization and population growth have intensified nutrient pollution (Ownby, Desrosiers, and Vaneeckhaute 2021). Human activities will always generate wastewater, but how it is managed will determine its environmental impact (Di Capua et al. 2022). Lake Winnipeg has been eutrophicated by excess P in Manitoba. As excess P escapes into rivers, lakes, and oceans, it causes eutrophication, toxic blue green algae, fish kills, and lowers water quality overall. Recycling phosphorus back into the supply stream is essential for ensuring a viable agriculture industry in the future (Ackerman and Cicek 2013).

Regulations for treated wastewater often specify the highest permissible level of phosphorus should be less than 1.0 mg/L or requires a removal rate of over 90% (D. Cordell et al. 2011). According to the Manitoba Water Quality Standards, Objectives, and Guidelines, as of January 1, 2016, all wastewater treatment facilities discharging greater than 820 kg TP per year (or communities with a population more than 2,000/equivalent due to industrial contributions) are required to meet 1 mg/L TP discharge limit if their effluents discharge to surface waters. This includes wastewater lagoons that are broadly used by numerous communities and municipalities across Manitoba. Most wastewater lagoons cannot naturally meet the provincial limits of 1 mg/L under cold climate conditions in Manitoba (Vahedi et al, 2022).

Most wastewater lagoons in Manitoba use a variation of chemical precipitation for phosphorous removal. Chemical precipitation is a process of binding soluble phosphate molecules with a positively charged metal (e.g., Al^{3+} , Fe^{3+} , Ca^{2+}) to form non-soluble precipitates that can be removed by sedimentation (Metcalf and Eddy, 2014). In municipal wastewater lagoons, the dosing of coagulants can be done in-situ by simply pouring the coagulating chemicals (typically Ferric Chloride (FeCl_3) or Alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$)) into the lagoon or ex-situ by dosing the wastewater in a separate plant and separating the formed sludge. A number of parameters including pH, metal salt dosage, dosage point, initial phosphate concentration, and wastewater retention time may affect phosphate precipitation efficiency using these metal salts (Szabó et al. 2008). As a result of this process, a large amount of chemical sludge is produced. Typically, chemical sludge is commonly disposed of in landfills due to the limited availability of viable reuse options. Landfilling is regarded as an emergency measure rather than a favorable choice, as it lacks benefits. As a part of its strategic plan, the City of Winnipeg is considering the application of sludge on land due to economic incentives and the advantageous utilization of nutrients (City of Winnipeg 2014). Phosphorus recovery from chemical sludge is of significant importance because of its positive environmental impact. The recovery of this scarce resource will aid to create a circular economy and lead to resource sustainability. It is a better way of sludge management.

Chemical sludge from lagoon plants has the potential to act as a valuable phosphorus source. Due to their nutrient content and as a means of recycling nature's gift, P recovery from sludge and sludge streams is considered essential regardless of the wastewater treatment method. P recovery assures sustainability, depreciating P rocks are mitigated, and renewable P resources are created.

On the other hand, the strong link that exists between P and the metals makes the recovery of P from the chemical sludge of Al or Fe difficult (Wilfert et al. 2020). However, consideration must be given to P recovery from sludge in order to ensure environmental sustainability and satisfy the expanding population's P needs (D. Cordell et al. 2011). In that contest, considerable progress has been made, particularly in the recovery of P from ferric phosphate sludge (Oleszkiewicz et al. 2015). Several industries can benefit from consideration and assessment of P recovery from chemical sludge (Wu and Williams 2013).

Chemical sludge has the potential to act as a valuable phosphorus source for high biomass crops, which can be utilized for biofuel production. The growth of the plant can be adversely impacted by the occurrence of Al toxicity, which can be influenced by the level of aluminum or ferric in the sludge and, in particular, the pH of the soil in which it is applied (Desmidt et al., 2015; Kluczka et al., 2017). Alum-P sludge serves as a productive source of accessible phosphorus for cultivating switchgrass in soils with high pH and low Olsen-P levels (Tolofari et al. 2021). Since P is thought to be potentially unavailable, recovery from aluminum and ferric P removal methods has been labelled as impractical. However, considerable progress has been made, particularly in the recovery of P from ferric phosphate sludge (Oleszkiewicz et al. 2015). Ferric salts are said to be economical and extremely effective at removing P from wastewater, but the precipitated ferric phosphate sludge needs to be disposed of correctly (Zhang et al. 2010). Several industries can benefit from consideration and assessment of P recovery from chemical sludge (Wu and Williams 2013). Although it has been stated that the availability of P in chemical sludge (alum and ferric phosphate) is limited and nearly impossible to recover due to the existing bond and the high cost of P recovery, chemical sludge still has availability of P (Oleszkiewicz et al. 2015).

The issue of sludge disposal has emerged as a pressing environmental problem in need of urgent resolution (Chen 2012). Municipal sludge normally has to be dewatered or treated before it can be reused or disposed of, in order to remove infectious organisms, viruses, and organic pollutants (Dong et al., 2014). A variety of technologies have therefore been developed, such as dewatering, anaerobic digestion, and aerobic composting (Dong et al., 2014). One of the most economical ways to manage and dispose of sludge is through composting and land application among these technologies (Wong et al. 2011).

In the study conducted in University of Manitoba, a class A compost has been produced using alum and ferric precipitate sludges in the Environmental Engineering laboratory in a controlled bench scale.

The main goal of this research was to assess the bioavailability of phosphorus (P) in composted alum-P and ferric-p sludge in comparison to commercial fertilizer (MAP) when utilizing switchgrass and canola. Switchgrass was selected for this study because of its ability to grow year after year, its capacity to thrive in less favorable areas, and its ability to produce a substantial amount of biomass (which can be readily used as a source for biofuels). Canola's efficient and rapid phosphorus uptake, and tolerance to seed-placed phosphorus fertilizer makes it a good choice for the experiment on phosphorus uptake in Manitoba.

4.3 Objectives

The objectives of this study are to investigate the bioavailability phosphorous in the final compost product by applying the matured compost products as a fertilizer, to the selected plants (switchgrass and canola), in controlled environments.

4.4 Methods and Material

4.4.1 Phosphorus sources

In the present investigation, three different phosphorus sources were applied to the experimental pots for the purpose of conducting assessments comparing parameters such as phosphorus uptake (PU), biomass yield (BY), and phosphorus recovery efficiency (PRE). These phosphorus sources used in this study are as follows:

Class A composted alum and ferric phosphate sludges were produced in the composting process to recover nutrients from chemically precipitated phosphate sludge. For the composting process, the dewatered alum and ferric precipitated sludges were thoroughly mixed with woodchips as a bulking agent in a controlled laboratory setting. The ratio of woodchips to sludge was 3:1. This process was carried out in two compost piles. The composting process involved monitoring several parameters, including moisture content, temperature, and pH of the compost mixtures. Both compost piles maintained a temperature of 55°C or higher for a minimum period of 15 days. The final compost products were analyzed for various parameters to assess their quality and suitability for different applications. These parameters included: maturity, foreign matter, pathogenic organisms, organic matter, moisture content, and pH. The findings indicated that both alum and ferric composts met the requirements for Category A compost according to CCME standards. (Table 4.1)

For the comparison, monoammonium phosphate (MAP, 11-52-0), which is a widely used commercial fertilizer in western Canada, was included in this study.

Parameter	Results		
	Alum Sludge Compost	Ferric Sludge Compost	CCME Guidelines – Class A compost
Bulk Density (kg/m ³)	478	464	-
Total Nitrogen (%)	1.90	1.50	-
Total Phosphorus (%)	0.80	1.43	-
Total Potassium (%)	0.59	0.83	-
Calcium (%)	5.02	3.19	-
Magnesium (%)	1.41	0.81	-
Sodium (%)	0.36	0.24	-
Organic Matter (%)	68.64	71.08	More than 50 %
Moisture (%)	59.36	58.57	Less than 60 %
C: N Ratio	12:1	17:1	Less than 25
Total Organic Carbon (%)	38.13	39.49	More than 30 – 40 %
pH	7.26	8.04	6 - 8
Total Solids (%)	40.64	41.43	-

Table 4-1 Composted Alum and Ferric sludge properties

4.4.2 Soil

The study was conducted using a composite soil mix developed by the plant science department, University of Manitoba, which was a mixture of 40% topsoil, 40% washed sand, and 20% peat moss. The soil was previously cropped to switchgrasses in 2021 and had a low available phosphate concentration of 3×10^{-3} gr/kg and a pH of 8.2 (Tolofari et al. 2021).

Prior to the start of planting, the soil was analyzed for different chemical properties. The analysis of the soil showed a low concentration of available phosphate (7.8×10^{-3} gr/kg), with a pH of 7.21, and electrical conductivity of 1.75 (mS/cm) (Table 4.2).

Table 4-2 chemical properties of the potting soil

Parameter	Results
pH	7.21
Conductivity (mS/cm)	1.75
Total Carbon (mg/kg)	60,000
Organic Matter (mg/kg)	85,200
Sulfur (mg/kg)	2320
Phosphate, available (as P) (mg/kg)	7.8
Nitrate (as N) (mg/kg)	236
Aluminum (mg/kg)	5800
Arsenic (mg/kg)	3.3
Boron (mg/kg)	7.8
Cadmium (mg/kg)	9.8×10^{-2}
Calcium (mg/kg)	29,200
Chromium (mg/kg)	10
Cobalt (mg/kg)	3.1
Copper (mg/kg)	8.5
Iron (mg/kg)	8370
Magnesium (mg/kg)	8480
Manganese (mg/kg)	150
Molybdenum (mg/kg)	0.18
Nickel (mg/kg)	8.9
Phosphorus (mg/kg)	349
Potassium (mg/kg)	1080

Sodium (mg/kg)	166
Zinc (mg/kg)	24

The soil was thoroughly blended and sieved through a 4-mm mesh to eliminate roots and stones. It was then left to dry naturally and stored until the beginning of the experiment. Around 1.5 kg of the dried soil was measured and placed into plastic pots with dimensions of 14.9 cm in diameter and 16.5 cm in height. To ensure that the soil is adequately hydrated, all pots were irrigated with reverse osmosis water. Subsequently, the pots were placed in a growth chamber for 24 hours before the planting process.

