RECOVERY OF PHOSPHORUS FROM CHEMICAL SLUDGE

by

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A Thesis

Submitted to the Faculty of Graduate Studies of

The University of Manitoba in partial fulfilment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

Department of Civil Engineering

University of Manitoba

Winnipeg, Manitoba

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To my amazing husband **Ofeoritse** and my awesome kids (**Favour** and **Hephzibah**), thank you for the support, encouragement and love as always.

ACKNOWLEDGEMENT

I would like to express my profound gratitude to my supervisor Dr. Qiuyan Yuan for your support and guide throughout this entire process. I am indebted to Dr. Francis Zvomuya for your availability, invaluable support, the encouragement and thoroughness at every stage. You have made me a better person and I am most grateful. I am thankful to all members of my advisory committee for their contribution and support towards my Ph.D. completion. I appreciate the funding support from Niger Delta Development Commission (NDDC) which was a steppingstone for me. I would also like to thank Rob Ellis for his support and kindness. Many more appreciation goes to Dr. Theresa Adesanya, thank you for your friendship, encouragement and support. Dr. Nicholson Jeke, you stepped in to support and I am most grateful. I appreciate the support of Dr. Ikechukwu Agomoh, you constantly wanted better, and it got me here, thank you. Special thanks to my profound youth members in RCCG Winnipeg, God bless you all. Thank you dear Tolu Bankole. I have only achieved this because of the support from many amazing friends and families in Winnipeg, the names are too numerous to mention but I have you all at heart. To the entire members of Environmental Engineering in Civil Engineering Dept. and Soil Science lab, thank you. To my siblings and parents, I am full of hearty thanks. Thank you, Mimi, for all you have given, you constantly challenge me to be better. I am indebted in thanksgiving to God for helping me successfully come to the end of this program.

ABSTRACT

The shortage of pure phosphate rocks may be a limitation to the availability of food and other resources to man and animals. Understanding how phosphorus (P) can be recycled from chemical sludge to make-up for the shortage in availability of pure phosphate rocks is necessary as the world continues to survive. The inclusion of chemical sludge for nutrient utilization purposes in a well-drained Entisol (dark-grey sandy Gleyed Regosolic sand) was demonstrated in this work by applying dewatered sludge from Headingley Wastewater Treatment Plant, Canada. Growth room experiments were conducted to determine the effect of chemical sludge (alum phosphate sludge) as a P source to soil and this was compared to commercial fertilizer (monoammonium phosphate). Maize and switchgrass were examined for a 45- and 50-day cycle with 3 replications each. Low-P soil pots of 1.455kg were treated with different P application rates of 9.7, 19.4, 29.1 and 38.8 mg P kg^{-1} dry soil.

For switchgrass, over the three growth cycles, sludge treated pots showed that P availability increased as the cropping cycle increased. The rate of P application to each pot showed no significant variations based on biomass generated in all cycles. Improved P availability was observed in sludge amended pots compared to monoammonium phosphate (MAP) treated and control pots. Switchgrass also experienced increase in aluminum uptake in the biomass as the cropping cycle increased. The application rate of 9.7 mg P kg $soil^{-1}$ was identified as the best rate for switchgrass growth and P recovery in biomass.

Low-P soil was also seeded with maize for four cropping cycles with each cycle lasting about 45 days. Soil pots were amended just once at the beginning of the first cycle and results were analyzed for dry matter yield, P uptake, aluminum uptake and phosphorus recovery efficiency at the end of each cycle. Results showed that sludge is as effective as MAP in P utilization for maize growth

and P uptake was higher in sludge than in MAP. Biomass generated from switchgrass and maize could be harnessed as feedstock for biofuel, however, proper analysis of all forms of P and N in the sludge is necessary to prevent overdosing.

Chemical sludge was also exposed to alkali solubilization where waste activated sludge (WAS) and dewatered sludge (DS) were treated with different strengths of sodium hydroxide (NaOH). Results highlighted the importance of floc content in the sludge as the solubilization is mostly dependent on the floc content. Statistical analysis showed that maximum sludge solubilization for P was achieved within the first 30min. Further alkali addition showed no significant release of P from the sludge however, P in resulting solution must be analyzed for its separation and recovery cost.

All results indicate the potential possibility of reuse of chemical sludge to reduce the challenges around the availability of P rock and provides some insight into the usability of P in chemical sludge.

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NOMENCLATURE

ATP - adenosine triphosphate

CAD - Canadian dollar

CCE - calcium carbonate equivalent

CMAP - coated monoammonium phosphate

COD - chemical oxygen demand

DAP – diammonium phosphate

DMY - dry matter yield

DNA - deoxyribonucleic acid

DS - dewatered sludge

EBPR - enhanced biological phosphorus removal

EPS - extracellular polymeric substance

MAP - monoammonium phosphate

PAC - poly-aluminum chloride

PAOs - phosphate accumulating organisms

PHB - poly-hydroxybutyrate

PRE - phosphorus recovery efficiency

Psludge - phosphorus in sludge

Psup - phosphorus in supernatant

rbCOD - readily biodegradable chemical oxygen demand

RNA - ribonucleic acid

SCOD - soluble chemical oxygen demand

SOC - soil organic carbon

SOM - soil organic matter

TP - total phosphorus

TSP - triple superphosphate

VFA - volatile fatty acids

VSS - volatile suspended solids

WAS - waste activated sludge

WWTP - wastewater treatment plant

CHAPTER 1

GENERAL BACKGROUND

1.0 The Need for Phosphorus Recovery

With acknowledged limitations around phosphorus (P) availability (depleting P rocks and rock quality, rock location, economic consequence of the location and rock exploitation), every sustainable recovery of P will help mitigate P scarcity (Pizzol et al., 2014; Egle et al., 2016). P is enlisted among the top 20 critical raw materials in the world, hence the urgency in recovery from wastewater stems from the need to support economic growth, life on earth and promote environmental sustainability (Anders et al., 2021; Ma & Rosen, 2021; European Commission, 2014).

Regardless of the wastewater treatment method employed, P recovery from sludge and sludge streams is considered vital due to the nutrients inherent in them and as a means of recycling nature's gift (Cornel & Schaum, 2009; Takiguchi et al., 2003). This recovery ensures sustainability, mitigates challenges associated with declining sources of P rocks while moving the world into a renewable P direction. With the remaining P rocks not evenly distributed worldwide [literatures have it that 71% of available rock reserves are in Morocco and Western Sahara (Jasinski, 2020; Desmidt et al., 2015; Kasprak, 2016)], this may result to geopolitical consequences as well as a socio-economic threat (Cordell and White, 2015). Nutrient recovery is one way of managing this vulnerability as well as protecting the environment.

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, most targeted is the enriched P side stream. Here, digested solution from the anaerobic zone has abundance of magnesium, phosphorus and ammonium in solution as well as potassium (Yuan et

al., 2012). In the ratio of 1:1:1 magnesium, phosphate and ammonium under the right conditions generate struvite, a white crystal that is a slow-release fertilizer that competes favourably with conventional fertilizer (Ackerman, 2012). Conditions for the precipitation of struvite bothers mostly on having the right pH in solution and the concentration of magnesium (Doyle & Parsons, 2002; Hester and Harrison, 2013). With too high a pH, ammonium leaves the system as ammonia and magnesium becomes unavailable as it is transformed into $Mg(OH)_2$ (Ackerman, 2012). Struvite can reduce P in sludge stream or ash to as low as 10 mg L^{-1} within a favourable pH greater than 8 (Yuan et al., 2012; Ackerman, 2012; Yuan; 2011) and is quite comparable to commercial fertilizer. Hydroxyapatite on the other hand reduces P below 10 mg L^{-1} however, its performance is limited in alkaline soils (Yuan et al., 2012).

Generally, recovery of P has been considered from sludge stream, sewage sludge ash and liquid stream and utilized over the years with technologies such as crystallization (struvite, hydroxyapatite), wet oxidation and thermochemical (incineration with chemical extraction) methods, these technologies can also be combined for best results (Peng et al., 2018; Stemann et al., 2015; Herzel et al., 2016). The dynamics for P recovery in the future will determine to a large extent the market forces (scarcity, cost, demand, supply and others) and also political influence.

1.1 Objective of the Research

The objective of this thesis is to analyse the impact of using chemical sludge as a source of P to reduce dependability on commercial fertilizer (monoammonium phosphate) and the competition associated with it. The objectives for this research include:

- Evaluate the impact of different alkali (sodium hydroxide, NaOH) strength and mixing time on chemical sludge for P solubilization.
- Evaluate the bioavailability of P from chemical sludge in a low-P soil.

- Understand the impact of different cropping cycles on the availability of P from chemical sludge.

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 fertilizer.

1.2 Research Scope

The main scope of this work was to study the usage of chemical sludge (specifically alum-phosphate sludge) for P recovery. This is mostly in two parts: i) to generate P in solution through a laboratory scale solubilization assessment and ii) as a substitute for P in fertilizers in a growth room study using different sludge application rates and different cropping cycles.

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 through 5) were prepared in manuscript format and are as follows:

Chapter 2: Literature review.

Chapter 3: Statistical modeling of P solubilization from chemical sludge and evaluation of optimal sodium hydroxide dose.

Chapter 4: Bioavailability study of P in alum-phosphorus sludge using switchgrass.

Chapter 5: Aluminum phosphate sludge as a P source for maize production in a low-P soil.

Chapter 6: Engineering significance.

Chapter 7: Recommendation and future study.

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CHAPTER 2

LITERATURE REVIEW

2.0 Background of Phosphorus and its Usage

Phosphorus (P) is an element that is naturally occurring and abundant in the earth crust. It exists in part as phosphate deposits in sedimentary and igneous rocks. Soluble phosphate released by weathering is rapidly converted into insoluble compounds because of its reactivity (Smil, 2000). With major world reserves of phosphate rocks in China, USA, Morocco and South Africa, other large deposits although restrained by cost of deep-sea mining, are found in the Pacific and Atlantic Ocean (Cordell et al., 2009; Desmidst et al., 2014). Utilized by all forms of life in one way or another, P stands out as an indispensable element. As a very vital component in the make-up of man, it is found in deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine triphosphate (ATP), bone, and teeth, it also determines how well plants and fruits grow (Ashley et al., 2011; Cornel and Schaum, 2009; Zhao et al., 2013).

The demand and usage of P as fertilizer have increased tremendously over the last two centuries with predictions of reserves depleting within the next 100 years moreso, the cost of extraction and transportation of P rocks are on the rise whereas there is a decrease in the quality of extracted rocks (Cordell et al., 2009). With an efficient fertilizer application mechanism and a sustainable P recovery means, this increasing P demand can be managed alongside the available P rocks. Depending on the type of fertilizer applied to the soil, both organic and inorganic P can be introduced into the soil. Inorganic P is in a form that is ready for plant uptake while organic P requires some mineralization for plant uptake. Breakdown can be aided by the right soil conditions and the presence of microorganisms in the soil. Just as mineralization takes place, inorganic P can

become immobilized in the soil by the presence of metals, this however limits its availability to plants.

Schroder et al. (2011) gave an in-depth explanation about the sustainable use of P within the agricultural sector to balance the disparities between P rock reserves and the ever-growing P needs of man. The inefficient use of P and the drive for intensified agriculture due to increasing population, increased food demand, advancements in technology, land and water scarcity have led to a lot of environmental issues; however, to ensure efficiency and sustainability, recovery from wastewater becomes a necessity. A lot of research (Ownby et al., 2021; Brunce et al., 2018; Fernandes et al., 2012) has been done in the past to describe the removal and recovery of P from wastewater which contains P from erosion and surface run-off from agricultural farmlands, detergent use, human waste, industrial waste, landfill, and fertilizers. With all of man's 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 and Schaum, 2009; Smil, 2000). An intensified removal and recovery of P from wastewater could be the bedrock for an efficient and sustainable P gap closure in the society. P removal from wastewater protects the environment since wastewater is a major nutrient carrier.

2.1 Phosphorus Removal from Wastewater

Nutrient pollution has intensified over the years due to rapid industrialization and increase in population (Huber et al., 2020; Ownby et al., 2021). P pollution comes from domestic and industrial activities as well as storm water, erosion, and run-off from farmlands. Domestic wastewater is mostly due to household activities such as washing, bathing, toilet, and kitchen activities. On the other hand, industrial wastewater is majorly from industrial activities while storm water and agricultural wastewater are from rainwater runoff and farmland runoff respectively (Shevah, 2019). Although wastewater generation is inevitable due to human activities, the level to

which it is managed would determine the effect it would have on the environment (UNESCO, 2020).