4.4.3 Experimental set up

The experiment took place in a growth room with a temperature cycle of 25°C during the day and 15°C at night. The relative humidity was set at 60%, and the corresponding photoperiod lasted for 16 hours. The experiment followed a completely randomized design, with a factorial treatment arrangement involving three sources of phosphorus (P) and five different application rates of P. Three replications were performed for all treatments, which included pots with control conditions. The P application rates on a dry weight basis were 0, 4.8, 9.7, 19.4, 29.1 and 38.8 mg P kg⁻¹ dry soil, which corresponded to 0, 26, 52, 103, 155, and 206 kg ha⁻¹ P. The pots were weighed and received daily watering to compensate for the moisture lost through evapotranspiration. Switchgrass and canola seeds were germinated in a potting mix for a duration of 4 and 2 weeks, respectively to ensure consistent growth (Figure 4.1)



Figure 4-1 Germinated Canola and Switchgrasses seeds

Following this, three evenly developed plants were transplanted into the prepared pots. This study included the examination of three crop growth cycles, each lasting for 50 days. The switchgrass and canola were harvested after 50 days of transplantation by cutting it 8 cm above the soil surface, ensuring that regrowth could occur easily. This process was consistently applied to all pots in a uniform manner. The harvested above-ground biomass was measured by weight, then placed inside paper bags and subjected to oven-drying at a temperature of 60°C for a duration of 72 hours. Oven-dried biomass samples were weighed for yield, chopped into bits and fine-ground in a mill grinder (<0.2 mm, Model 8000D Spex Sample Prep, Metuchen, NJ). Soil subsamples were collected at the end of the final growth cycle. The roots were rinsed using reverse osmosis water and subsequently dried in the open air.

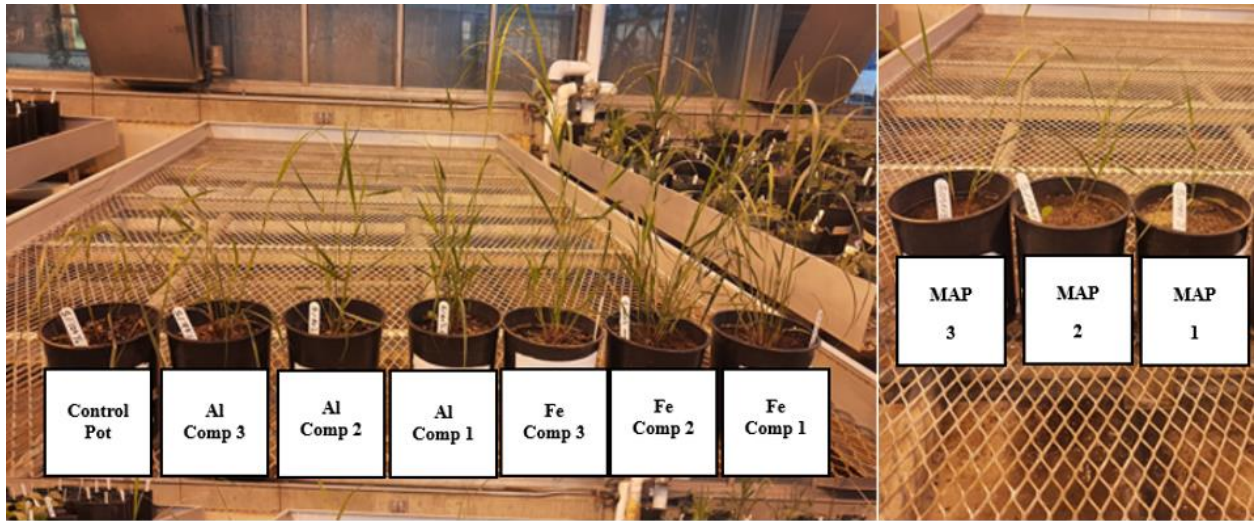


Figure 4-2 Switchgrass pots comparison

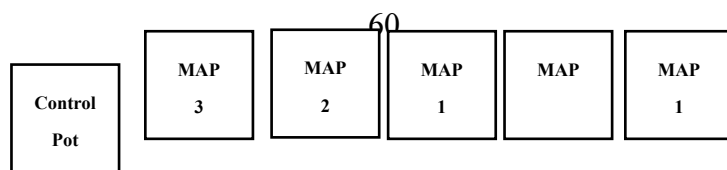




Figure 4-3 Canola pots comparison



Figure 4-4 Canola pots on day 40

4.4.4 Laboratory analysis

The total phosphorus (TP) concentrations in plant tissues were assessed using the wet oxidation method. In this process, samples of dried and chopped plant tissue were digested with a mixture of sulfuric acid (99.7%) and hydrogen peroxide (30%) in an acid block digester. (Parkinson and Allen, 1975). The concentrations of the element in the digested solution were subsequently analyzed using an inductively coupled plasma optical spectrophotometer (ICP-OES Thermo Electron ICAP 6300 Radial).

4.5 Statistical analysis

Analysis of variance was performed using the ANOVA. The influence of different phosphorus sources on the growth of switchgrass (*Panicum virgatum*) was examined. The study investigated

three critical response variables: Phosphorus Uptake, Biomass Yield, and Phosphorus Recovery Efficiency. The data was collected and analysed from the experiment based on the three distinct phosphorus sources: Al Compost, Fe Compost, and MAP (Monoammonium Phosphate). Following the ANOVA, a Tukey's Honestly Significant Difference (HSD) test was performed to determine which specific pairs of groups are significantly different from each other in terms of the variable in question.

The ANOVA table comprises three critical components: "Between (SSB)" examines the variation in P uptake, biomass yield, and PRE% attributed to differences between phosphorus sources. The "Within (SSW)" component signifies the variability within specific treatment groups, whereas the "Total (SST)" reflects the overall variability in P uptake, biomass yield, and PRE%.

4.6 Results and discussion

4.6.1 Phosphorus uptake

4.6.1.1 Switchgrass

The ANOVA table provides a comprehensive analysis of P uptake in switchgrass, with a specific focus on the influence of different phosphorus sources (Table 4.3). Notably, it yields a substantial F-statistic of 33.31 and an exceedingly low p-value of 0.0000, highlighting a statistically significant difference in P uptake among these phosphorus sources. This outcome underscores the profound impact of the choice of phosphorus source on P uptake in switchgrass. In summary, the ANOVA results indicate that the selection of phosphorus source plays a pivotal role in influencing P uptake in switchgrass. These findings hold great significance for enhancing P uptake and optimizing switchgrass cultivation practices, with direct implications for agricultural productivity.

Table 4-3 ANOVA table for comprehensive analysis of P uptake in switchgrass

P Uptake	Sum of Squares	Degrees of Freedom	Mean Squares	F-statistic	p-value
Between (SSB)	6952.31	2	3476.15	33.31	0.0000
Within (SSW)	16592.79	159	104.36		
Total (SST)	23545.10	161			

There was a statistically significant difference in phosphorus uptake among different Phosphorus sources ($p = 0.0000$) (Figure 4.1). The Phosphorus source with the greatest P uptake for switchgrass was Ferric Compost. This indicated that among the different Phosphorus sources tested, Fe Compost resulted in the highest uptake of phosphorus by switchgrass plants. During the first growth cycle of switchgrass, the amount of mean phosphorus uptake by switchgrass when using Fe Compost, was 21.93 mg/kg of soil. Al Compost followed closely with a mean uptake of 18.98 mg/kg of soil. MAP (Monoammonium Phosphate), on the other hand, had a significantly lower mean uptake of 6.80 mg/kg of soil.

Al Compost showed a P uptake that was approximately 13.43% lower than Fe Compost. This means that, on average, switchgrass plants using Al Compost as the phosphorus source absorb 13.43% less phosphorus than those using Fe Compost. MAP had a significantly lower P uptake, approximately 69.01% lower than Fe Compost. This suggested that MAP was less effective in terms of phosphorus uptake compared to Fe Compost, during the first growth cycle.

Among the three different phosphorus sources, Fe Compost appeared to be the most effective for promoting phosphorus uptake by switchgrass. This could be due to its composition, which provided a favorable environment for nutrient absorption. While Al Compost was effective, its mean phosphorus uptake was slightly lower than that of Fe Compost. MAP, a synthetic fertilizer, showed the lowest mean uptake among these three sources. This suggested that it might be less efficient in providing phosphorus to switchgrass plants in this context (Figure 4.1).

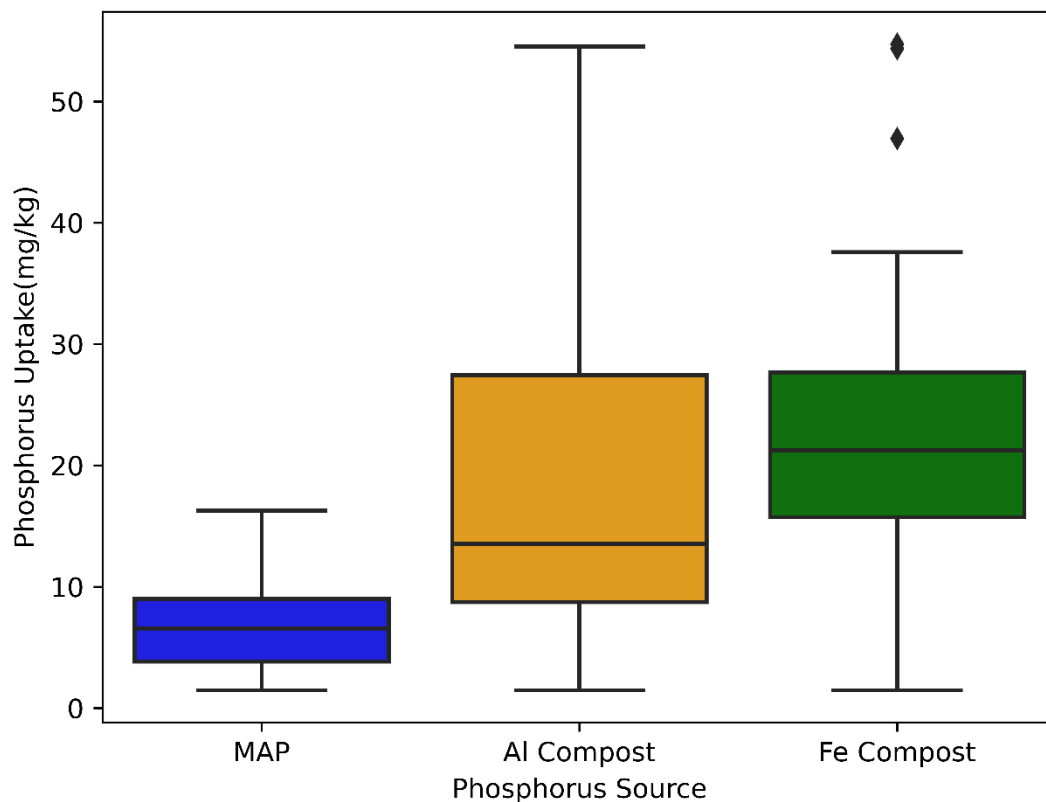


Figure 4-5 Switchgrass phosphorus uptake for different phosphorus sources

The analysis of P uptake across different growth cycles revealed notable variations (Figure 4.2). While using the MAP, in the first growth cycle, switchgrass plants displayed the lowest mean P uptake of 3.46 ± 1.70 mg/kg. The second growth cycle also showed an intermediate mean P uptake of 6.41 ± 1.87 mg/kg, which suggested an intermediate response to phosphorus levels. In contrast, during the third growth cycle, the mean P uptake significantly increased to 10.52 ± 2.74 mg/kg, which indicated a substantial phosphorus uptake.

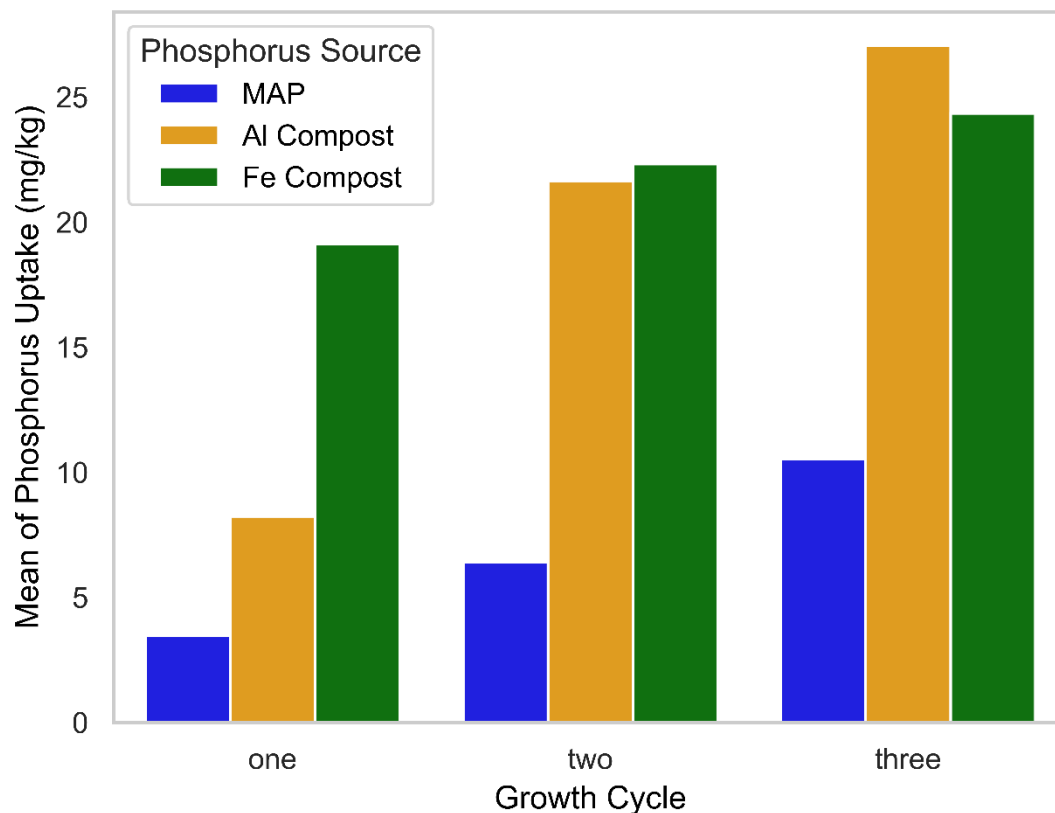


Figure 4-6 Switchgrass Phosphorus uptakes change over the growth cycles for different P sources

In the first growth cycle for Al compost application, the mean P uptake was 8.24 ± 3.47 mg/kg of soil. This indicated relatively low phosphorus uptake with a moderate level of variability within this cycle. In the second growth cycle, the mean P uptake was 21.65 ± 11.74 mg/kg of soil. This cycle showed an intermediate level of phosphorus uptake compared to the other two cycles, with a moderate level of variability. In the third growth cycle, we observed a substantially higher mean P uptake of 27.06 ± 13.10 mg/kg of soil. This suggested that the switchgrass plants had significantly increased their phosphorus uptake compared to the first cycle, which had a wider variation in uptake among the plants. The gradual rise in phosphorus uptake observed in relation

to the cycle indicated a gradual release of phosphorus from composted alum and ferric precipitated sludges (figure 4.2).

The analysis of P uptake across the three growth cycles, for Fe compost revealed that there were differences in P uptake levels. In growth cycle one, while using Fe compost, the mean P uptake was 19.12 ± 10.76 mg/kg of soil. In growth cycle three, the mean P uptake was higher at 24.35 ± 13.06 mg/kg of soil. Growth cycle two fell in-between, with a mean P uptake of 22.32 ± 10.69 mg/kg of soil. These results suggested that growth cycle three had the highest mean P uptake, while growth cycle one had the lowest mean P uptake. The differences in means and medians between the cycles indicated variations in P uptake levels during different growth stages. The increase in phosphorus uptake from composted chemical sludge indicated a gradual release of P from the organic source over time through the mineralization process (Lee, 2009). Missaoui et al., 2005, in their investigation of genetic variation and heritability of phosphorus uptake in Alamo switchgrass within a controlled environment, the researchers observed a rise in the concentration of phosphorus in the biomass. They hypothesized that this outcome could be attributed to the specific fertilizer employed in the study, namely soluble ammonium phosphate, and its elevated application rate (Missaoui et al., 2005).

4.6.1.2 Canola

The ANOVA table for P uptake in Canola offers a comprehensive analysis of the impact of different phosphorus sources on the uptake of phosphorus by Canola plants (Table 4.4). Notably, the "Between (SSB)" component shows a remarkably high F-statistic of 34.43 and an extremely low p-value of 0.0000, providing strong evidence for a statistically significant difference in P uptake among the various phosphorus sources. This suggests that the choice of phosphorus source has a substantial and influential effect on the uptake of phosphorus by Canola plants. The "Within

(SSW)" source of variation represents the variability within the treatment groups, although specific F-statistic and p-value values are not provided. Lastly, the "Total (SST)" accounts for the overall variability in P uptake. In conclusion, the results point to the critical role of selecting the appropriate phosphorus source in optimizing P uptake in Canola cultivation, with significant implications for agricultural practices and crop yield enhancement.

Table 4-4 ANOVA table for comprehensive analysis of P uptake in Canola

P Uptake	Sum of Squares	Degrees of Freedom	Mean Squares	F-statistic	p-value
Between (SSB)	24583.86	2	12291.93	34.43	0.0000
Within (SSW)	51406.56	144	356.99		
Total (SST)	75990.42	146			

During the first growth cycle, the rate of P uptake for Canola when using Fe Compost, Al compost and, MAP as the Phosphorus sources was approximately 47.18, 37.48 and, 15.91 mg/kg of soil, respectively. This suggested that during the first growth cycle, Canola plants using Fe Compost as the Phosphorus source tend to absorb the most phosphorus. The percentage difference compared to other sources provided a comparison of P uptake with Fe Compost as the reference. It indicated how much higher or lower the P uptake was for the other Phosphorus sources compared to Fe Compost. Al Compost had a P uptake that was approximately 20.56% lower than Fe Compost. MAP had a significantly lower P uptake, approximately 66.28% lower than Fe Compost. In summary, Fe Compost was the most effective Phosphorus source for Canola in terms of P uptake, with a rate of 47.18 mg/kg of soil during the first growth cycle ($p = 0.0000$) (Figure 4.3).