The concentrations of P in the influent wastewater depends on the loading of the system involved. For example, for a typical municipal wastewater, influent P concentration can vary between 5 mg L^{-1} to 20 mg L^{-1} (Gray, 2004; Huber et al., 2020) while effluent P concentrations can be as low as < 0.5 mg L^{-1} (Oleszkiewicz & Barnard, 2006) but can sometimes be given as <1 mg L^{-1} (Huber et al., 2020; Desmidt et al., 2014; Tchobanoglous et al., 2003) depending on the receiving water body and the regional law. Wastewater treatment must be considered very crucial and an obligation before it is disposed into the environment, as excess P in surface water creates an imbalance in the environment. The level of P removal from the wastewater is mostly dependent on the type of treatment applied, P composition, and the specific regional discharge limits (Huber et al., 2020). A major risk with excess nutrient loading into surface water bodies is eutrophication. To preserve aquatic habitats and prevent the bloom of algae, P, the primary source of eutrophication, must be at minimal acceptable concentrations before its discharge into the receiving waters. Excess nutrients must be removed to meet up with the rising demand for fresh water and fertilizers for agricultural purposes (Cordell et al., 2009).

Eutrophication occurs in water bodies due to the presence of excess nutrients especially P and nitrogen (N). Naturally, eutrophication can happen with the aging of water bodies, nevertheless, nutrient accumulation is mostly accelerated by man-made activities (Carpenter et al., 1995). The excess algae bloom from these anthropogenic activities reduces the amount of dissolved oxygen in water and results in the subsequent death of aquatic habitats. This is detrimental to man and the environment (Schindler et al., 2008).

Despite the detrimental effect of excess P in the environment, P from wastewater can be recovered and used as an alternative nutrient source. As a limited resource, there has been intensified efforts to remove and recover P from wastewater (Cornel and Schaum, 2009; Hester and Harrison, 2013; Mohammed and Shanshool, 2009). P 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 (Morse et al., 1998). The established methods of removal are chemical precipitation and the enhanced biological phosphorus removal (EBPR).

2.1.1 Chemical Precipitation of Phosphorus

The removal of P from wastewater using chemical precipitation is described as a significant and more effective treatment process since it has high removal efficiency (Eliassen and Tchobanoglous, 1991). Also known as the traditional method, it involves the conversion of soluble P into insoluble precipitates by the addition of metal salts of calcium (Ca), aluminum (Al) and iron (Fe). The multivalent metal salts precipitate orthophosphates present in wastewater and conveniently reduces the P level in the effluent to very low concentrations (Thistleton et al., 2002). Depending on the need of the system, chemical precipitation/dosing can be done at different stages (Figure 2.1) of the treatment plant to reduce the P load on the system. When metal salts are added before or in the primary settling tank, it is described as pre-precipitation. In co-precipitation, chemical dosing is implemented after the primary settling tank, in the digestion tank or before the secondary settling tank. Post-precipitation metal dosing occurs after the secondary clarifier (Derco et al., 2016; Henze et al., 2002; Kazadi Mbamba et al., 2019). Post-precipitation ensures the effluent is mostly within 1 mg L^{-1} with possible P recovery from the chemical sludge (Cornel and Schaum, 2009). The quantity of chemical sludge generated decreases as the dosing operation changes from pre-precipitation to post-precipitation (Parsons and Stephenson, 2004; USEPA,

2010). With chemical precipitation, effluent low in P is discharged while the metal phosphate precipitate is collected in the sludge which can be easily recovered as fertilizer (Fernandes et al., 2012). In most cases, chemical dosing to the supernatant is done after anaerobic digestion with over 90% of P is precipitated into the sludge (Yuan, 2011).

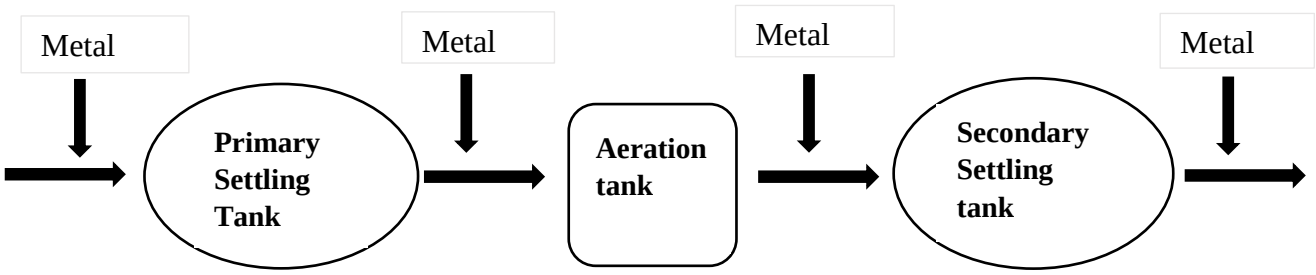

Figure 2. 1: Chemical dosing options for phosphorus precipitation

Some key factors that affect the efficiency of phosphate precipitation using these metal salts are pH, dosage of metal salt, dosage point, initial phosphate concentration and retention time of wastewater (Szabó et al., 2008). Most important is the metal salt dosage as it depends on the concentration of orthophosphates in solution. The pH is another key factor as this determines the solubility of the precipitates for effective removal as it varies with pH. For example, the stoichiometric molar ratio of metal to P for ferric salts is between 1.5:1 at a pH range of about 4 to 5 while that for Al varies mostly between 2:1 and 3:1 at an optimal pH between 5 and 6.5 (De Haas et al., 2001). To achieve effluent P concentrations lower than 1 mg L^{-1}, metal salts dosage should be in excess stochiometric ratio at a range of 1.5:4 for Al and Fe salts (MPCA, 2006). To achieve effluent P below 0.5 mg L^{-1}, not only would metal salts be dosed in excess of stoichiometric requirements but sophisticated filtration of the effluent must be added to the process (Derco et al., 2016). Effluent P concentrations as low as 0.005 - 0.05 mg L^{-1} were

thermodynamically simulated as chemical precipitation best prediction performance (Neethling & Gu, 2006; Takács, 2006) with limitations bothering on the temperature of the system, ionic strength of the coagulant in addition to pH and P concentration (Song et al., 2002). Kazadi Mbamba et al. (2019) reported that increasing the stoichiometric ratio at low P concentrations of about 0.2 mg L^{-1} does not influence P precipitation. Challenges associated with efficient chemical precipitation of P include the increased volume of chemical required and sludge generated as well as sludge handling and its disposal (Eliassen and Tchobanoglous, 1991). Other notable challenges that have been highlighted in several literatures are poor sludge dewaterability of the sludge and reduced denitrification efficiency (USEPA, 2010; Burton et al., 2014).

Chemical precipitation has also been induced into the pond system which serves as a natural purifier. In Canada, this system has been successfully used in small communities although with upgrade challenges (Federation of Canadian Municipalities, 2004; Steinmann et al., 2003). With the build-up of sludge in these lagoons, the challenge of sludge disposal becomes an issue (Zhan et al., 2015; Schneiter et al., 1984; Maynard et al., 1999, Heinke et al.; 1988). Cost of dredging, transportation and dumping of sludge are other major challenges in lagoon system aside meeting the discharge requirements (Hosetti and Frost, 1995). To meet up the P discharge requirement of 1.0 mg L^{-1}, most stabilization lagoons add metal salts to precipitate P in the lagoon.

2.1.2 Enhanced Biological Phosphorus Removal

Enhanced biological P removal (EBPR) is a more recent P removal advancement that was discovered in 1959 whereas the behaviour and characteristics of the microbes were fully understood in the 1980s (Yuan, 2011; Van Loosdrecht, 1997). This method is fully recognised and is applied in full scale in a variety of ways worldwide.

Microorganisms called phosphate accumulating organisms (PAOs) are utilised under anaerobic condition (no oxygen) to store P in excess. Under this condition, when fed with volatile fatty acids (VFAs) or acetate (formed from fermented organic matter), the PAOs use up their polyphosphates as energy source and release orthophosphates into the solution. The energy from polyphosphates breakdown enables the storage of VFAs as poly-hydroxybutyrate (PHB). The stored poly-hydroxybutyrate (PHB) is then oxidized in the aerobic zone to enable their growth and subsequent uptake of all orthophosphates in the solution (Morse et al., 1998; Stratful et al., 1999; Tchobanoglous et al., 2003). The oxidation of carbon reserves in the aerobic zone enables the uptake of orthophosphate to replenish the energy used up in the anaerobic zone. Seeing that more energy is released in the oxidation of carbon reserves than during the energy storage in the anaerobic zone, this results in an increased uptake in orthophosphate compared to that released in the anaerobic zone (Hui et al., 2014). The P can be collected in the form of wasted activated sludge (WAS) while a percentage is recycled into the anaerobic zone to ensure the active growth of PAOs is maintained in the system. Benefits of this method are seen in the form of cost reduction for chemical handling and usage, reduction in the volume of sludge produced (Strom, 2006). It also produces a dischargeable effluent low in residual P (Tchobanoglous et al., 2003). High level of P removal has been achieved with the incorporation of EBPR into granola sludge reactors, membrane bioreactors and sequencing batch reactors processes (Bunce et al., 2018). A summary of the enhancements made in the P removal process from wastewater and the efficiencies are documented in Bunce et al. (2018). The use of this method is impacted by some of the following: i) The availability of adequate readily biodegradable chemical oxygen demand (rbCOD) with a minimum requirement of 1:13 P: rbCOD for PAOs to thrive significantly in the anaerobic zone (Hartley, 2013; Wang et al., 2010; Bertanza et al., 2020). ii) Establishing a perfect anaerobic zone

and maintaining it would ensure PAOs thrive, take up VFAs and store them as poly-hydroxybutyrate. The presence of oxygen and nitrates would deter this and prevent orthophosphate uptake in the aerobic zone. iii) Reduced fluctuations in influent flow and load as huge variabilities could affect the P: rbCOD load as well as the VFA availability and disrupt the anaerobic zone status. iv) Temperature, pH and sludge retention time may influence the effectivity of PAOs (Anders et al., 2021; Broughton et al., 2008; Zheng et al., 2014;).

To achieve an effluent P concentration as low as 0.1 mg L^{-1}, a combination of chemical dosing and EBPR can be applied and with some efficient effluent filtration however, this is not without its challenges and shortcomings (Kazadi Mbamba et al., 2016; MPCA, 2006).

2.2 Phosphorus Recovery

The recovery of P is essential in today's economy since there are both environmental and economical challenges associated with phosphate rock mining. In the light of a sustainable yet circular economy, wastewater has been identified as a broad resource for P which when removed and recovered should bridge some of the existing gap in P demand and also improve the environment. For example, Yuan et al. 2012 reported about 3 MT yr^{-1} of P in domestic waste that can be harnessed and recovered to meet about 20% of the world P demand.

Regardless of the wastewater treatment method employed, P recovery from sludge and sludge streams is considered vital due to the nutrients inherent in them and as a means of recycling nature's gift (Cornel & Schaum, 2009; Takiguchi et al., 2003). This recovery ensures sustainability, mitigates challenges associated with depreciating sources of P rocks and plunges the world into a renewable P source era.

Phosphorus recovery considers concentrating P using removal methods and recovering P in a way that it can be reused effectively with little or no contaminants. Recovery from wastewater and

sludge streams have been extensively documented with the highest P recovery up to about 90% been recorded from sewage sludge and sludge ash (Cornel & Schaum, 2009). The cost of recovery is one of the basic challenges encountered in P recovery. There is continuous push for improved research into P recovery methods that would ultimately improve recovery cost when compared to mining cost. Recovery methods have been extensively reviewed in literatures (Rajasekar et al., 2015; Ma & Rosen, 2021; Cornel & Schaum, 2009).

2.2.1 P recovery methods

The finite nature of P is very sensitive because it is a crucial resource for essential wellbeing. World P supply is very limited but, it is on record that less than 15% of P from wastewater treatment plants (WWTP) can satisfy the yearly P fertilizer demand (Rittmann et al., 2011; Perera et al., 2019). With increase in world population and P demand, there is heightened need for sustainable recovery of P.

The recovery of P from sludge has mostly been facilitated from biological P removal method either from the sludge or side stream. In the enriched side stream, solution rich in P are recovered from anaerobic section of the removal process while in the sludge stream, the anaerobically digested sludge supernatant which is rich in P and other ions is treated for P recovery (Perera et al., 2019). Struvite and hydroxyapatite have both been enabled using the above-mentioned streams, with struvite been the most applicable method due to its utilization of both P and N in waste streams (Rajasekar et al., 2015).