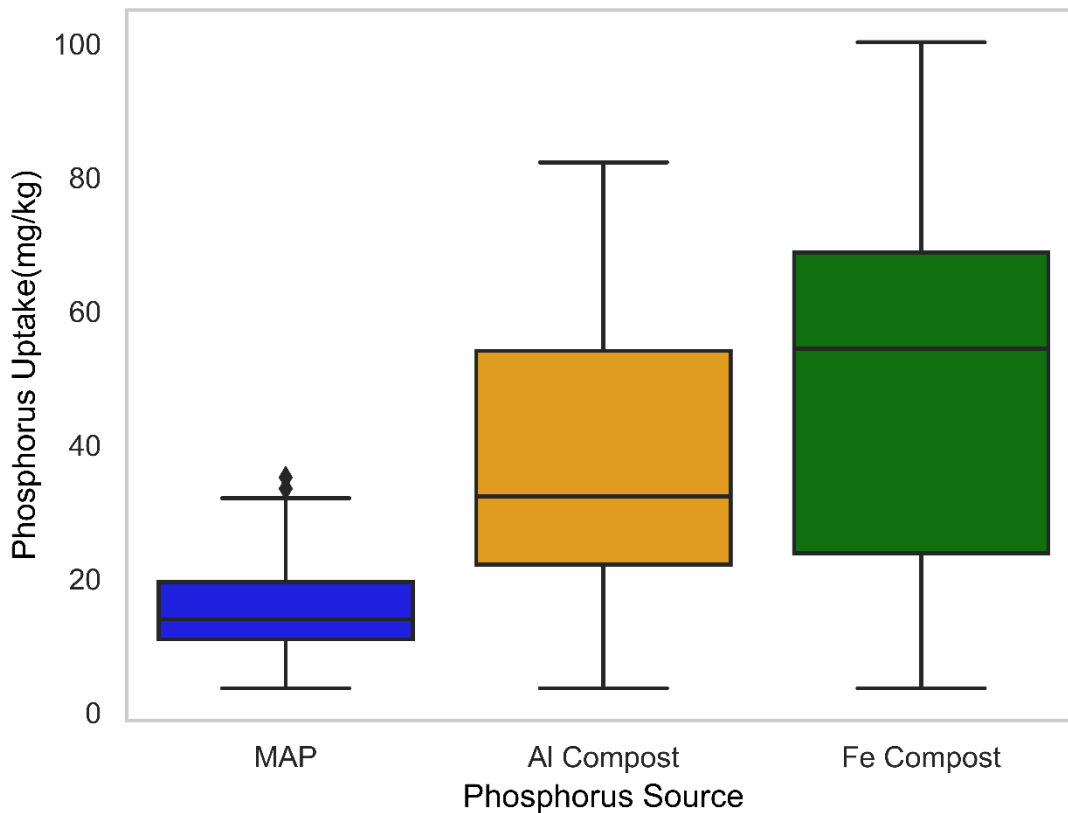


Figure 4-7 P uptake for Canola by different phosphorus source

In terms of using MAP for different growth cycles of canola, the mean P uptake values varied, with growth cycle three having the highest mean P uptake of 20.36 ± 9.13 mg/kg of soil. This was followed by growth cycle two, which had a mean phosphorus uptake of 14.31 ± 2.87 mg/kg of soil. Growth cycle one had the lowest mean P uptake of 13.05 ± 8.47 mg/kg of soil. The standard deviations indicated the degree of variability in P uptake within each cycle (Figure 4.4).

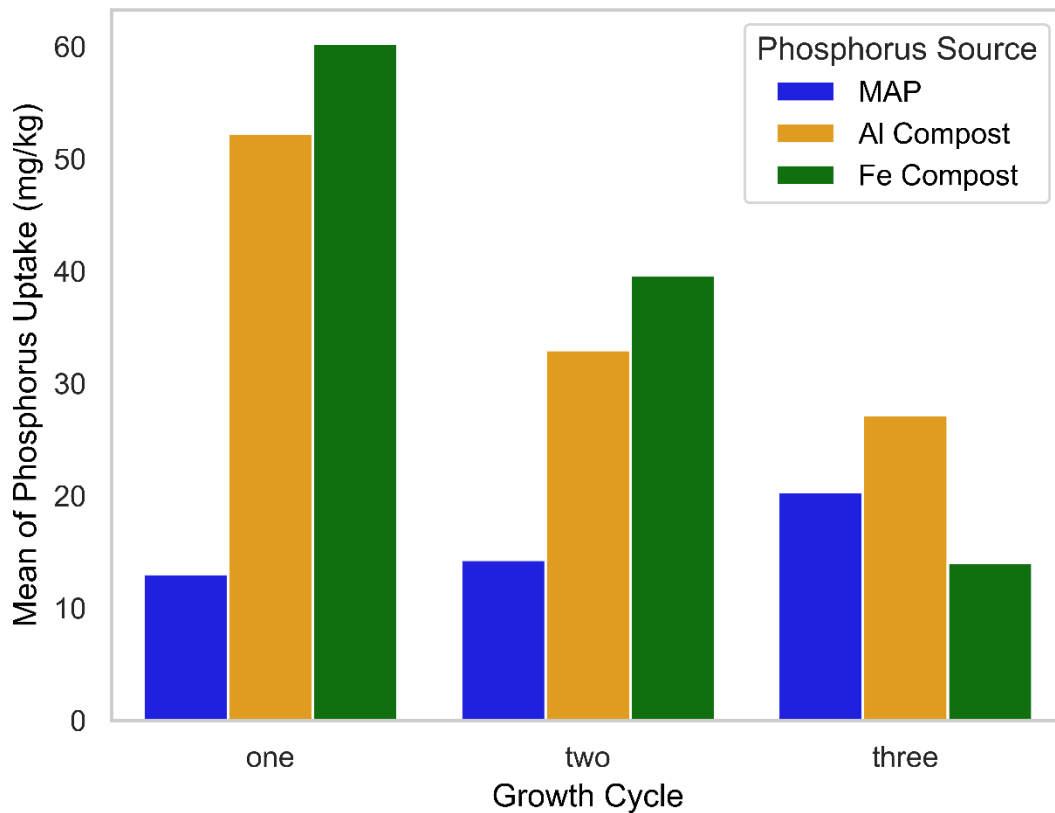


Figure 4-8 Canola Phosphorus uptakes change over the growth cycles for different P sources

In terms of using Al compost for the first growth cycle, the mean P uptake was relatively high at 52.27 ± 22.65 mg/kg. While in growth cycle three, P uptake was lower with a mean of 27.19 ± 9.78 mg/kg. Growth cycle two fell in-between with a mean of 32.98 ± 16.98 mg/kg (Figure 4.4).

In the analysis of using Fe compost to determine P uptake for different growth cycles, growth cycle one exhibited the highest mean P uptake of 60.25 ± 27.41 mg/kg while growth cycle three has the lowest mean P uptake 14.04 ± 6.19 mg/kg. Growth cycle two fell in-between with a mean P uptake of 39.63 ± 19.36 mg/kg. This suggested significant variation in P uptake across three growth cycles.

4.6.2 Biomass yield

4.6.2.1 Switchgrass

The ANOVA table presents an analysis of Biomass yield, with a particular focus on the impact of different phosphorus sources within the context of switchgrass (Table 4.5). Notably, it yields a substantial F-statistic of 57.03 and a significant p-value of 0.0000, underlining a statistically significant difference in Biomass yield across these phosphorus sources within the switchgrass variable. In summary, the ANOVA result underscores the profound impact of different phosphorus sources on Biomass yield within the switchgrass context, thus emphasizing the critical role of switchgrass conditions in influencing the desired outcome. These findings have significant implications for the management and cultivation practices related to switchgrass.

Table 4-5 ANOVA table for comprehensive analysis of Biomass yield in switchgrass

Biomass yield	Sum of Squares	Degrees of Freedom	Mean Squares	F-statistic	p-value
Between (SSB)	298.31	2	149.16	57.03	0.0000
Within (SSW)	415.87	159	2.62		
Total (SST)	714.18	161			

Analysis of variance for biomass yield of switchgrass showed a statistically significant difference among phosphorus sources ($p = 0.0000$) (Figure 4.5). In the first growth cycle, the mean biomass yield varied significantly based on the phosphorus source used. Fe Compost resulted in the highest mean biomass yield at 5.31 ± 2.31 g/kg of soil. Al Compost followed with a mean yield of 3.26 ± 1.47 g/kg of soil. MAP had the lowest mean yield at 2.02 ± 0.61 g/kg of soil. The standard deviation for biomass yield indicated the variability within each group.

Fe Compost not only led to high phosphorus uptake but also resulted in the highest biomass yield. This made it a promising choice for maximizing switchgrass growth and potential bioenergy

production. While Al Compost was effective, its mean biomass yield was lower than that of Fe Compost. MAP appeared to be the least effective phosphorus source in terms of promoting biomass yield.

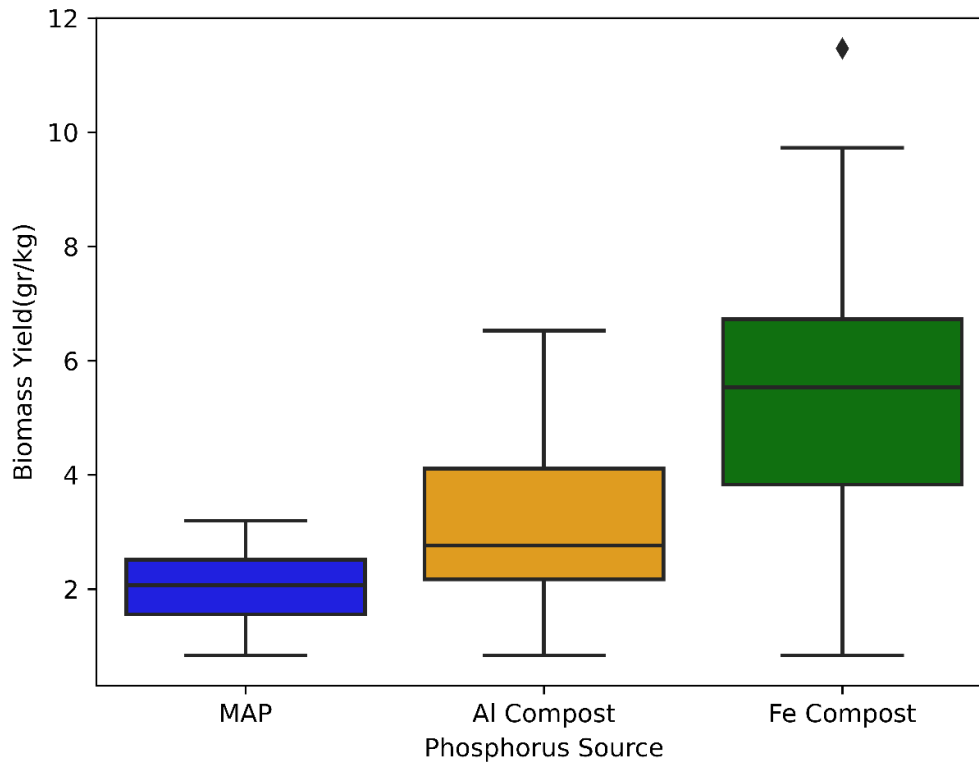


Figure 4-9 Switchgrass biomass yields for different phosphorus sources

In the context of biomass yield in different growth cycles, these results illustrated variations in plant biomass production (Figure 4.6). In terms of MAP application for growth Cycle one, the mean Biomass yield was 1.47 ± 0.45 g/kg of soil. This variation suggested a relatively consistent biomass production. Conversely, in growth cycle three, there was an increase in mean (2.32 ± 0.49 g/kg of soil) biomass yield, which indicated slightly more variability in biomass. Growth cycle

two closely resembled cycle three in terms of mean biomass yield (2.28 ± 0.47 g/kg of soil). This suggested similar biomass production trends between these two cycles.

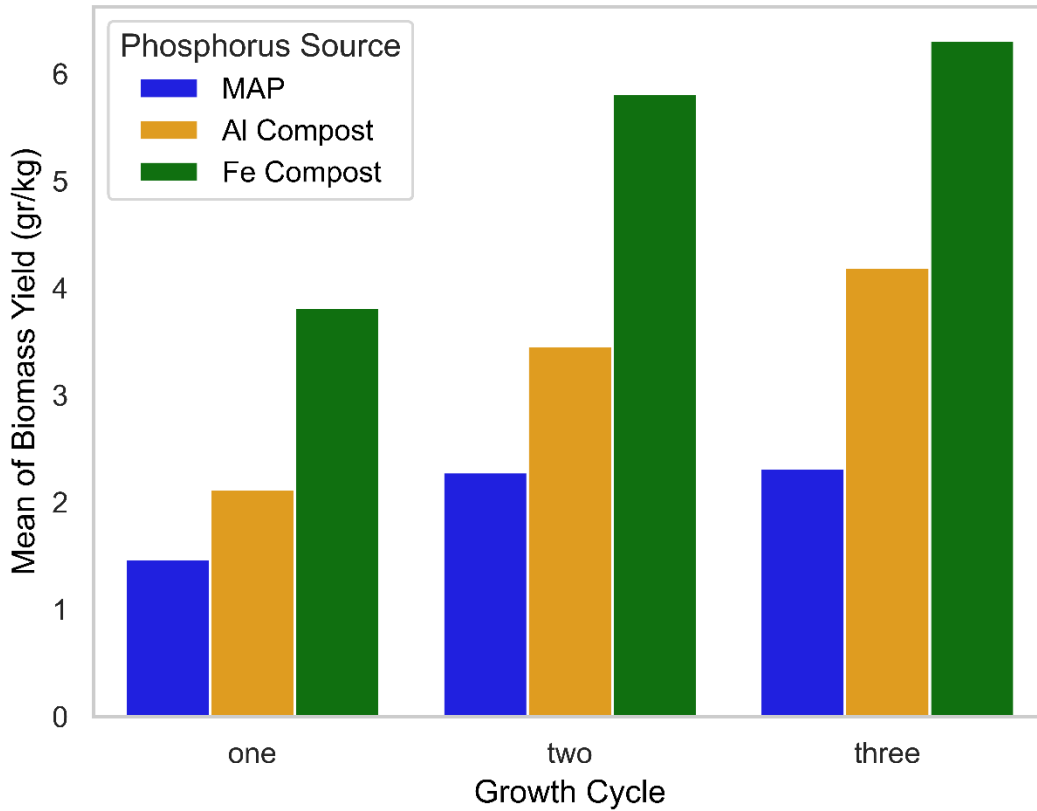


Figure 4-10 Switchgrass biomass yields change over the growth cycles for different P sources

Following the ANOVA, a Tukey's Honestly Significant Difference (HSD) test was performed to determine which specific pairs of groups were significantly different from each other in terms of the variable in biomass yield. The results of this post-hoc test showed that growth cycles one and two, as well as one and three, had significantly different means in the variable. However, there is no significant difference between growth cycles two and three. The improvement in biomass yield during cycles 2 and 3 compared to cycle 1 may be attributed to enhanced growth and development

of switchgrass roots, leading to an increased capacity for phosphorus scavenging (Tolofari et al. 2021).

In terms of Al compost application, in the context of three growth cycles, it was observed that there were distinct patterns in biomass yield. In the first growth cycle, the mean biomass yield was 2.12 ± 0.65 g/kg of soil, which indicated a relatively narrow distribution of biomass values. In contrast, the third growth cycle displayed notably higher biomass yield, with a mean of 4.19 g/kg of soil. Although, it also exhibited a wider spread as indicated by the higher standard deviation of 1.64 g/kg. This suggested that while the overall biomass was higher in the third cycle, there was greater variability in the measurements. The second growth cycle fell between the other two in terms of mean biomass yield (3.46 ± 1.14 g/kg of soil). This suggested that the second growth cycle represented a middle ground in terms of biomass production compared to the first and third cycles (Figure 4.6).

The analysis of biomass yield across the three growth cycles for Fe compost indicated significant differences. In growth cycle one, the mean biomass yield was 3.81 ± 1.65 g/kg of soil. Growth cycle three showed the highest mean biomass yield at 6.31 ± 2.51 g/kg of soil. Meanwhile, Growth cycle two fell in-between, with a mean biomass yield of 5.81 ± 1.96 g/kg of soil. These results suggested that growth cycle three had the highest mean biomass yield, while growth cycle one had the lowest mean biomass yield, and growth cycle two was in the middle (Figure 4.6).

4.6.2.2 Control and Test

In the control group for P uptake, the mean value was around 5.03 ± 2.99 mg/kg of soil. Values ranged from 1.48 to 9.28 mg/kg. In the test group for P uptake, the mean value was significantly higher at approximately 18.08 mg/kg, with a larger spread (standard deviation around 12.06 mg/kg) and a wider range from 1.86 to 54.73 mg/kg. For biomass yield, the control group had a

mean value of 1.76 ± 0.70 g/kg. The values ranged from 0.84 g/kg to 2.73 g/kg. In the test group for biomass yield, the mean value was notably higher at 3.89 ± 2.12 g/kg. The values ranged from 1.06 to 11.47 g/kg.

There was a statistically significant difference in the mean biomass yield between the control group and the test group. In other words, the data provided strong evidence to conclude that the two groups had different average biomass yields and the difference was not likely due to random chance. There was a statistically significant difference in the mean P uptake between the control group and the test group. In this case, the data also provided strong support for the idea that the two groups had different average P uptake values. The observed differences in P uptake were not likely due to random variation in the data. Significant differences in both biomass yield and P uptake between the two groups were observed.

4.6.2.3 Canola

The ANOVA table presents an analysis of Biomass yield in Canola, specifically examining the impact of different phosphorus sources (Table 4.6). Between (SSB), which assesses the variability between Phosphorus sources, reveals a high F-statistic of 6.91 and a low p-value of 0.0013. This suggests that there is a statistically significant difference in Biomass yield among the various phosphorus sources. Within (SSW) reflects the variability within groups or treatment levels, although the exact F-statistic and p-value are not provided. In conclusion, the ANOVA result indicates that the choice of phosphorus source significantly influences Biomass yield in Canola, as evidenced by the statistically significant differences found among the Phosphorus sources, making it a crucial factor to consider in Canola cultivation practices.

Table 4-6 ANOVA table for comprehensive analysis of Biomass yield in Canola

Biomass yield	Sum of Squares	Degrees of Freedom	Mean Squares	F-statistic	p-value
Between (SSB)	364.92	2	182.46	6.91	0.0013
Within (SSW)	4198.34	159	26.40		
Total (SST)	4563.26	161			

Among the three phosphorus sources (Al Compost, Fe Compost, and MAP), Al Compost resulted in the highest biomass yield for Canola. The highest biomass yield of 9.32 g/kg of soil was observed during the first growth cycle. This value (9.32 g/kg of soil) represented the amount of biomass (plant material) produced by the Canola plants per unit of soil under the influence of Al Compost. Fe Compost had a lower biomass yield (7.08 g/kg) compared to Al Compost. MAP had the lowest biomass yield at 5.68 g/kg.

Fe Compost had a biomass yield that was 24.03% lower than Al Compost, while MAP had a biomass yield that was 39.09% lower than Al Compost. In summary, the analysis suggested that among the three phosphorus sources, Al Compost resulted in the highest biomass yield for Canola during the first growth cycle. These results provided valuable insights into which phosphorus source was most effective in promoting biomass yield in Canola ($p = 0.0013$) (Figure 4.7).

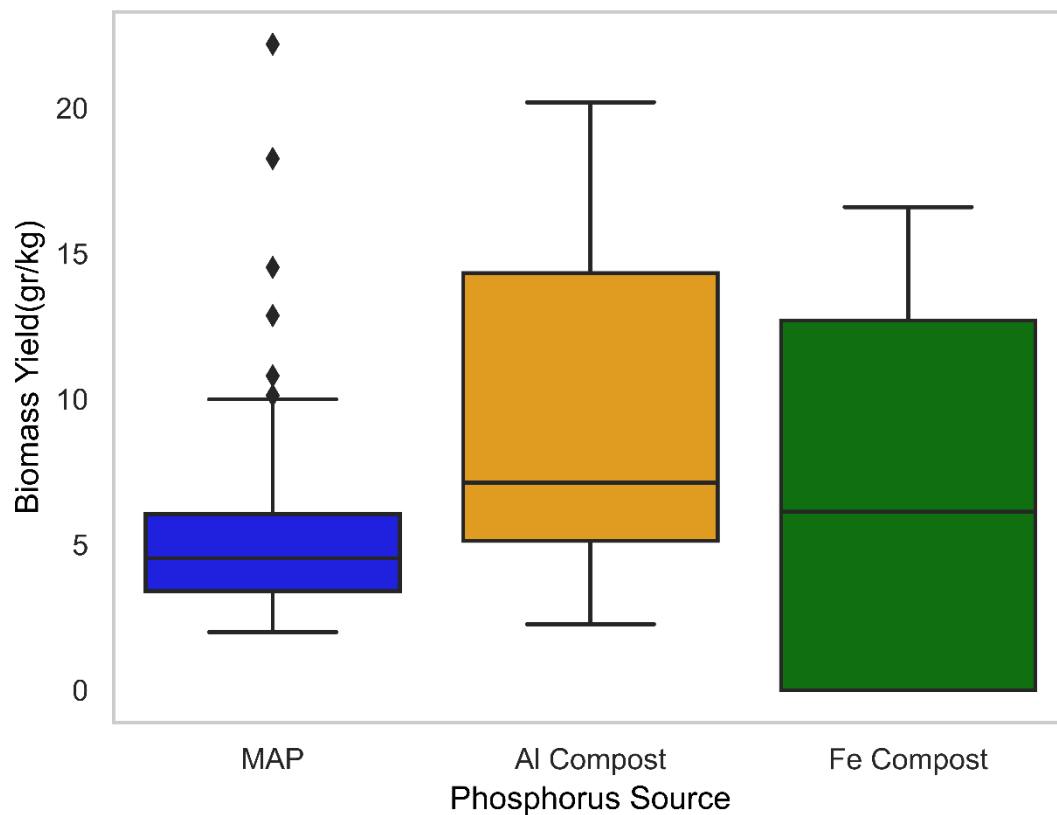


Figure 4-11 Biomass yield for Canola by different phosphorus source

In terms of MAP, growth cycle one had the highest mean biomass yield at 9.01 ± 5.2 g/kg. This was followed by growth cycle three at 4.25 ± 1.49 g/kg. While growth cycle two had the lowest mean biomass yield at 3.78 ± 0.65 g/kg (Figure 4.8).