Struvite (magnesium ammonium phosphate) recovery from the side stream combines the P rich solution with ammonium stream for its formation. From the digested stream, the P rich solution is also rich in ammonium and struvite is precipitated by some pH adjustments (Monea et al., 2020; Ackerman, 2012). Hydroxyapatite on the other hand can also be precipitated by the addition of

lime to the P rich side stream and is impacted by pH, P concentration, and other ions in solution. This process starts with nucleation as first step or nucleation can also be induced artificially. Both struvite and hydroxyapatite have been employed in countries like Canada, USA, Japan, Germany etc in identified processes such as Phosptrip, Phosnix, Ostara, Prisca, Pearl, Kurita etc (Monea et al., 2020; Rajasekar et al., 2015; Yuan, 2011).

In 2012, Ackerman did a study on recovering P from hog manure via batch reactors and the precipitated manure derived struvite was compared with pure struvite and other commercial fertilizers (Ackerman, 2012). Also, Bowers and Westerman (2005) recovered struvite from swine lagoon liquor using a fluidized bed reactor. The molar ratio of $Mg:NH_4:PO_4$ and pH are crucial factors for successful struvite precipitation (Rajasekar et al., 2015; Bowers & Westerman, 2005).

Phosphorus can also be recovered using chemical leaching where acid or alkali is contacted with the activated or/and chemical sludge. Chemical leaching can also lead to the release of unwanted organic pollutants or metals into solution, and this may impact the quality of precipitated struvite (Monea et al., 2020). Contact time, pH, composition of sludge, and concentration of leaching agent are some of the factors that may affect the extent of leaching (Xu et al., 2018; Monea et al., 2020).

Other technological advances such as nano-enhanced electrochemical processes where cathodes and anodes are used to improve the crystallization potential of P from wastewater to form struvite and hydroxyapatite. The driver for this method is the green theory where process electrification reduces chemical demand, chemical waste generated, and green house gases emitted during the process. Also, the cost-benefit of electrode regeneration makes this process attractive and environmentally friendly (Zhang et al., 2021).

Thermal pretreatment and thermochemical processes have also been employed to recover P from solid sludge. The thermochemical processes allow for high temperature treatment of sludge via

incineration and pyrolysis where dry sewage sludge is turned into ash and then washed in acids for maximum P extraction. Wet pyrolysis and gasification followed by acid dissolution can also be employed to wet sludge for P recovery (Rajasekar et al., 2015).

Nano-enabled processes, membrane enhanced recovery, adsorption and ion exchange are also considered techniques to sequester P for maximum recovery (Zhang et al., 2021; Rajasekar et al., 2015; Cornel and Schaums, 2009).

Overall, an integration of several technologies may be the solution to a cost-effective P recovery process.

2.2.2 Need for recovery from chemical sludge

With chemical precipitation, there is an increase in the volume of sludge produced which is mostly due to the increase in chemical needs of the process. Sludge generated during this treatment process must be properly disposed, albeit, minimal contamination and pollution is the target of this disposal quest. The need to enhance environmental quality and protect water bodies is a major drive for the proper management of sludge (Hassan Basri et al., 2019; Kundu & Dutta, 2018).

The disposal of sludge is affected by factors such as the cost of handling, transportation and disposal (Bunce et al., 2018; Keeley et al., 2012; Likosova et al., 2014). Oftentimes, chemical sludge is deposited in landfill due to very few available reuse options which has led to significant loss in P (Hassan Basri et al., 2018); while the average cost of landfill, the shortage of landfill sites and the ban on landfill in some countries are hindering factors to this effect. (Keeley et al., 2012; Tay et al., 2001; Kato et al., 2006). Recovery of P from chemical sludge of Al or Fe has been tagged impracticable as the reusability of P is questioned (Wilfert et al., 2020; Oleszkiewicz et al., 2015) due to the bond that exist between the respective metals and P.

With a short lifespan for the reserves of P rocks and the recurrent decline in quality of rock-extracted P, the cost of extraction/purification and transportation are adversely affecting P availability to mankind (Cordell et al., 2011). To ensure environmental sustainability and meet the P needs of growing population, P recovery from sludge must be considered (Cordell and White, 2015). The fact that stringent discharge limits are enforced daily means more sludge (increased sludge volumes) will be produced to ensure these limits are met (Doyle and Parsons, 2002). With an estimated 50% P need recoverable from wastewater (Cornel and Schaums, 2009) and the sheer volume of wastewater produced daily all over the world, there is every tendency that the challenges the world may face due to P can only be addressed by wastewater P recovery.

2.2.3 Advances in recovery from chemical sludge via alkaline dissolution

Several studies exist on alkali dissolution of sludge however, the major focus has been on the breakdown of readily biodegradable carbon (Lin et al., 2009; Torres and Llore´ns, 2008; Chang et al., 2011). For instance, Lin et al. (2009) analyzed the breakdown of pulp and paper sludge to improve biogas generation using alkali. They observed that the alkaline addition resulted in the increase in soluble chemical oxygen demand (SCOD) and a complementary increase in the volatile fatty acid (VFA) concentration, hence a general increase in biogas production. Similarly, Chang and colleagues observed an increased biogas yield after alkali pretreatment was carried out on waste activated sludge (WAS) from a pulp and paper for 60 mins at pH of 12. They observed about 47% and 20% biogas recovery improvement over the control samples due to increases in chemical oxygen demand (COD) and volatile suspended solids (VSS). Observations from these studies, imply that during alkali solubilization of sludge, increases in chemical oxygen demand and volatile fatty acids are a direct indication of the breakdown and lysis of protein with a potential P release from the phosphates and nucleic acids (Zhang et al.; 2013).

Kato et al. (2006) investigated the alkali dissolution of pre-coagulated sludge followed by the recovery of P as calcium phosphate. This calcium phosphate was recovered from the supernatant at a pH of 12 using poly-aluminum chloride (PAC).

Although recovery from aluminum and ferric P removal methods have been tagged as impracticable since P is deemed potential unavailable (Oleszkiewicz et al., 2015), some recent advancements have been carried out especially on recovery of P from ferric phosphate sludge.

Salts of ferric are described as both highly efficient in P removal from wastewater and inexpensive (Zhang et al., 2010) however, the precipitated ferric phosphate sludge must be properly disposed (Keeley et al., 2012; Likosova et al., 2014). Based on an experimental analysis in 1978, Soon and coworkers documented that ferric phosphate sludge is a very slow-release P source when used as a fertilizer since it is highly insoluble (Soon et al., 1978). With very limited reuse options, the ferric phosphate sludge is landfilled. Ferric can leach over time and contaminate groundwater. Therefore, the disposal of ferric phosphate sludge does not just have an impact on the overall cost of the plant; it also has associated long term environmental issues (Kato et al., 2006). Therefore, a critical consideration and assessment of P recovery from chemical sludge can open opportunities for reuse options by several industries (Hester and Harrison, 2013; Likosova et al., 2014).

P recovery from ferric phosphate sludge was first proposed about 26 years ago by Ripl and colleagues; the proposal involved the simultaneous recovery of P and ferric from ferric phosphate sludge using sulphides (Ripl et al.; 1988). This method has since been analysed by Kato et al. 2006, Likosova et al. 2013a and Likosova et al. 2014.

Kato et al. (2006) validated this proposal by using sodium hydrogen sulphide ($NaHS$) to treat ferric phosphate sludge with the aim of maximizing the extraction efficiency of the process, here it is expected that majority of the phosphate is chemically bound to the ferric. On a laboratory-

scale level, experiments were carried out on both synthetic sludge and pre-coagulated sludge of $FePO_4$. The rationale behind the use of $NaHS$ were due to the associated cost of NaS and its manageability. Below was the chemical reaction as given by Kato et al. (2006):

$$2FePO_4 + 3NaHS + 3HCl \rightarrow 2FeS + S + 2H_3PO_4 + 3NaCl \qquad 1$$

At a loading rate of $S/_{Fe}$ between 1-2 and pH range of 5.26 - 6.96, phosphate recovery of approximately 93% and 43% were reported for both synthetic and pre-coagulated sludge respectively. Also reported were precipitates of 98.5% ferric and 98.3% sulphide by mass in the extracted residue while 44% of phosphate was recovered by mass in the supernatant. Low extraction efficiency for the pre-coagulated sludge was attributed to the inability of $NaHS$ to reduce non-$FePO_4$ phosphates (other different forms of Fe associated with phosphate and any other compounds of phosphates) in the sludge. For effective and efficient P recovery from $FePO_4$ sludge, high concentration of sludge and proper mixing are recommended (Kato et al., 2006). Likosova et al. (2013a) had analyzed P recovery from $FePO_4$ sludge with consideration on the effect of mixing time, dosing rate, pH and settling time (Likosova et al., 2013a). They simulated their experiment first using synthetic sludge of $FePO_4$, this was to prevent the interfering effect of organic substances in the sludge. Using sodium sulphide *(Na_2S)*, pH values of 4, 5 and 6 were considered with different dosing rates, mixing time, and settling rates for P recovery. At a low pH of 4, under a settling time of 1 h, the highest P recovery of about 70% ± 9% was achieved at a dosing ratio of 1.5; upon the analysis of pre-coagulated sludge, about 70, 75% and 90% P were recovered at pH 4 and dosage ratios $S/_{Fe}$ of 1.5, 1.7 and 2.5 respectively (Likosova et al., 2013b). Apparently, increasing the dosing rate improves the recovery of P. This analysis was done using sodium sulphide based on the stoichiometry of the chemical equations written below, originally presented by Wei and Osseo-Asare (1996):

$$2FePO_{4\,(s)} + 3H_2S \rightarrow 2FeS_{(s)} + S^0_{(s)} + 2H_2PO_4{}^- + 2H^+ \quad 2$$

$$2Fe^{3+} + HS^- \rightarrow 2Fe^{2+} + S^0 + H^+ \quad 3$$

$$Fe^{2+} + HS^- \rightarrow FeS_{(s)} + H^+ \quad 4$$

$$FeS + S^0 \rightarrow FeS_{2\,(s)} \quad 5$$

Here, they concluded that the formation of a stable product of ferric sulphide is dependent on the pH and molar ratio of ferric to sulphide (Fe:S). The above was formed at a pH range of 3.6-5.7 with a 99.46% extraction of ferric sulphide (Wei and Osseo-Asare, 1997). Furthermore, an electrochemical cell recovery for ferric and sulphide was done on the residual ferric sulphide (Likosova et al., 2014). With carbon graphite cathode and anode, the cell generated about 60% ± 18% ferric and 46% ± 11% sulphide. This shows the possibility of recycling ferric to precipitate P from wastewater and the further use of sulphide for P recovery from ferric phosphate sludge. For ferric and sulphide recovery, the electrochemical cell was maintained under anaerobic condition. This was achieved by purging both cathode and anode with nitrogen to ensure no oxygen was available (Likosova et al., 2014).

More recently in 2020, Wilfert and colleagues worked on synthetic and digested sludge of ferric phosphate, where they considered P recovery from the sludge using iron reduction with sulfide. They cautioned that the type of colloids and complexes ferric forms with sulfide would largely impact the recovery of P. They recorded a 75% P recovery using synthetic ferric phosphate solution at Fe:P ratio of 1.55. For the various digested sludges analyzed, a 31% P recovery was achieved at 1.18:1 Fe:P ratio as the maximum possible recovery (Wilfert et al., 2020). This reduced recovery was attributed to the nature of the sludge used (digested sludge) and low molar ratio of Fe:P used as sulfides specifically extracts the P that are ferric bound (Wilfert, et al., 2020; Kato et al., 2006).

The table below illustrates work done on synthetic and real ferric phosphate sludges and their % P recovery.

Table 2. 1: Sulphide-induced analysis in ferric phosphate sludge and the associated P recoveries

P Recovery %	Sludge type	Molar ratio (S:Fe)	pH	Author
31	Digested Sludge	0.7	7 – 7.5	Wilfert et al., 2020
75	Synthetic sludge	1.0	7 – 7.5	Wilfert et al., 2020
90	Pre-coagulated Sludge	2.5	4	Likosova et al., 2013b
75	Pre-coagulated Sludge	1.7	4	Likosova et al., 2013b
70 ± 6	Pre-coagulated Sludge	1.5	4	Likosova et al., 2013b
70 ± 9	Synthetic sludge	1.5	4	Likosova et al., 2013b
43	Pre-coagulated Sludge	1 - 2	5.26 - 6.96	Kato et al., 2006
93	Synthetic sludge	1 - 2	5.26 - 6.96	Kato et al., 2006

2.2.4 P demand from chemical sludge and its bioavailability

Phosphorus has been identified as a limiting nutrient in agriculture since it is a major determinant of plant growth (Sattari et al. 2012). In their work on P reuse from waste stream, Rajasekar and colleagues illustrated that P in the soil is in a continuous cycle with transitions between biotic and abiotic processes including mineralization, uptake, precipitation, weathering and leaching among others (Rajasekar et al., 2015). Organic and inorganic P are mostly present in soil. Organic phosphates are readily converted to inorganic P based on soil conditions and are utilized by plants. Microorganisms and carbon content of soil can aid organic P mineralization while soil pH and metal content can easily immobilize inorganic P availability in the soil (Yossif & Gezgin, 2019).