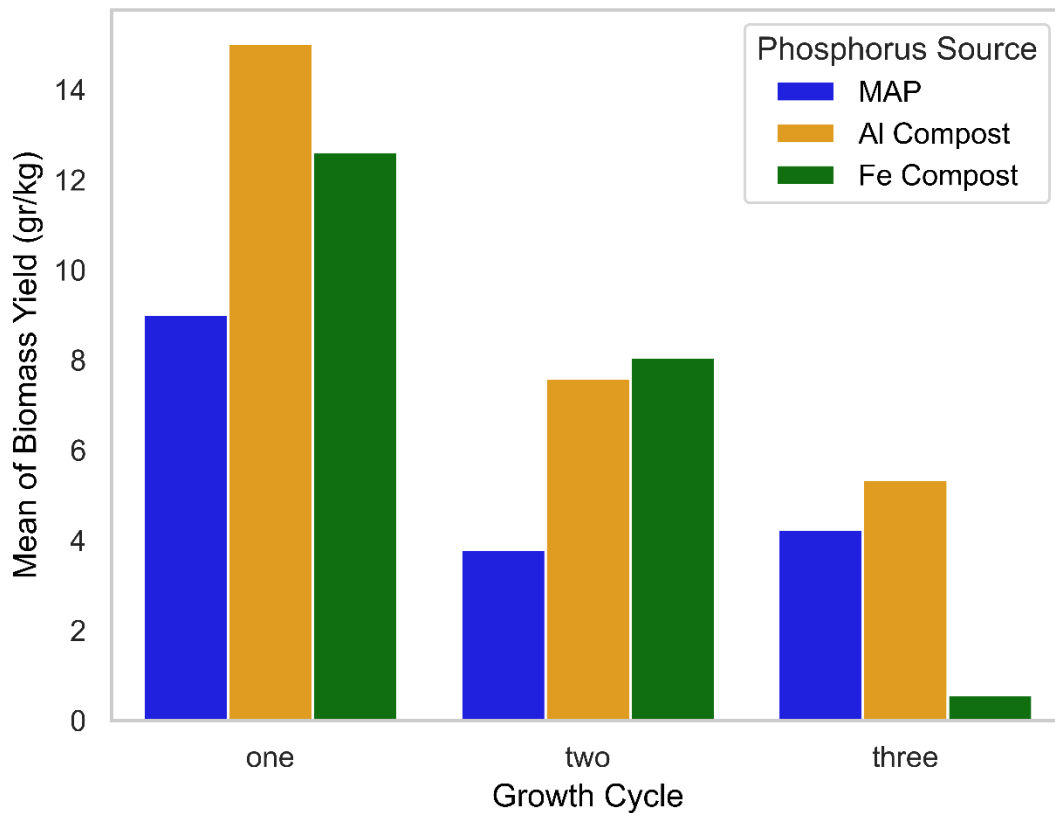


Figure 4-12 Canola Biomass Yield changes over the growth cycles for different P sources

In the first growth cycle, while using Al compost, the mean biomass yield was relatively high at 15.03 ± 4.90 g/kg. The third growth cycle observed a significant decrease to a value of 5.35 ± 1.75 . The second growth cycle fell in-between at 7.60 ± 3.41 g/kg. This reflected variations in biomass production across these cycles (Figure 4.8).

In this analysis of biomass yield, while using Fe compost across different growth cycles, growth cycle one stood out with the highest mean biomass yield (12.63 ± 3.68 g/kg). In contrast, growth cycle three displayed a significantly lower mean biomass yield (0.56 ± 1.39 g/kg). Growth cycle two fell in-between these extremes with a mean biomass yield of 8.06 ± 3.54 g/kg.

4.6.2.4 Control and Test

In the control group for both P uptake and biomass yield, the data appeared to have moderate variability, with means around 11.20 mg/kg and 4.06 g/kg, respectively. In the test group for P uptake, there was a wider range of values with a higher mean of approximately 36.84 mg/kg and significant variability. In terms of biomass yield, there was higher variability with a mean of approximately 8.02 g/kg. There was a statistically significant difference in the mean biomass yield between the control group and the test group, but no significant difference in P uptake was indicated.

4.6.3 Phosphorus recovery efficiency (PRE %)

4.6.3.1 Switchgrass

The ANOVA table provides a comprehensive analysis of PRE % within the switchgrass context, with a specific emphasis on the influence of different Phosphorus sources (Table 4.7). The table reveals a compelling and statistically significant difference in PRE % among these various phosphorus sources, supported by the remarkably low p-value of 0.0000 and the substantial F-statistic of 31.77. These findings offer invaluable insights for optimizing PRE % within the switchgrass context, providing crucial guidance for enhancing agricultural practices and crop management in this specific scenario.

Table 4-7 ANOVA table for comprehensive analysis of PRE % in Switchgrass

PRE %	Sum of Squares	Degrees of Freedom	Mean Squares	F-statistic	p-value
Between (SSB)	487190.95	2	243595.48	31.77	0.0000
Within (SSW)	1012099.84	132	7667.42		
Total (SST)	1499290.79	134			

The descriptive statistics for PRE % in switchgrass, categorized by Phosphorus sources (Al Compost, Fe Compost, and MAP), reveal distinct patterns. Switchgrass grown with Fe Compost exhibited the highest mean PRE at approximately 153.25%, which indicated efficient Phosphorus uptake. In contrast, plants utilizing MAP as a source had the lowest mean PRE, around 12.27%. This suggested less effective Phosphorus uptake. Al Compost fell between these extremes, with a mean PRE of roughly 119.27 % ($p = 0.0000$) (Figure 4.9).

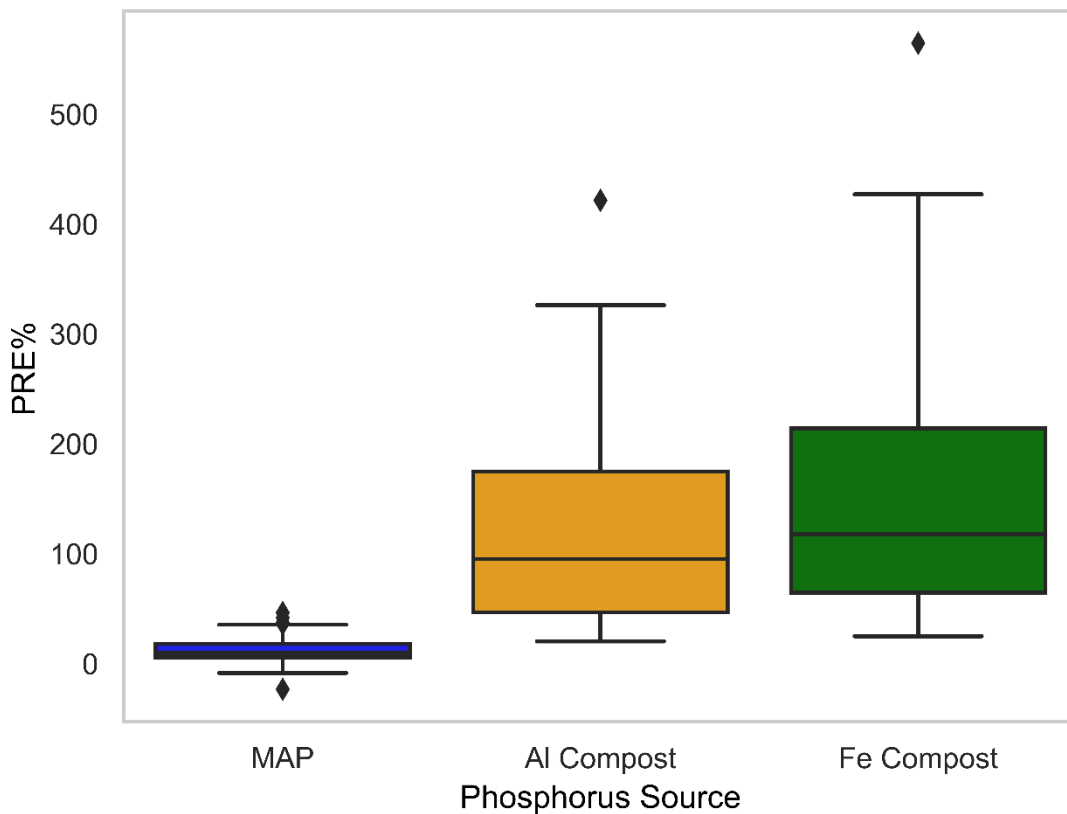


Figure 4-13 PRE % of switchgrasses for different phosphorus sources

The analysis of PRE % in switchgrass, considering different Phosphorus Sources and Growth Cycles, revealed interesting insights. Among the sources, Al Compost exhibited a significant

increase in PRE % from the first cycle (58.36 %) to the second (164.50 %) and third (134.97 %) cycles, with notable variability. In contrast, Fe Compost started relatively high (154.36 15 %) in the first cycle but experienced a decrease in the third cycle (140.36 %) with substantial variability throughout. MAP, on the other hand, maintained lower PRE % values across all cycles, with higher variability observed in the third cycle (13.93 %). These findings provided valuable information for optimizing phosphorus source selection and understanding how PRE % changes over different growth cycles in switchgrass (Figure 4.10).

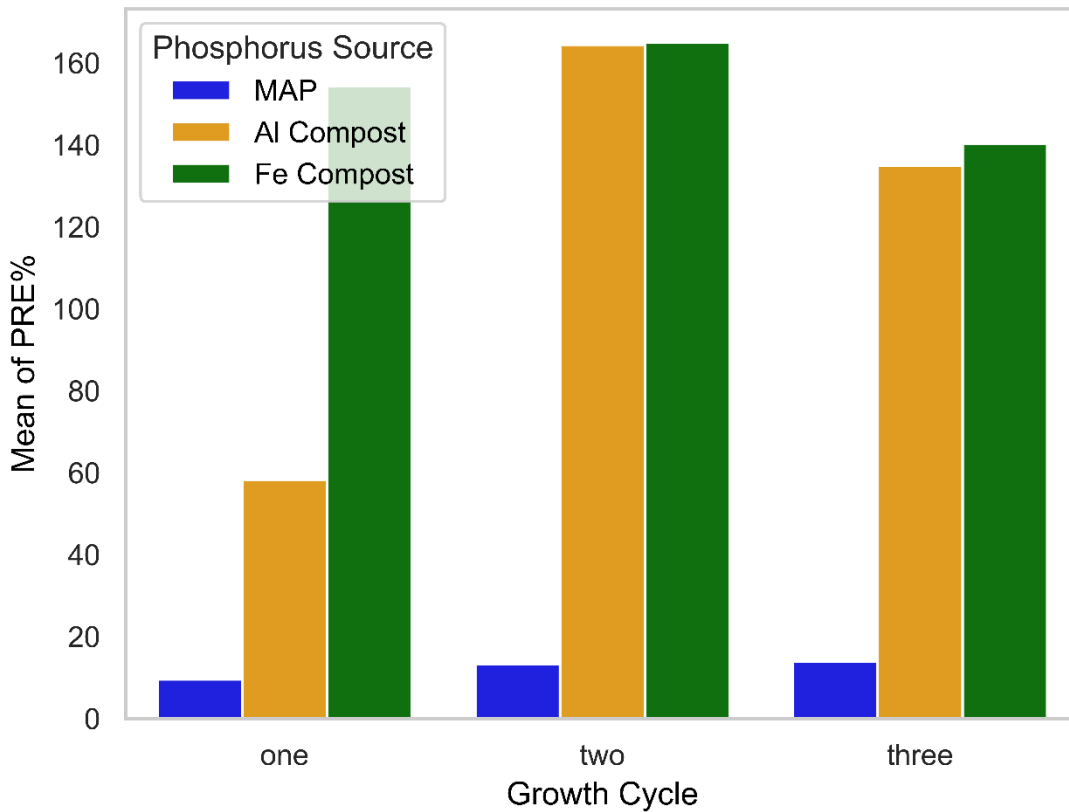


Figure 4-14 PRE % of Switchgrass by different phosphorus sources and growth cycles

4.6.3.2 Canola

The ANOVA table for PRE % in Canola provides crucial insights into the impact of different phosphorus sources on the content of PRE % in Canola plants (Table 4.8). Notably, the "Between (SSB)" component demonstrates a substantial F-statistic of 17.90 and an exceedingly low p-value of 0.0000, indicating a highly statistically significant difference in PRE % among the various Phosphorus sources. This suggests that the choice of phosphorus source has a profound influence on the PRE % in Canola plants. The "Within (SSW)" component accounts for variability within treatment groups, although specific F-statistic and p-value values are not provided. In conclusion, these results underscore the critical importance of selecting the appropriate phosphorus source when aiming to optimize PRE % in Canola cultivation. This information is invaluable for agricultural practices and achieving specific targets for Canola crop attributes.

Table 4-8 ANOVA table for comprehensive analysis of PRE % in Canola

PRE %	Sum of Squares	Degrees of Freedom	Mean Squares	F-statistic	p-value
Between (SSB)	2548471.22	2	1274235.61	17.90	0.0000
Within (SSW)	8330174.14	117	71198.07		
Total (SST)	10878645.36	119			

For Al Compost, the data exhibited a relatively high mean PRE value of 238.94%, which signified a moderate average phosphorus retention efficiency ($p = 0.0000$). However, substantial variability was observed and indicated by the high standard deviation of 279.99%. Fe Compost demonstrated a notably higher mean of 392.28%. This implied that more effective phosphorus retention than Al Compost, yet with a similarly widespread in values. Conversely, MAP presented the lowest mean at 25.39%, which indicated lower phosphorus retention due to a relatively lower standard deviation of 81.63% compared to the compost sources (Figure 4.11). The analysis provided valuable insights

into the influence of phosphorus sources on PRE % in Canola plants. Fe Compost resulted in the highest mean PRE %, which suggested that it was an effective source of Phosphorus. Al Compost and MAP had lower mean PRE % compared to Fe Compost.

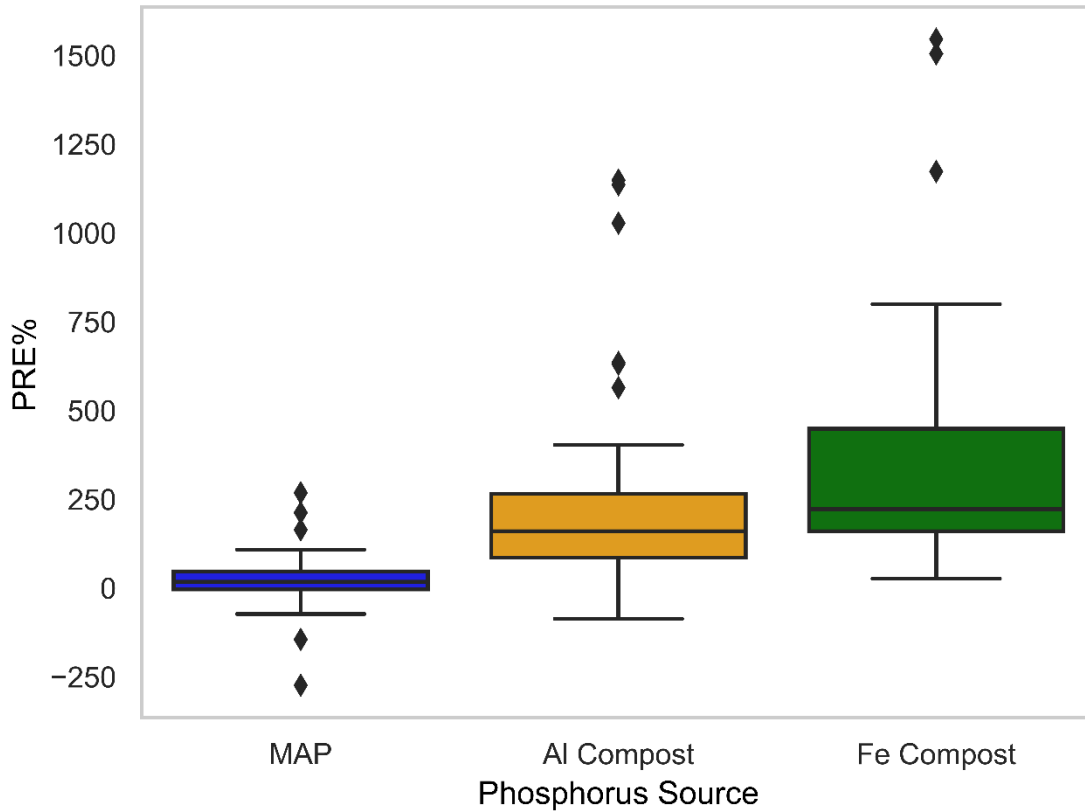


Figure 4-15 PRE % of Canola for different phosphorus sources

For Al Compost, during growth cycle one, there was a substantial mean PRE of 457.88%. In contrast, during growth cycle three, the mean PRE % dropped significantly to 91.47 %. Growth cycle two exhibited an intermediate mean PRE of 167.48%. A similar trend was observed for Fe Compost, with notably high PRE % levels during growth cycle one (566.30) compared to growth cycle two (218.26). On the other hand, MAP showed relatively lower PRE % levels across all

cycles, with growth cycle one having the highest mean (59.92). These findings underscore the dynamic nature of PRE % influenced by both phosphorus source and growth cycle (Figure 4.12).

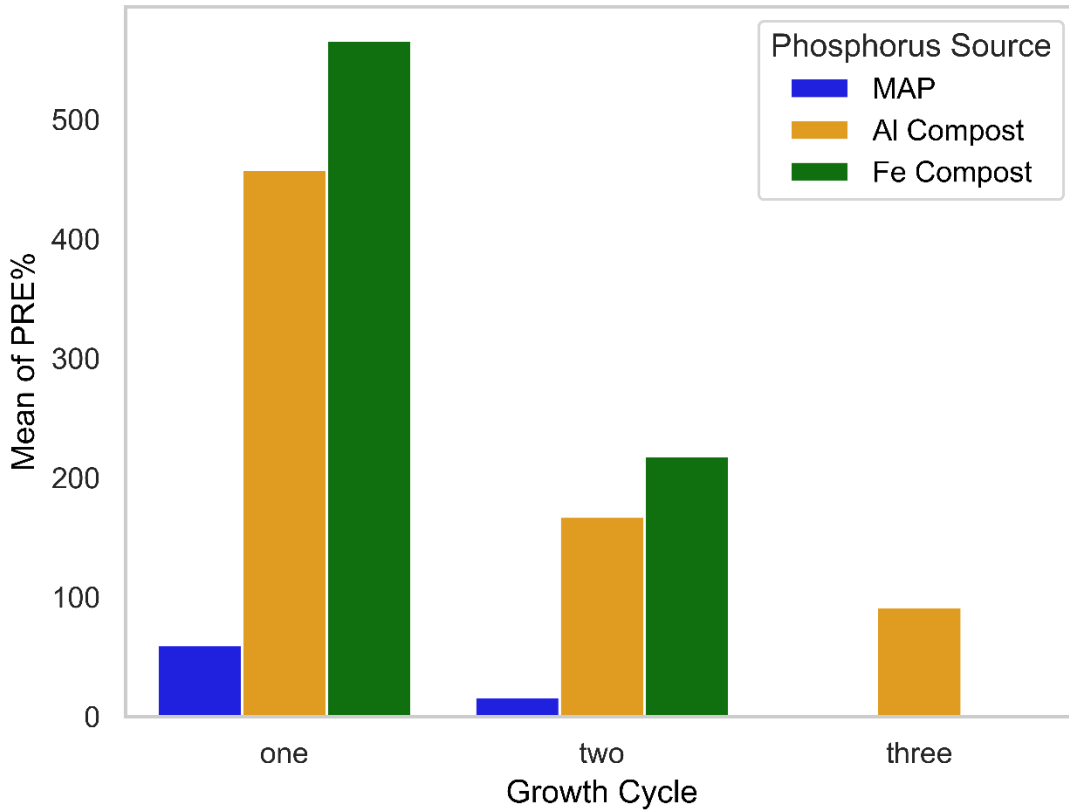


Figure 4-16 PRE % of Canola by different phosphorus sources and growth cycles

4.7 Conclusion

In conclusion, the research findings demonstrate the potential of Fe Compost as a superior phosphorus source for promoting the growth of switchgrass, contributing to more sustainable and efficient agricultural practices. The analysis of phosphorus uptake in switchgrass and canola revealed distinct patterns for different treatments, emphasizing the importance of considering the source and timing of phosphorus application for optimizing P uptake in both crops. The study also