Orthophosphates are the most common inorganic P with the most applicable form of fertilizer known as monoammonium phosphate (MAP). Diammonium phosphate and trisuperphosphate are other common inorganic fertilizers that are applied to enhance crop productivity (Yossif & Gezgin, 2019; Vogel et al., 2015). Green manure and other forms of manure are also added to boost the richness of nutrients in the soil. For instance, Ackerman (2012) reported the sensitivity of the use of struvite generated from hog manure to commercial fertilizers. In this study, struvite from hog manure (manure derived struvite) was compared with pure struvite, monoammonium phosphate (MAP) and coated monoammonium phosphate (CMAP). P response to different application rates showed that biomass yield was similar for manure derived struvite and pure struvite while MAP and CMAP had similar yields; biomass yields from MAP and CMAP were higher than those from manure derived and pure struvite. At higher rates, there was no significant difference in P uptake for manure derived struvite and pure struvite while MAP and CMAP continued to increase linearly. Although commercial fertilizers showed better yield and P uptake, He concluded that P from manure derived struvite was effective for crop growth and can improve manure management efficiently (Ackerman, 2012).

Achat et al. (2014) in their work on plant P availability had carried out pot experiments to analyze the responses of ryegrass and fescue to the application of recycled pig manure and diary effluent. These sources were compared with TSP (triple superphosphate), synthetic struvite, and hydroxyapatite at a P application rate of 50 mg kg^{-1} in a deficient soil with pH of 6.49. Pot experiments were run for about 60 d with shoot harvest done on days 34, 40 and 50. Aboveground and belowground biomass yield was reported to be highest for TSP followed by recycled pig manure and diary effluent. Also, increase in P uptake was in the order of TSP followed by pig manure, diary effluent and synthetic P sources. The increase in P uptake was attributed to an

increase in root biomass and more importantly, the source of P utilized in the process. Overall, there was no significant statistical difference identified throughout the experiment both in plant biomass and P uptake. Recycled pig manure and diary effluent could be utilized as potential fertilizer sources as they showed responses that had similar variances with TSP. Moreso, the presence of organic C in the recycled products could have improved the soil microbial structure (Achat et al.; 2014).

A 2 yr pot experiment was done comparing the effectiveness of P from TSP, phosphate rock (PR), struvite, calcium phosphate and P from thermal process (sewage sludge ash, cupalo slag, meal ash, sinter phosphate) in two soils of pH 4.7 and 6.6 by cropping maize. Results indicated that both TSP and struvite were more effective in plant growth with similar responses in both soils (Cabeza et al., 2011). They concluded that P products such as struvite and calcium phosphate can effectively be applied directly as fertilizer due to the exchangeable P compared to thermal products in soil, however, thermal products could potentially be considered as raw materials for fertilizer production (Cabeza et al., 2011).

The need for the efficient use of P has stimulated the drive for economic growth and environmental sustainability, this would entail moving P from a region of high concentration to where it is needed as a means of maintaining the ecosystem. The entire drive to ensure P is recycled and reused is to build a sustainable economy that is rooted in circularity as this would tackle P inefficiencies (Wali et al., 2021). Sustainable P usage ensures food security but so far, there is a disparity between P supply and consumption pattern (Childers et al., 2011). Having a proper roadmap and management structure for P waste systems could be one of the best ways of integrating all parts of P ecosystem to ensure future sustainability. Fertilizer serves a great need, and generally is necessary for food production (with P being useful for root development among others). Nevertheless, environmental

protection from excess P is an ever-pressing need as algae bloom and eutrophication increases acidification of water due to the formation of carbonic acid. This CO_2 generation in the water interacts with the anthropogenic atmospheric CO_2 and prevents the global target of Net-Zero 2050 agenda (William and Wei-Jun, 2012). Chemical sludge has abundance of P although it has been reported that the availability of P in chemical sludge (alum and ferric phosphate) is limited and almost impossible to recover due to the existing bond and the incurred high cost of P recovery (Oleszkiewicz et al., 2015; Carliell-Marquet et al., 2010).

Significant impact on P availability is driven by the type of chemical used in the wastewater treatment while the mechanism and release rate of P in chemical sludge varies according to the soil characteristics (sorption, pH) (Vogel et al., 2015). Reports have been controversial with some indicating that P would be unavailable to plants and that excess metal hydroxide in the chemical sludge may lead to precipitation of available P in the soil (Vogel et al., 2017). Some older studies still showed that the availability of P in the sludge was not deterred by the chemical nature of the sludge and the excess metal hydroxide did not do limit the availability of P in the soil (Kirchmann et al., 2017; Cohen et al 2011; Kirkham, 1982). Some literatures report that the immediate availability of P can be limited by the addition of chemical sludge, however the addition will increase the formation of oxalates of metals which would increase soil P sorption capacity and in the long run P availability (Bøen et al., 2013).

Although the organic P content of chemical sludge varies, P availability is described to be mostly from the breakdown of organic P due to the abundance of organic matter in the sludge. The mineralization of organic P would lead to the accumulation and release of inorganic P on the soil surface below 30 cm of the soil depth (Kyle & McClintock, 1995). In comparison, Kyle & McClinton (1995) also highlighted that available P in Al bound sludge was more compared to that

in Fe bound sludge, this they attributed to be as a result of the complex bounding of Fe with P and soil particles. They also stated that from experiments carried out, Al and Fe sludges are more likely to be soluble in alkaline soils than acidic soils due to the formation of metal hydroxides. Vogel et al. (2015) in their work reported a reduced P availability for alum and ferric P sludge on 5 different crops compared to struvite and trisuperphosphate. This was attributed to the formation of amorphous metal compounds and subsequent increase in P sorption capacity of the soil. Krogstad et al. 2005 suggested that the unavailability of P in metal P sludge may be transformed over a long time into availability due to improved soil characteristics. On the positive, the low P availability could serve as the right incentive for proper administration of chemical sludge for slower release and future usage since it has higher P sorption rate (Vogel et al., 2017; Bøen et al., 2013; Kyle and McClintock, 1995). Generally, the use of alum and ferric sludge would reduce waste of P and envisaged losses in the environment (Pritchard et al., 2010; Huang et al., 2007). Rigby et al. (2008) from their work had reported that plants could be grown using alum P sludge however, they observed a reduction in the concentration of P found in the shoot.

Some concerns on the application of alum sludge are that free aluminum may leach into the soil that could result in environmental and health risk, whereas there is also the concern with colloidal matter as well as other heavy metal leaching and changes in soil properties (Awab et al., 2012; Kim et al., 2002). Understanding the right application rates for sludge could improve cost competitiveness with inorganic fertilizer, continue to improve ground water quality and enhance soil properties due to the organic content in the sludge. The original landfilling of chemical sludge needs to be reviewed due to the useful nutrients and organic content of sludge with a regulated application approach. One of the reuse concepts for chemical sludge could be its usage for the growth and production of bioenergy crops specifically dedicated to biofuel generation. This may

eliminate the already existing fertilizer competition with food crop and prevent world hunger as well as contribute to the achieving of net-zero emission. The growth and production of bioenergy crops can be seen as part of the gap-fillers to ensuring a reduced emission of green house gas as this allows for blending with natural gas or as a stand-alone renewable fuel (Maghsoodi et al., 2020; Kering et al. 2012). The application of chemical sludge with several crops to determine the availability would improve groundwater quality, protect environment, reduce waste and also reduce greenhouse emission (Hoekman et al., 2018).

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CHAPTER 3

PHOSPHORUS SOLUBILIZATION FROM CHEMICAL SLUDGE USING SODIUM HYDROXIDE

3.0 Abstract

Phosphorus (P) recovery from sludge has drawn widespread attention across the world to minimize the P load to the watershed, a concern for eutrophication, and to meet the stringent effluent discharge regulations in some countries. Waste activated sludge (WAS) and dewatered sludge (DS) were treated with a wide range of NaOH doses (0 ~ 0.75 g g^{-1} total solid {TS}). The DS sludge was diluted to 4.5% ~ 2.25% of TS before the treatment to make comparable amount of TS as of WAS (2.25% ~ 1.5%). The time-based study illustrated that P solubilization reached equilibrium within the first 20 min of treatment duration. Significant positive correlation was found between solution pH and P solubilization, whereas effect of TS was mostly insignificant. The experimental data was fitted to the exponential models and exhibited maximum P recovery of about 67% and 56% from the DS and WAS at NaOH doses of 0.71 and 0.27 g g^{-1} TS, respectively. The optimal P recovery dose of 0.36 g g^{-1} TS for DS and 0.20 g g^{-1} TS for WAS were obtained with 64% and 48% of P recovery, respectively. The optimal dose of NaOH illustrated in this study could be utilized for other types of sludges as well as the modeling approach and P recovery mechanisms could be further extended to other type of P recovery techniques.

3.1 Introduction

The indispensable nature of P can never be overemphasized. Scientists estimated the extinction of available P reserves due to the increased consumption rate to meet the demand of ongoing world population growth and industrialization (Daneshgar et al., 2018). Phosphorus is also considered as a serious environmental polluting agent while it remains in water body and enhances

eutrophication. Nutrients (especially P and nitrogen) enhance excessive formation of algae bloom and ultimately create dead zone (Guzman et al., 2017). Therefore, the need to recover, recycle and reuse P to ensure a sustainable system is eminent.

Wastewater, which is a major conveyor of P, has been treated using biological, bio-chemical and chemical methods over the years and P is accumulated in the sludge produced from these treatment methods (Bardi et al., 2017; Droste and Gehr, 2018; Islam et al., 2019). Various technological approaches are used to stabilize sludge including aerobic and anaerobic digestion (Berenjkar et al., 2018) along with the P recovery options. In biological treatment method, P accumulating organisms (PAOs) are employed to remove P from wastewater which can then be recovered from sewage sludge in the form of struvite ($MgNH_4PO_4$), which is a crystal fertilizer with economic and market value (Doyle and Parsons, 2002). Although fully established and in full force, biological treatment may face some challenges with unstable microorganisms and operational conditions, also the are cost implications in overhauling old and existing treatment plants to biological treatment plants (Morse et al., 1998; Stratful et al., 1999; Tchobanoglous et al., 2003).

On the other hand, P recovery in the form of chemical precipitation from wastewater treatment plants (WWTPs) has been reported in the literature using metal salts of calcium (Ca), aluminum (Al) and iron (Fe) (Cieślik and Konieczka, 2017). The advantages of these treatment methods include solid state recovery of P as metal-P compounds and stable process operability (Desmidt et al., 2015; Tchobanoglous et al., 2003). The challenges associated with sludge disposal are considered imperative (Rai et al., 2004; Smil, 2000), whereas main challenges include landfill availability, transportation cost, handling and dumping, leachate generation and treatment costs (Kato et al., 2006; Keeley et al., 2012; Mejia Likosova et al., 2014).

Various metal forms of P (Ca, Al and Fe phosphate) precipitate in chemical sludge. Calcium phosphate [$Ca_3(PO_4)_2$] is easily reusable and works almost similarly as extracted rock. But Al and Fe phosphates are not reusable as P is tightly bound in the compounds, almost insoluble and not easily accessible to plants; therefore, generally discarded in landfills (Fernandes et al., 2012; Hosni et al., 2007). Although there is a global concern over the depletion of phosphate rocks, the extracted P rocks contain substantial amount of heavy metal that calls for high purifying cost. With more stringent environmental policies and increasing demand of P by the ever-rising world population, P recovery from chemical sludge (Al and Fe phosphate) could be considered as a viable option to bridging some of the P gap. Since Al and Fe phosphate compounds have little or no reuse options, dumping of these compounds adversely impacts the environment and can affect groundwater quality with problems such as high Al concentration impact to the surrounding waterbody (Kluczka et al., 2017). Therefore, recovering and reusing this important nutrient could also serve as a form of waste management.