highlighted the dynamic nature of phosphorus uptake in canola and switchgrass cultivation, influenced by both the growth stage and the source of phosphorus application. Furthermore, the examination of biomass yield across various growth cycles underscored the importance of considering both the growth stage and the type of amendment applied when aiming to optimize biomass production in switchgrass and canola cultivation. The research identified Al compost as a standout for promoting the highest biomass yield in canola during the first growth cycle, while Fe Compost demonstrated significant differences in biomass yield across cycles in switchgrass cultivation. Moreover, the analysis of phosphorus recovery efficiency (PRE %) revealed intriguing trends, with Al compost showing a potential cumulative effect over time in switchgrass cultivation, while Fe compost exhibited fluctuating efficiency. Monoammonium phosphate (MAP) consistently maintained lower PRE % values across all cycles. In canola cultivation, dynamic trends were observed for Al compost, Fe compost, and MAP, emphasizing the varying efficiency of different phosphorus sources across different growth cycles.

5 CHAPTER 5 - General Conclusions and Recommendations

The investigation into the feasibility of composting chemically precipitated phosphate sludge, specifically alum and ferric sludges, has provided valuable insights into a sustainable approach for managing wastewater byproducts. The controlled laboratory-scale composting process, with a woodchip to sludge ratio of 3:1, demonstrated successful phosphorus recovery from the sludge while meeting the criteria for Category A compost as per CCME standards.

The investigation into different phosphorus sources and their impact on the growth of switchgrass and canola has yielded valuable insights for agricultural practices. The findings emphasize the significance of selecting an appropriate phosphorus source to enhance plant growth and productivity.

The key findings and conclusions derived from the study are as follows:

- **Effective Temperature Maintenance:** Both compost piles, containing alum and ferric sludges, maintained temperatures exceeding $55\pm 3^{\circ}\text{C}$ for a minimum of 15 days during the composting process. This thermophilic phase is crucial for pathogen elimination and successful composting.
- **Moisture Content Reduction:** The composting process effectively reduced the high moisture content of the sludge, enhancing the efficiency of decomposition. Moisture content steadily decreased throughout the composting period, aligning with optimal decomposition requirements.
- **pH Regulation:** The pH levels of both alum and ferric compost piles remained within the favorable range of 7-8 throughout the composting period. This pH regulation supports aerobic microbial activities, ensuring efficient composting.

- **Quality Assessment of Final Compost Products:** The final compost products were subjected to a comprehensive analysis, including assessments of maturity, foreign matter, and the presence of pathogenic organisms. Both alum and ferric sludge composts met the criteria for Category A compost, indicating their suitability for various applications.
- **Nutrient-Rich Compost Products:** The compost products exhibited desirable characteristics, including organic matter content, moisture content, and pH, meeting the standards set by CCME. The nutrient-rich nature of these composts positions them as valuable organic soil conditioners.
- **Fe Compost emerged as a standout phosphorus source,** demonstrating superior performance in terms of phosphorus uptake and biomass yield for switchgrasses. The results suggest that Fe Compost could be a preferred choice for promoting the growth of this crop, potentially contributing to more sustainable and efficient agricultural practices.
- **In term of switchgrass, the analysis of P uptake across various growth cycles revealed distinct patterns for different treatments.** When using MAP, switchgrass plants exhibited varying levels of P uptake over three growth cycles, with a significant increase observed in the third cycle, indicating a substantial response to phosphorus levels. Conversely, the application of Al compost resulted in relatively low P uptake during the first cycle, followed by an intermediate increase in the subsequent cycles, suggesting a gradual release of phosphorus from the composted material. Similarly, the use of Fe compost showed differences in P uptake levels across the three cycles, with the highest uptake observed in the third cycle, indicating a progressive release of phosphorus over time. These findings underscore the importance of considering the source and timing of phosphorus application for optimizing P uptake in switchgrass cultivation.

- When utilizing MAP, canola plants exhibited varying levels of P uptake across the three growth cycles, with the highest uptake observed in the third cycle, indicating a potential cumulative effect over time. Conversely, the application of Al compost resulted in varying P uptake levels across the cycles, with the first cycle showing the highest uptake and a decrease in subsequent cycles, suggesting a potential depletion, or altered availability of phosphorus. Similarly, the use of Fe compost showed significant variation in P uptake across the growth cycles, with the highest uptake observed in the first cycle and a notable decrease in the third cycle. These findings underscore the dynamic nature of phosphorus uptake in canola cultivation, influenced by both the growth stage and the source of phosphorus application.
- The examination of biomass yield across various growth cycles, for switchgrass highlights distinct patterns influenced by different treatments. When considering MAP application, variations in biomass production were evident, with an increase observed in cycles two and three compared to cycle one, potentially attributed to enhanced root growth and phosphorus scavenging capacity. Conversely, Al compost application showed differing trends in biomass yield across the cycles, with the third cycle exhibiting the highest mean biomass but also greater variability, while the second cycle presented a middle ground. Similarly, the use of Fe compost demonstrated significant differences in biomass yield across cycles, with the third cycle showing the highest mean biomass yield, the first cycle the lowest, and the second cycle falling in between. These findings underscore the importance of considering both the growth stage and the type of amendment applied when aiming to optimize biomass production in switchgrass cultivation.
- Among the three sources, Al compost stands out for its ability to promote the highest biomass yield in canola during the first growth cycle, suggesting its effectiveness in early-stage growth

promotion. Conversely, MAP application resulted in varying biomass yields across the cycles, with the highest observed in the first cycle and a subsequent decrease in cycles two and three. Meanwhile, the use of Fe compost exhibited contrasting patterns, with the first cycle showcasing the highest mean biomass yield, the third cycle displaying the lowest, and the second cycle falling in between.

- The analysis of phosphorus recovery efficiency (PRE %) in switchgrass, considering various phosphorus sources and growth cycles, highlights intriguing trends. Among the sources, Al compost showed a significant increase in PRE % from the first to the subsequent cycles, indicating a potential cumulative effect over time, albeit with notable variability. In contrast, Fe compost started with a relatively high PRE % in the first cycle but experienced a decrease in the third cycle, suggesting a fluctuating efficiency with substantial variability. Monoammonium phosphate (MAP) consistently maintained lower PRE % values across all cycles, with higher variability observed in the third cycle.
- The analysis of PRE % for Al compost, Fe compost, and MAP across different growth cycles in canola cultivation reveals dynamic trends. For Al compost, a substantial mean PRE % was observed during growth cycle one, followed by a significant decrease in cycle three, with cycle two presenting an intermediate level. Similarly, Fe compost exhibited notably high PRE % levels in the first cycle compared to the second, indicating a fluctuating efficiency. In contrast, MAP consistently displayed relatively lower PRE % levels across all cycles, with the highest mean observed in cycle one.

Recommendations for future studies and works are as follows:

- **Scale-Up and Field Testing:** Consideration should be given to scaling up the composting process for alum and ferric sludges to assess its viability on a larger scale. Field testing in real-

world wastewater treatment scenarios would provide practical insights into the process's applicability.

- **Long-Term Monitoring of Compost Products:** Long-term monitoring of the alum and ferric sludge compost products in field conditions is recommended to assess their stability, impact on soil health, and long-term nutrient release patterns.
- **Exploration of Agricultural Applications:** Investigate potential agricultural applications for the nutrient-rich compost products. Collaboration with agricultural experts and stakeholders can provide insights into the best practices for utilizing these composts for crop cultivation.
- **Economic and Environmental Assessment:** Conduct a comprehensive economic and environmental assessment of the composting process, including cost-effectiveness, resource savings, and environmental benefits. This assessment will aid in decision-making for widespread implementation.
- **Fe Compost Preference:** Based on the research outcomes, it is recommended to consider Fe Compost as a preferred phosphorus source for cultivating switchgrass. Fe Compost demonstrated consistent effectiveness, leading to higher phosphorus uptake and biomass yield. Farmers and agricultural practitioners may benefit from incorporating Fe Compost into their nutrient management practices in term of switchgrass.
- **Al Compost as an Alternative:** While Fe Compost showed superior performance, Al Compost proved to be a viable alternative with slightly lower effectiveness but higher variability. Depending on specific conditions and objectives, Al Compost may serve as a suitable phosphorus source, providing flexibility in agricultural practices.
- **Consideration of Growth Cycles:** The research demonstrated variations in phosphorus uptake and biomass yield across different growth cycles. Agricultural practices should consider the

specific growth stage of the crops when applying phosphorus sources, recognizing the dynamic nature of nutrient requirements over time.

- **Further Research on Nutrient Release Dynamics:** Given the observed gradual availability of phosphorus over time for composted sources, further research into the nutrient release dynamics of different phosphorus sources could provide deeper insights. Understanding how nutrients become available to plants over various stages of growth can contribute to more precise nutrient management strategies.
- **Soil Management:** Given the gradual release of phosphorus from composted sources, soil management strategies should incorporate regular monitoring of phosphorus levels to ensure optimal nutrient availability throughout the growth cycles.

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