Alkali dissolution of sludge has been studied extensively, although most studies focused on dissolution of readily biodegradable carbon i.e. soluble chemical oxygen demand (SCOD), only a few have investigated P solubilization. For instance, Lin et al. (2009) performed alkaline treatment of sludge and observed an increase in the concentrations of supernatant SCOD and NH_4^+–N , which indicated decomposition of protein and potential release of P from nucleic acids and phospholipids. Other studies have also reported similar SCOD increase as a result of alkaline treatment of sludge (García Becerra et al., 2010; Torres and Llore´ns, 2008; Chang et al., 2011). In a different study, Chen et al. (2007) outlined the benefits of high pH in alkaline sludge hydrolysis with substantial increases in phosphates and discovered increasing trend of protein and carbohydrate solubilization at pH range 7 to 11 with subsequent phosphate release. Similarly, Li et al. (2008) examined the

effect of high NaOH concentration on sludge treatment and found 60 to 71% of organic matter solubilization within 30 min reaction time from 0.05 mol L^{-1} of NaOH treatment. Bi et al. (2014) carried out two-stage alkali hydrolysis of sludge and reported 41.96% release efficiency of P in the form of monoammonium phosphate (MAP) by treating 16.44 g L^{-1} of sludge with 10 mol L^{-1} of NaOH within a pH range of 7.67 to 12.44. Kato et al. (2006) carried out alkaline dissolution of sludge followed by the precipitation of Ca-P compounds (i.e. amorphous calcium phosphate: $Ca_3(PO_4)_2 \cdot H_2O$ or monetite: $CaHPO_4$) from the supernatant to recover P using poly-aluminum chloride (PAC) and discovered the highest amount of soluble P at pH 12.

In a more recent study, Kim et al. (2015) analysed the release of total phosphorus (TP), inorganic phosphate (IP), and polyphosphate (poly-P) through alkali treatment under a range of NaOH concentration with pH between7.7 and 13.6. They recorded the increase of P release with the increase of alkali concentration and reported the release of 64%, 86%, 90% of TP; 21%, 17%, 16% of IP and 26%, 49%, 51% of poly-P at 0.02, 0.1 and 1 M NaOH concentrations, respectively.

All the aforementioned studies have investigated alkali treatments at various NaOH concentrations for P recovery; however, the optimal dose for P recovery has not been reported. Since P in sludge is associated with the sludge biomass cell, the amount of P in sludge is proportionally related to the total solids (TS) content, which significantly vary depending on the sludge source. Moreover, the concentration of NaOH reported by the previous studies may not be adaptable for other sludges as high TS content sludge would require higher dose of NaOH, even though the volume of sludges could be the same. The current study has addressed this knowledge gap by exploring the optimum NaOH dose based on the TS content of the sludge to optimize P recovery from the chemical sludge (containing alum: $Al_2(SO_4)_3 \cdot nH_2O$) using alkaline solution. The objectives of this study were: 1) to perform time-based study of P solubilization, 2) to fit the P solubilization experimental data to

appropriate models, and 3) to evaluate the optimal dose of NaOH for optimum P recovery as well as to investigate the P solubilization mechanisms.

3.2 Materials and Methods

3.2.1 Sludge characterization

The chemical sludge was collected from Headingley Wastewater Treatment Facility, Manitoba, Canada. Two sequencing batch reactors operating at the Headingley Wastewater Treatment Facility removed organic matter and ammonia nitrogen. Alum was added to precipitate P at the end of the aeration step before the settling phase. Two sets of sludge were collected for this study: 1) waste activated sludge (WAS) having 1.5% to 2.25% of TS, and 2) dewatered sludge (DS) having 18% of TS. Sludge was transferred to the laboratory and stored in the refrigerator at 4°C. Table 3.1 shows the characteristics of the sludge.

Table 3. 1: Characteristics of sludge samples

Properties	DS	WAS
Moisture Content (%)	82	98
Total Solids (%)	18	2
TP (g P kg^{-1} dry TS)	64.22	38.75
pH	5.9 ± 0.2	6.03 ± 0.2

3.2.2 Phosphorus solubilization

To compare the P solubilization between DS and WAS sludges, the DS sludge was diluted 2.25 to 4.5% to maintain comparable amount of TS in both sludges. Solubilization of P was carried out in Erlenmeyer flask containing 200 ml of sludge and each treatment was triplicated including the control. Stock solutions of 0.5, 1.0, 1.5 and 2.0 M NaOH were used for the alkali treatment. Volumes of 5, 10, 15, 20, 40, 60, or 80 ml of alkali solutions were used to obtain desired level of NaOH dose. The total reaction time was 100 min. Experiments were carried out at room

temperature (25°C). Samples of 10 ml were collected at intervals of 20 min and centrifuged at 3000 rpm for 20 min. Supernatant was collected and filtered using 1 to 5 µm plain filter paper for further analysis.

3.2.3 Analytical procedures

Supernatant was analysed for ortho-phosphate concentration (calorimetric method) using a Flow Injection Analyzer (FIA) (Quik Chem 8500, LACHAT Instruments, Loveland, CO, USA), following the Quik Chem ortho-phosphate method 10-115-01-1-O. Total phosphate (TP) content was determined by digesting the samples on the Kheldjal digester at 400°C and further analyzed by using the above-mentioned FIA. Dissolved aluminum concentration was determined using Inductively Coupled Plasma (Vista MPX: ICP-OES, Varian Inc., Palo Alto, CA, USA) with CCD array detector design. A pH meter (Oakton pH meter, Eutech Instruments, Singapore) was used to determine the solution pH. The sludge samples were dried in an oven at 105°C for 24 hours to determine the moisture and solid content.

3.2.4 Statistical analysis

Statistical analysis was carried out using SAS software for Windows 10 (SAS 9.4, SAS Institute Inc., Toronto, ON, Canada). Analysis of variance (ANOVA) was conducted on time-dependent solubilization data using PROC GLIMMIX for repeated measures in SAS 9.4 to determine main and interaction effects of dose and time on P solubility. Each sludge type was analyzed separately. Based on the Akaike Information Criterion (AIC), the heterogenous autoregressive (1) arh (1) was the most suitable covariance structure. Solubilization data was lognormally distributed, therefore the distribution “DIST” was specified as lognormal. Treatment means were compared at $\alpha = 0.05$ using the Tukey multiple comparison procedure. PROC REG and PROC NLIN procedures were also used to fit other experimental data to the linear regression (remaining P in sludge) and

nonlinear (exponential) regression (relationship between P in sludge and NaOH concentration) models respectively. The experimental data was fitted with the models based on the maximum value of R^2 and minimum values of root mean square error (RMSE) and coefficient of variance (CV). The slope and intercept of the linear regression model were considered significant at $p < 0.05$. PROC CORR procedure was used to compute Pearson Correlation Coefficients.

3.3 Results and Discussion

3.3.1 Change analysis of P

The study was conducted for 100 min with low and high doses of NaOH (g g^{-1} TS). The control treatments for both DS and WAS sludge showed no significant changes of P release over the experimental period (Table 3.2). The low dose of NaOH (0.09 g g^{-1} TS) was applied for two different methods using DS sludge with successive addition of 0.5 M NaOH solution for the first 60 min at a rate of 3.33 ml every 5 min and a required amount of NaOH solution was added at the beginning of the test for the second process. Successively adding NaOH solution gradually increased the P solubilization from 74 mg L^{-1} to 524 mg L^{-1} within 100 min, whereas addition of NaOH at the beginning significantly increased the P solubilization to 412 mg L^{-1} within the first 20 min. Although further P solubilization reached 545 mg L^{-1} at the end of 100 min treatment period for the second process, no significant difference was observed between P release at 20 min and 100 min. Same phenomenon was observed for all the treatments. For instance, NaOH doses of 0.53 g g^{-1} TS in DS sludge and 0.09 and 0.63 g g^{-1} TS dose in WAS sludge promptly increased the P solubilization to 695, 188, and 284 mg L^{-1} within the first 20 min, respectively. After the first 20 min of treatment period, no significant P solubilization trend was observed except for the successive addition of NaOH treatment, which confirmed equilibrium conditions within the first 20 min. Results corroborate with several other studies (Kim et al., 2015; Li et al., 2008) where

sludge disintegration and releasing of P from sludge reached equilibrium within the first 30 min of reaction time.

Table 3. 2: The effect of NaOH dose on the solubility of P from DS and WAS Sludges

	Dewatered Sludge (DS)				Waste Activated Sludge (WAS)		
NaOH dose → (g g^{-1} TS)	0	0.09	0.09	0.53	0	0.09	0.63
Treatment →	Control	Low [a]	Low [b]	High [c]	Control	Low [b]	High [c]
Time (min) ↓	P (mg L^{-1})						
0	75 g	74 g	80 hg	49 kj	5 fg	5 g	2 h
20	74 hg	220 ed	412 f	695 a	6 f	188 b	284 a
40	65 hi	353 d	426 fe	692 a	7 e	196 b	284 a
60	62 i	509 d	439 edc	708 a	7 e	196 b	284 a
80	53 j	530 cd	496 cb	711 a	10 d	201 b	289 a
100	46 k	517 b	545 cba	708 a	11 c	201 b	290 a

Effect	**Num DF**	**Den DF**	**F value**	**p-value**
Main Effect				
DS				
NaOH/TS ratio	3	1	718	<.009
Time	5	6	2033	<.0001
WAS				
NaOH/TS ratio	2	1	9283	<.007
Time	5	1	21973	<.005
Interaction Effect				
DS: NaOH/TS ratio * Time	15	6	384	<.0001
WAS: NaOH/TS ratio * Time	10	1	5987	<.0001

Note: The effect is significant when $p < 0.05$ at 95% confidence level.

Note:

[a] NaOH was successively added for the first 60 min at a rate of 3.33 ml (0.5 M NaOH) every 5 min.

[b] NaOH was added at the beginning of the test (0.5 M NaOH).

[c] NaOH was added at the beginning of the test (1.5 M NaOH).

The change in letters (a-e) suggest statistical significance at $p < 0.05$.

It was noticeable that for both NaOH addition processes (successive addition and instantaneous addition at the beginning), there was no significant difference of P release at the end of the 100 min treatment period (524 and 545 mg L^{-1} of P release for successive addition and addition at the beginning, respectively). The breakdown of most cells and flocs occurred within the first 20 min for the instantaneous addition of NaOH at the start of experiment and released most available P into solution, therefore, P solubilization peak was observed early in the process. Similar observations were reported by other studies (Bi et al., 2014; Li et al., 2008; Xiao and Liu, 2006), where highest solubilization occurred within the first 30 min of reaction period.

P present in the sludge as organic phosphate is very tightly embedded in the extracellular polymeric substance (EPS) which is mostly made up of proteinous, humic and nucleic substances. Application of NaOH provides the energy to overcome the binding force between sludge and organic phosphates (Wang et al., 2017), thereby enabling breakdown of the P bonding. Kim et al. (2015b) reported that poly-P release reached a maximum level within the first 30 min and then gradually decreased due to the hydrolysis of poly-P to inorganic phosphate, which was not observed from the P concentration in this study.

3.3.2 Phosphorus solubilization model

Several doses of NaOH were tested on both 4.5% TS in DS and 2.25% TS in WAS sludge. The relationship of remaining P in sludge (mg g^{-1} TS) after the treatment period with the equilibrium supernatant P and NaOH application rate was carefully investigated. Linear relationship was observed between the remaining P in sludge and the equilibrium P in solution for both sludges (Fig. 3.1 (a)), which validated the assumptions that the P solubilization was increased with increasing rate of NaOH doses and therefore, remaining amount of P in sludge was reduced. Table 3.3 illustrates the linear regression model as:

$$\text{DS:} \quad P_{sludge} = 65.92 - 0.032 \times P_{sup} \quad (1)$$

$$\text{WAS:} \quad P_{sludge} = 37.17 - 0.054 \times P_{sup} \quad (2)$$

Where, P_{sludge} represents P in sludge (mg g^{-1} TS) and P_{sup} represents P in supernatant (mg L^{-1}).

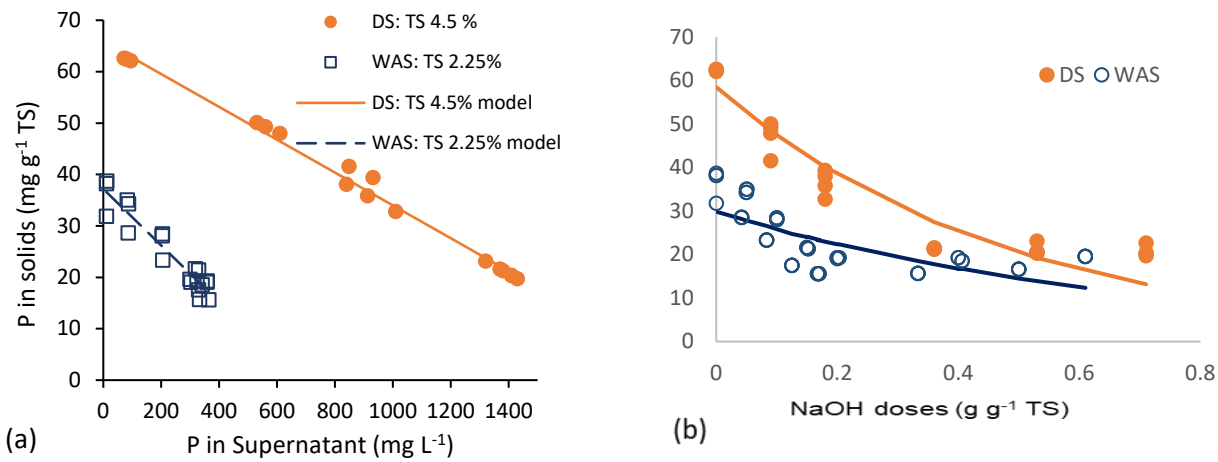

Figure 3.2. 1: P solubilization model. (a) Linear relationship between P in sludge and supernatant. (b) Two-step relationship (exponential and linear) between P in sludge and NaOH application doses.

Table 3. 3: Parameter estimation of the linear regression models in relation to P in sludge and equilibrium P in supernatant

Linear Regression Model: $P_{sludge} = a + bP_{sup}$

Sludge	Variable	DF	Parameter	SE	t Value	p-value	Root MSE	R^2	CV
DS	Intercept	1	65.92	0.64	102.99	<.0001	1.39	0.99	3.52
	Slope	1	-0.032	0.001	-48.03	<.0001			
WAS	Intercept	1	37.17	1.145	32.45	<.0001	2.51	0.91	9.94
	Slope	1	-0.055	0.004	-12.14	<.0001			

Note: P_{sup} = Concentration of P in supernatant (mg L^{-1}), P_{sludge} = Concentration of P in sludge (mg g^{-1} TS), a = intercept, b = slope, SE = standard error, SS = sum of square, MSE = mean square error, and CV = coefficient of variance.

The intercept and slope had a significant effect on the linear regression model ($p < 0.05$). The root MSE, R^2 and CV values validated the fitness of the data for both the linear and non-linear

regression models, although the model for DS was comparably a better fit (higher R^2 and lower root MSE and CV values) than the WAS sludge (Table 3.3). The models articulated that the P in DS and WAS sludges were 65.92 and 37.17 mg g^{-1} TS respectively (Equation 1 ~ 2), when there was no P in supernatant (P_{sup} = 0), which were very close to the original P values in raw sludges of 64.22 and 35.09 mg g^{-1} TS, respectively. The slopes of the regression lines indicated that the reduction of P in sludge was sharper for WAS than DS. For instance, one unit increase of P in supernatant caused 0.054- and 0.032-unit reduction of P in sludge for WAS and DS, respectively. The relationship between remaining P in sludge and NaOH application doses is depicted in Fig. 3.1(b). The remaining amount of P in sludge after the treatment, as an exponential function of the concentration of NaOH is given by the equation below. This modelled equation is described in Table 3.4:

$$\text{DS:} \quad P_{sludge} = 58.50\, e^{-2.1\, D_{NaOH}} \tag{3}$$

$$\text{WAS:} \quad P_{sludge} = 29.87\, e^{-1.45\, D_{NaOH}} \tag{4}$$

Where, P_{sludge} represents P in sludge (mg g^{-1} TS) and D_{NaOH} represents NaOH application dose in (g g^{-1} TS). Hence the general exponential model is given by:

Exponential model: $P_{sludge} = P_0 e^{-kD_{NaOH}}$

Table 3. 4: Parameter estimation of the non-linear models in relation to the amount of P in sludge and NaOH application doses

Sludge	P_0	k	RMSE
DS	58.50	2.1	5.07
WAS	29.87	1.45	4.99

The exponential model equations (Equations 3 & 4) exhibited that the available P for DS and WAS sludges were 58.50 and 29.87 mg g^{-1} TS for the treatments without the application of NaOH (D_{NaOH} = 0), which were close to the values of the blanks (62.43 and 36.27 mg g^{-1} TS for DS and WAS respectively). It is evident from the graph, that at high doses of NaOH (> 0.36 and > 0.2 g g^{-1} TS

for DS and WAS) resulted in no change in the available content of P in sludge and no further P solubilization was observed. The analysis confirmed that the NaOH doses up to 0.36 g g^{-1} TS for DS and 0.2 g g^{-1} TS for WAS were effective for P solubilization and the amount of NaOH beyond these doses could be considered as the excess amount.

The model equations became horizontal lines parallel to the x-axis having constant values of P in sludge around 21.50 mg g^{-1} TS for DS and 18.22 mg g^{-1} TS for the WAS, respectively. Similar values were observed for remaining P in sludge for DS and WAS at excess NaOH doses, although, the initial P content in DS was quite higher than the WAS. This demonstrated that the remaining P in sludge could be considered as unrecoverable amount of P (21.50 mg g^{-1} TS for DS and 18.22 mg g^{-1} TS for the WAS from this study) and the current NaOH application method is not effective to recover that fraction.

Application of NaOH causes the microbial cells to undergo lysis due to the turgor pressures and cell membranes become saponified (Tyagi and Lo, 2013). High pH facilitates electrostatic repulsion and desorption of EPS from sludge resulting in the transfer of intracellular P to the liquid phase. Exposure of high NaOH content to the sludge for an extended period enables break down of bonds between EPS and sludge and causes significant amount of P solubilization (Wang et al., 2017). The mechanism of P transformation from sludge to liquid is a complex phenomena and it could be assumed that some forms of P are more tightly bonded with sludge such as organic P associated with higher molecular weight compounds of humic and fulvic substances (Crews and Brookes, 2014), which are difficult to be released by the current NaOH application treatment method.

3.2.3 Effect of pH and TS on P solubilization

Further investigation was carried out to explore the relationship of solution pH and TS on the supernatant P concentration and recovered percentage of P from the sludge. The Pearson Correlation Coefficients (R^2) showed that pH was strongly correlated with the equilibrium supernatant P concentration and recovered percentage of P (Table 3.5). The solution pH increases with the increasing of NaOH application dose. Since, the NaOH doses influence the P content, the P solubilization rose up to a certain level, and this increasing level of pH also contributed to higher level of P solubilization, which is validated from the correlation analysis.

Table 3. 5: Correlation analysis – pH and TS versus supernatant P and percentage P recovered

Simple Statistics					**Pearson Correlation Coefficients**		
Sludge	**Variable**	**N**	**Mean**	**SD**	**Variable**	P_{sup}	P_{recov}
DS	pH	27	11.08	2.15	pH	0.81*	0.92*
	TS		3.33	1.26	TS	0.72*	0.29
	P_{sup}		780.27	418.92			
	P_{recov}		42.67	23.52			
WAS	pH	24	10.75	2.63	pH	0.91*	0.93*
	TS		1.97	0.32	TS	-0.41	-0.38
	P_{sup}		256.33	135.16			
	P_{recov}		35.72	19.89			

Note: P_{sup} = Supernatant P (mg L^{-1}), P_{recov} = percentage P recovered, TS = total solids percentage (%), N = Observation number, SD = Standard deviation about the mean. Parenthesis value indicates p-value. Asterisk (*) indicates significant correlations ($p < 0.0001$).

The average pH of solution at intervals and at the end of the entire experiment was around 11 ~ 13 for all treatments except the blanks. The amount of solubilized P was at its peak under this pH range, which has also been recorded in several studies for such sludge-alkali processes (García Becerra et al., 2010; Kato et al., 2006; Li et al., 2008), although Chen et al. (2007) reported highest soluble phosphate concentrations (≈ 150 mg L^{-1}) at pH 9 ~ 11.

Higher pH is beneficial to P solubilization since it leads to better hydrolysis of sludge flocs and protein cells, which in turn leads to breakdown of the innermost organic matter, subsequently

releasing and solubilizing P (Bi et al., 2014; García Becerra et al., 2010; Xiao and Liu, 2006). The proteinaceous materials of sludge contain P that undergoes microorganisms' metabolism processes (Tyagi and Lo, 2013). Hydrolyzation of organic P into inorganic P under neutral pH condition is a complicated process, eliciting lower P release in the blanks with deionized water. At higher pH range, the competition between NaOH and P to form compound with metals ions (Al, Ca, Fe, Mn etc.) plays important roles to release P from sludge. Strong alkaline conditions favour the hydrolysis of organic P compounds (proteins, polysaccharides, nucleic acids etc.) (Bi et al., 2014; Wang et al., 2017). Cell osmotic pressure of sludge biomass changes in presence of higher solution pH and causes cell lysis or solubilization of EPS and eventually releases P to the solution (Zhang et al., 2015). In conclusion, strong alkaline condition (high pH) enhanced solubilization of P. This solubilized P can be treated under the right conditions to generate inorganic fertilizer such as struvite ($MgNH_4PO_4$) and $CaHPO_4$ (Hester and Harrison, 2013; Ackerman, 2012; Hosni et al., 2008). Also, the resulting solution containing high concentration of aluminum could be rechannelled for P coagulation in WWTP after pH adjustment (Nguyen et al., 2022).

The percentage of total solids (TS) in the treatments were 4.5% and 2.25% for DS and 2.25% and 1.5% for WAS. It can be seen from Table 3.5 that TS was not significantly correlated with the recovered percentage of P for both DS and WAS. The correlation between TS and supernatant P was significant only for DS. The insignificant correlation between TS and P solubilization could be due the limited level or range of TS in the treatments employed in the current experiment. Further investigation is recommended to explore the relationship under a wide range of TS in the treatment solution.

3.3.4 Phosphorus recovery model

The percentage recovery of P from sludge after the treatment period was evaluated against a wide range of NaOH application doses (0 ~ 0.75 g g^{-1} TS) and the experimental data was fitted to the model to predict the optimum dose of NaOH for optimization of the P recovery process for both DS and WAS sludge (Fig. 3.2.2). It was observed that the percentage recovery of P was exponentially increased with the increase of NaOH application dose. The minimum value of root-mean-square error (RMSE) and coefficient of variance (CV) about RMSE and the maximum value of R^2 illustrated that the data was a good fit to the following exponential models:

$$\text{DS:} \quad P_{recov} = 69.998\left(1 - e^{-5.167 D_{NaOH}}\right) \tag{5}$$

$$\text{WAS:} \quad P_{recov} = 54.658\,(1 - e^{-9.097 D_{NaOH}}) \tag{6}$$

Where, P_{recov} represents recovered percentage of P and D_{NaOH} represents NaOH application doses (g g^{-1} TS).

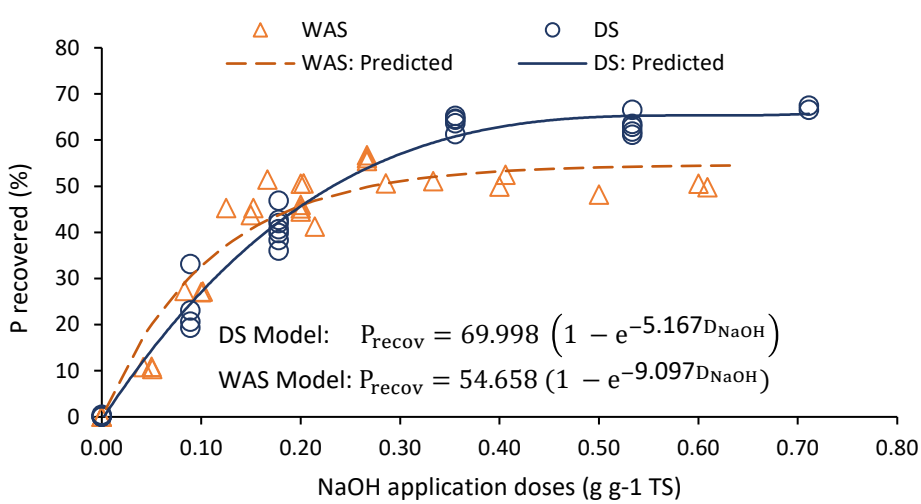

Figure 3.2. 2: Exponential model for percentage P recovered to predict the optimum NaOH application dose.

The RMSE, CV and R^2 values indicated that the model was a better fit for DS than WAS in terms of higher R^2 value and lower RMSE and CV values (Table 3.6). Equations (5 and 6) illustrated that the maximum recoverable percentages of P (P_{max}) could be predicted as 70% and 55% for DS

and WAS, respectively, using unlimited amount of NaOH (when $D_{NaOH} = \infty$). The experimental data showed that the maximum recovered percentages of P were 67% and 56% (predicted values: 68.2% and 49.8%) with the NaOH application doses of 0.71 and 0.27 g g^{-1} TS from the DS and WAS, respectively. The t-tests of P recovery percentages between the NaOH doses of 0.20 and 0.61 g g^{-1} TS for DS and 0.36 and 0.6 g g^{-1} TS for WAS exhibited no significance difference (p values: 0.06 and 0.12, respectively). This phenomenon confirmed that the higher dose of NaOH beyond 0.36 g g^{-1} TS for DS and 0.20 g g^{-1} TS for WAS sludge did not have a significant effect on further P recovery. The reason could be the existence of tight bonding of P in biomass cells, which did not break down by employing only NaOH. Chen et al. (2003) and Wang et al., (2017) highlighted five types of substances containing P in sludges: aromatic protein I, aromatic protein II, fulvic acid, microbial by-product, and humic acid like substances. Among these five groups, P is more tightly bonded with humic acid like substances and simultaneously, humic acid like substances are very stable and not easily biodegradable (Muller et al., 2014). But high doses of NaOH (i.e. high alkaline condition) could break down most of the bonding between P and humic like substances in the sludge.

Table 3. 6: Parameter estimated from the non-linear exponential model of percentage P recovery and NaOH application dose

Exponential model fitting: $P_{recov} = P_{max}(1 - e^{-kD_{NaOH}})$					
Sludge	P_{max}	k	R^2	RMSE	CV
Dewatered Sludge (DS)	69.998	5.167	0.973	3.878	9.09
Waste Activated Sludge (WAS)	54.658	9.097	0.960	5.124	13.54

The increase in recovered percentage of P was significant for NaOH application doses up to 0.36 g g^{-1} TS for DS and 0.20 g g^{-1} TS for WAS, which were considered optimum doses for P recovery from sludge. The optimum NaOH doses correspond to the application of 80 ml and 40 ml of 1 M

NaOH solution in 200 ml DS sludge having 4.5% and 2.25% TS, respectively. Similarly, applications of 20 ml and 15 ml of 1 M NaOH solution in 200 ml sludge corresponding to 2.25% and 1.5 % TS were optimum doses for the WAS sludge. The experimental data revealed that 64% and 48% of P were recovered from the DS and WAS sludges at the optimum doses of NaOH, while the recovery models exhibited 59% and 46% of P recovery, respectively. Several previous studies have highlighted the alkali dissolution of P from sludge, but none of the studies emphasized on the optimum alkali dose for the sludge treatment (i.e. g of NaOH use per g of TS) to recover P. One such study by Bi et al. (2014) recorded 42% release efficiency of P in the form of monoammonium phosphate (MAP) within 30 ~ 60 min under the pH range of 10.5 ~ 12.44, where the recovery percentage was less than the current study. In another study, Kato et al. (2006) exhibited the highest P dissolution of 60% from the poly-aluminum chloride (PAC) treated sludge at pH 12 followed by 50% of P recovery from the supernatant in the form of Ca-P precipitation. Another recent study reported about 80% of P leaching after 2 h of treatment duration from PAC treated sludge using 1 M NaOH (Ali and Kim, 2016). Similarly, Kim et al. (2015) recorded an increase in P release with the increase in NaOH concentration under pH 7.7 ~ 13.6 and observed 64%, 86%, 90% of TP release with 0.02, 0.1 and 1M NaOH, respectively. All these previous studies reported the concentration of NaOH used in the treatment for the P recovery, which may not be adaptable for other sludges as different sludge has different TS content. The TS content of sludge varies significantly among the different sources of sludge; therefore, the required amount of NaOH for optimal P recovery would also vary accordingly. Henceforth, it is important to explore the optimum NaOH dose based on the TS content of the sludge to optimize P recovery and the current study has addressed this knowledge gap.

Figure 2 illustrated that the recovered percentage of P for WAS is higher than DS when NaOH application dose was 0 ~ 0.2 g g^{-1} TS. At higher NaOH dose, P recovery was almost negligible for WAS, but kept increasing for DS up to the NaOH dose of about 0.36 g g^{-1} TS. The reason could be due to the presence of higher amount of TP in DS than WAS with the values 64.22 and 35.09 mg g^{-1} TS, respectively. When the content of P in sludge reached to 21.50 mg g^{-1} TS for DS and 18.22 mg g^{-1} TS for the WAS, no further significant P recovery was observed, which confirmed that this fraction of P was very tightly bonded with sludge biomass cells and could be incorporated with other technological approaches in a sequential manner along with the current treatment option to recover this fraction of P. For instance, Kim (2014) reported higher percentage of P release than the organic compounds' solubilization with thermal treatment and later on recorded about 94% of P release with the combined application of thermal and alkali treatment (Kim et al., 2015). In this study, it was clearly visible that the optimum dose of NaOH and the corresponding recovered percentage of P were expressively higher for the sludge having high content of initial P than the sludge with lower initial P concentration. Herein, initial P concentrations of DS and WAS sludges were 64.22 and 35.09 mg g^{-1} TS, whereas the optimum doses of NaOH were 0.36 and 0.2 g g^{-1} TS, and corresponding P recovery percentages were 64% and 48%, respectively. At the end of the treatment period, the unrecovered concentrations of P in sludges were almost the same for both sludges, which showed that the remaining amount of P in sludge (unrecovered P concentration) were 21.50 and 18.22 mg g^{-1} TS after the treatment at optimum NaOH doses. To summarize, the initial P concentration of sludge influenced the determination of optimum doses of NaOH and the prediction of optimum P recovery percentages.

As the NaOH application dose increased from 0.09 to 0.6 g g^{-1} TS, P release increased from 24% to 63% for DS, and from 27% to 48% for WAS, respectively, whereas the recovered percentage

of P was almost zero for the blanks. Kim et al. (2015) reported about 26% of more P release with 1 M NaOH treatment than 0.02 M NaOH treatment. Moreover, the P releasing rate was much higher at low NaOH concentration than the rate of organic carbon solubilization and the selective release of P was decreased with the increase in NaOH concentration (> 0.005 M) as compared to the organic carbon solubilization (Kim et al., 2015).

3.3.5 Mechanisms of P solubilization in chemical sludge

High solution pH contributed to substantial amount of P release from both sludges. Table 3.7 showed that significant amount of P was released, i.e. 319.9 and 388.4 mg L^{-1} of P with the NaOH application doses of 0.15 and 0.20 g g^{-1} TS, respectively, from the WAS sludge having 2.25% of TS after the treatment duration, which was significantly higher than the blanks. Phosphorus exists in proteins and nucleic acids of sludge cell as well as in the phospholipid's bilayer of cell membrane of sludge biomass. The cell membrane starts disrupting when pH is higher than 10 and proteins and nucleic acids become hydrolyzed, consequently, P is released from the sludge (Bi et al., 2014).

Table 3. 7: Release of Al and P from WAS sludge having 2.25% of TS

Sampling Time	NaOH dose (g g^{-1} TS)	pH	Al (mg L^{-1})	P (mg L^{-1})
Before Treatment	0	5.6	0.45 c	18.6 c
After Treatment	0.15	11.01	380.3 b	319.9 b
After Treatment	0.20	12.6	610.0 a	388.4 a

Means within a column followed by the same alphabet are not significantly different from each other at $p \leq 0.05$

The release of Al was analogous to the release of P illustrating that $AlPO_4$ and $Al(OH)_3$ could dissolve efficiently under strong alkaline condition. Xu et al. (2018) reported that the concentration of Al increased up to a certain level and became stable when dissolution of $AlPO_4$ and $Al(OH)_3$

was stopped, but P concentration continued to increase due to the continuous release of P from the sludge biomass. The molar ratios of Al and P were 1.36 and 1.80 after the treatment duration with NaOH application doses of 0.15 and 0.20 g g^{-1} TS, respectively. Since the ratio of Al/P (mol/mol) in $AlPO_4$ is 1, it could be assumed that $Al(OH)_3$ was released and more P was adsorbed by $Al(OH)_3$, which increased the Al/P ratio greater than 1. The ratio of Al/P was also increased with the increase in NaOH application dose.

3.4 Conclusion

This study was conducted to investigate the optimum doses of NaOH required for the optimization of P recovery process by using dewatered sludge (DS: 4.5% and 2.25% TS) and waste activated sludge (WAS: 2.25% and 1.5% TS). Phosphorus solubilization process reached equilibrium within the first 30 min of treatment period and solubilization occurred in two steps: exponentially (at NaOH doses of 0 ~ 0.36 and 0 ~ 0.2 g g^{-1} TS for DS and WAS) and then remained unchanged (at NaOH doses > 0.36 and > 0.2 g g^{-1} TS for DS and WAS). The percentage P recovery models showed that optimum NaOH doses were 0.36 and 0.2 g g^{-1} TS for DS and WAS, respectively, and the corresponding P recovery percentages were 64% and 48% from experimental data and 59% and 46% from the proposed models. P recovery percentage greatly influenced by the initial P concentration of the sludge and further exploration is recommended using sludges having a wide range of initial P concentration, as the current study is investigated with only one type of sludge with two levels of initial P concentration in sludges. The model could be tested for other sludges to analyze how well they fit. In addition, the experimental rate could be repeated several times to develop a kinetic model that showcases P solubilization rate for the first 20mins of the process which was an intent in the initial set-up of the experiment.

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CHAPTER 4

BIOAVAILABILITY STUDY OF PHOSPHORUS IN ALUM-PHOSPHORUS SLUDGE USING SWITCHGRASS

4.0 Abstract

The study investigated biomass yield and the uptake of phosphorus (P) and aluminum (Al) by switchgrass grown in a low-P soil amended with alum-P sludge and a conventional fertilizer, monoammonium phosphate (MAP), at rates of 9.7, 19.4, 29.1 and 38.8 mg P kg^{-1} dry soil. Potted soil (amended and control) units were seeded with pre-germinated switchgrass and harvested three times at 50-day intervals. Over the three growth cycles, P from alum-P dewatered sludge gradually became available. Amendment rate showed no significant effect on switchgrass biomass yield. P availability was greater for alum-P sludge than MAP and this may have been enhanced by the properties and activities of the plant root system. Aluminum uptake by switchgrass increased with the number of cycles but did not differ significantly among treatments. Cumulative Al uptake over the 3 cycles was greater for below-ground biomass than for above-ground biomass. Maximum P recovery efficiency of 28% was achieved at the 9.7 mg P kg $soil^{-1}$ rate. These results demonstrate that alum-P sludge is an effective source of available P for cropping switchgrass in a high pH and low Olsen-P soil.

4.1 Introduction

The reuse of sludge-P as a form of fertilizer is critical to ensure the non-renewable nutrient P is maximally utilized. As an indispensable and irreplaceable element for living organisms, P is a limiting nutrient in agriculture since it is a major determinant of plant growth (Sattari et al. 2012; Syers et al. 2008). Many studies have raised concern over the depletion of finite P reserves; with some projecting that P will be depleted within 50 to 100 years (Cordell et al. 2009; Smil 2000)

while others believe it would last further into the future (Syers et al. 2008; Vaccari 2009). A 2011 US Geological Survey report inferred that world P reserves are about 65 billion metric tonnes, with the bulk of these reserves in Morocco, Algeria and China (Jasinski 2011; Roberts and Stewart 2002; Cooper et al. 2011). While P finite depletion is in clear view, there is a continuous rise in world population, meaning enough fertilizer is needed to feed and cater for the rising population (Yan et al. 2010; Cordell et al. 2012). Whether or not these projections are exact, one cannot deny the challenges P extinction may pose and the need for efficient use and distribution of this non-substitutable resource. Wastewater, a major carrier of nutrients, is constantly being treated for P and other nutrients; this is with the intent of recovering P, thereby preventing eutrophication, which would result in excessive algal growth (Smil 2000; Cordell et al. 2009). The agricultural sector currently consumes over 90% of mined P, meaning there is every reason to reclaim all forms of P (Vaccari 2009; Roy 2017; Cordell et al. 2009). Exploring all options of P recovery is crucial at this stage. Both chemical and biological methods have been applied to treat wastewater of nutrients such as P with the generation of sludge depending on the actual method used (Tchobanoglous et al. 2003; Droste and Gehr 2018). Alum-P sludge is generated from the use of alum salts as flocculants, a process widely-utilized by over 80% of wastewater treatment plants in the United Kingdom (Peter and Augustine 2018).

Noteworthy is the fact that most smaller communities in Manitoba, Canada generally practise chemical precipitation of wastewater since aluminum salts are generously abundant, making it an easy and reliable method of conventional wastewater treatment (Berg et al. 2007; Desmidt et al. 2015; Tchobanoglous et al. 2003). This method prevents issues of capital cost and instability of microbes associated with biological wastewater treatment (Stratful et al. 1999; Morse et al. 1998). Common practice is to landfill chemical sludge since it has little, or no reuse options and landfilling

is considered an emergency option and not a beneficial option. As part of its masterplan, the City of Winnipeg is interested in land application of sludge for economic reasons and for the beneficial reuse of nutrients (City of Winnipeg 2014).

Alum-P sludge can serve as a useful source of P for high biomass crops which can be used for biofuel. Depending upon the level of Al present in the sludge and more especially the pH of the receiving soil, it is possible to induce Al toxicity which can affect the growth of the plant (Yang et al. 2015; Smoliński et al. 2009; Kluczka et al. 2017). Barszczak and Bilski (1983) investigated some species of wheat and their adaptability to concentrations of Al in soil stating that above concentrations (soluble Al) of 2.4 mg kg^{-1}, the crop is less tolerant to Al and stresses such as reduced shoots, roots, heat stress and drought can be easily noticed. Koslowsky and Boener (1989) showed that plant growth, Al content and P uptake were related. Plant growth and P uptake decreased with increasing Al concentration in the soil when tested in pot experiments of 0.5, 2.0 and 5.0 mM Al concentrations; however, the Al effect on the plant growth was less at high P than at low P concentration (Koslowsky and Boener 1989).

The overall objective of this study was to determine the availability of P in alum-P sludge compared to commercial fertilizer (MAP) using switchgrass. The choice of switchgrass was due to its perennial nature, adaptability even on marginal lands and high biomass yield which is a readily available source for biofuels. It was hypothesized that (1) P uptake would be in the order of MAP > alum-P sludge > unamended soil. (2) Uptake of Al by plants will be less due to the soil pH; (3) P uptake decreases with continuous cropping; and (4) biomass yield decreases with continuous cropping. In order to achieve efficient utilization of the P, amendments are applied on P basis as this would protect surface water quality (Nelson and Janke 2007; Shock and Pratt, 2003).

4.2 Materials and Methods

4.2.1 Phosphorus sources

The dewatered sludge (18% total solids content) used in this study was collected from the Headingley wastewater treatment plant in Manitoba, Canada (49°52' 25.4" N; 97°26'16.1" W). The sludge was transported in plastic bags in a cooler and then stored in a refrigerator at 4°C prior to analysis to minimize microbial activity.

Phosphorus application was based on the bicarbonate-extractable P (Olsen-P) concentration of the sludge in order to aid treatment comparison between sludge and MAP, but also because much of the total P in the sludge was not expected to be available for plant uptake in the short term. Nonetheless, caution is needed when basing sludge application on available (bicarbonate-extractable) P concentration since the excessive amounts of total P added with the sludge may become available over time. Additionally, it is possible that bicarbonate-extractable P may underestimate the amount of sludge P that is actually bioavailable.

4.2.2 Soil

The study was conducted using surface soil (0-15 cm) from Roseisle, Manitoba, Canada (49°33.577' N; 98°24.824' W). The soil was a well-drained Entisol (dark-grey sandy Gleyed Regosolic sand). The soil was previously cropped to soybean in 2014 and 2015 and had a low Olsen P concentration of 3 mg kg^{-1} and a pH of 8.2 (Table 4.3). Prior to the start of the bioassay, soil was analyzed for plant available [(Olsen or bicarbonate-extractable) P (extraction with 0.5 M $NaHCO_3$ at a pH of 8.5 (Olsen et al., 1954) using the ascorbic acid-molybdate method (Murphy and Riley, 1962) and a Skalar SAN++ segmented flow analyzer (Skalar Analytical B.V., Breda, Netherlands)], nitrate concentration (Cd reduction method; Mulvaney, 1996); exchangeable Ca, Mg, K, and other cations [atomic absorption spectroscopy following extraction of 5 g of soil with 33 mL of 1 M NH_4OAc at pH 7 (Hendershot et al., 2008)]; cation exchange capacity (summation

of exchangeable Ca, Mg, K, and Na); electrical conductivity and pH (1:1 soil/water suspension); soil organic matter (SOM) concentration [loss on ignition method (Nelson and Sommers, 1996)]; soil organic carbon (SOC) concentration (multiplying SOM by 0.58); and carbonates [pressure calcimeter method (Loeppert and Suarez, 1996), expressed as calcium carbonate equivalent (CCE)].

The soil was thoroughly mixed and passed through a 4-mm sieve to remove roots and stones, air-dried and stored until the start of the experiment. Approximately 1.5 kg of air-dried soil was weighed into plastic pots (14.9 cm diameter x 16.5 cm height). All pots were watered with reverse osmosis water with a full-strength nutrient solution without P (Zvomuya et al., 2006) (Table 4.2) to bring the soil moisture content to field capacity. The pots were then stored in a growth chamber for 24 h before planting.

4.2.3 Experimental set up

The experiment was carried out in a growth room maintained at a day/night temperature regime of 25/15°C, relative humidity of 60% and a corresponding photoperiod of 16 h. The experiment was laid out as a completely randomized design with a factorial treatment layout of two P sources × four P application rates. All treatments were replicated three times and included control pots. The P application rates on a dry weight basis were 0, 9.7, 19.4, 29.1 and 38.8 mg P kg^{-1}dry soil, which corresponds to 0, 52, 103, 155 and 206 kg ha^{-1} P. The pots were supplied with essential macronutrient solutions as described in Table 4.2; these solutions were added once for each growth cycle. The pots were weighed and watered every day to replenish moisture lost by evapotranspiration.

Table 4. 1: Dewatered Sludge Properties from Headingley Wastewater Treatment Plant

Sludge Properties	
Moisture content (%)	82
Total solid (%)	18
VSS	
TP (g P kg^{-1}dry TS)	64.22
pH	5.9 ± 0.2
Bicarbonate extractable-P (mg kg^{-1})	808
NH_3-N (mg kg^{-1})	73.84
Al (mg kg^{-1})	10995
Mg (mg kg^{-1})	815.83
K (mg kg^{-1})	916.2

Table 4. 2: Composition of nutrient solution (Zvomuya et al. 2006)

Nutrient	Source	Rate (mg kg^{-1} soil)
N	NH_4NO_3	100
K	KCl	100
S	$MgSO_4.7H_2O$	20
Zn	$ZnCl_2$	4.0
Mn	$MnCl_2.4H_2O$	2.0
Mo	$NaMoO_4.5H_2O$	0.4
B	H_3BO_4	1.0
Cu	$CuSO_4.5H_2O$	1.0

Fe	Fe.EDTA	4.0

Table 4. 3: Selected chemical properties of the soil

Properties	Roseisle
Nitrate (mg kg^{-1})	33.6
Olsen P (mg kg^{-1})	3
Potassium (mg kg^{-1})	46
Organic C (g kg^{-1})	25
Carbonates (CCE) (g kg^{-1})	12
Soil pH	8.2
Cation exchangeable capacity $cmol_c$ kg^{-1}	25.1
Sulfur (mg kg^{-1})	26.9
Baron (mg kg^{-1})	2
Zinc (mg kg^{-1})	0.44
Iron (mg kg^{-1})	32.3
Manganese (mg kg^{-1})	1.7
Copper (mg kg^{-1})	0.2
Magnesium (mg kg^{-1})	912
Calcium (mg kg^{-1})	3402
Sodium (mg kg^{-1})	86
Electrical conductivity (dS m^{-1})	0.25

Switchgrass seeds were pre-germinated in a potting-mix for 4 wk to ensure growth uniformity after which four uniform plants were transplanted into already prepared pots and further thinned to three plants after 2 wk. Three crop growth cycles of 50 d were tested in this study. Switchgrass was

harvested 50 d after transplanting by cutting at 8 cm above the soil surface to ensure easy regrowth. This was uniformly carried out for all pots. Harvested biomass was weighed, placed in paper bags and oven-dried for 72 h at 60°C. Oven-dry biomass samples were weighed for yield, chopped into bits and fine-ground in a mill grinder (< 0.2mm, Model 8000D Spex Sample Prep, Metuchen, NJ). Soil subsamples were taken after the last growth cycle. Roots were washed with reverse osmosis water and then air-dried.

4.2.4 Laboratory analysis

Total P (TP), potassium (K), calcium (Ca), magnesium (Mg) and aluminum (Al) concentrations in plant tissues and roots were determined using the wet oxidation method in which plant tissue samples were digested with H_2SO_4 (99.7%) and H_2O_2 (30%) in an acid block digester (Parkinson and Allen, 1975). The concentrations of the elements in the digested solution were then measured using an inductively coupled plasma optical spectrophotometer (ICP-OES Thermo Electron ICAP 6300 Radial). Available P concentration in soil was determined using the Olsen P $NaHCO_3$ (99.7%) extraction method (Olsen et al. 1954; Olsen and Sommers 1982).

3.2.5 Statistical Analysis

Analysis of variance was performed using the GLIMMIX procedure of SAS (SAS Institute Inc., 2012). P source, cycle and rate were modeled as fixed factors while growth cycle and replicates as a repeated measure. Treatment means were compared using the Tukey–Kramer multiple comparison procedure at $\alpha = 0.05$. Phosphorus recovery efficiency (PRE) for each harvest was calculated as [(uptake in P treated soil – Uptake in control) ÷ P application rate] and % PRE was normally distributed according to Shapiro Wilk's W-test from PROC Univariate in SAS. For P uptake, biomass yield and PER, rate main effects and interactions were partitioned into linear and quadratic components. Regression equations were fitted to the response data, using PROC REG in

SAS 9.4, and the regression coefficients compared, only if the orthogonal contrasts were significant.

4.3 Results and Discussion

4.3.1 Phosphorus uptake

Averaged across growth cycles, there was a significant cycle by treatment interaction for P uptake (p = 0.006; Table 4.4). In the first cycle, there was no significant difference in P uptake between alum-P sludge and MAP. Both cycles 2 and 3 showed a significantly greater P uptake for alum-P sludge than for MAP (Fig. 4.1). Phosphorus uptake from MAP did not differ significantly among the three cycles, although there was a slight decrease in the uptake with increasing cycles. On the other hand, alum-P sludge amended plants showed an averaged increase in P uptake concentration of 33.8% across all rates in Cycle 3 relative to Cycle 1. The decreased uptake for MAP could be as a result of inorganic P being bound to soil metals of calcium and magnesium. The increase in P uptake from sludge indicates a gradual release of P from the organic source over time through the mineralization process (Lee et al. 2009). Missaoui et al. (2005) in their growth room study of genetic variation and heritability of P uptake in Alamo switchgrasss experienced an increase in biomass P concentration. They speculated this was due to the type of fertilizer used in the analysis (soluble ammonium phosphate) and its high application rate (Missaoui et al. 2005). Phosphorus accumulation in root (P recovered in the root calculated as P concentration in root multiplied by the mass of the root) biomass was significantly different among P sources, with alum-P sludge resulting in the highest uptake compared to MAP and the control ($p < 0.0001$; Table 4.5). Switchgrass could access more P from alum-P sludge than MAP using its root system as P is gradually being released from alum-P sludge (Kering et al. 2012). The gradual release of P in the sludge amended soil could mean that P loss is minimized as the remaining P in the soil is preserved

in the soil P–pool for future use (Vanden Nest et al. 2015; Sattari et al. 2012). The larger amount of total P added from alum-P sludge (relative to MAP) likely produced a larger residual P pool in sludge-amended soil. Previous studies have demonstrated the importance of utilizing and accounting for the role of this residual P pool (both labile and non-labile forms) in the face of a looming P decline as well as the environmental challenges associated with excessive residual P in the soil (Sattari et al., 2012; Al-Rohily et al., 2013; Neidhardt et al., 2019).

Table 4. 4: Switchgrass biomass yield, P uptake and phosphorus recovery efficiency (PRE) as affected by P source and rate in a low Olsen-P soil[*,**]

Effect	P Uptake *mg kg^{-1} soil*	Biomass Yield *mg kg^{-1} soil*	PRE (%)
P source (P)			
Control	2.35	2891a	–
MAP	3.30	3636a	3.89
Sludge	5.31	3986a	15.62
Application Rate (R) *mg kg^{-1} soil*			
0	2.35b	2891a	–
9.7	3.89ba	3762a	15.88
19.4	4.30a	3815a	10.05
29.1	4.56a	3912a	7.60
38.8	4.48a	3776a	5.50
Cycle (C) (50-day/cycle)			
1	3.95	4600b	4.02b
2	4.42	7794a	11.02a

3	4.55	8828a	14.23a
P values			
P source	<.0001	0.36	0.0001
Rate	0.58	0.99	0.03
Linear (P_{lin})	0.2440	0.7152	0.0022
Quad (P_{quad})	0.5295	0.9326	0.3683
Cycle	0.16	<.0001	0.0002
P × R	0.68	0.40	0.03
C × R	0.94	0.44	0.17
C × P	0.006	0.50	0.17
C × R × P	0.10	0.22	0.91

* Means within a column followed by the same letter are not significantly different from each other at p ≤0.05; ** Quadratic effects, tested separately for the two P sources (consistent with the significant P rate x P source interaction) were not significant for PRE at α = 0.05

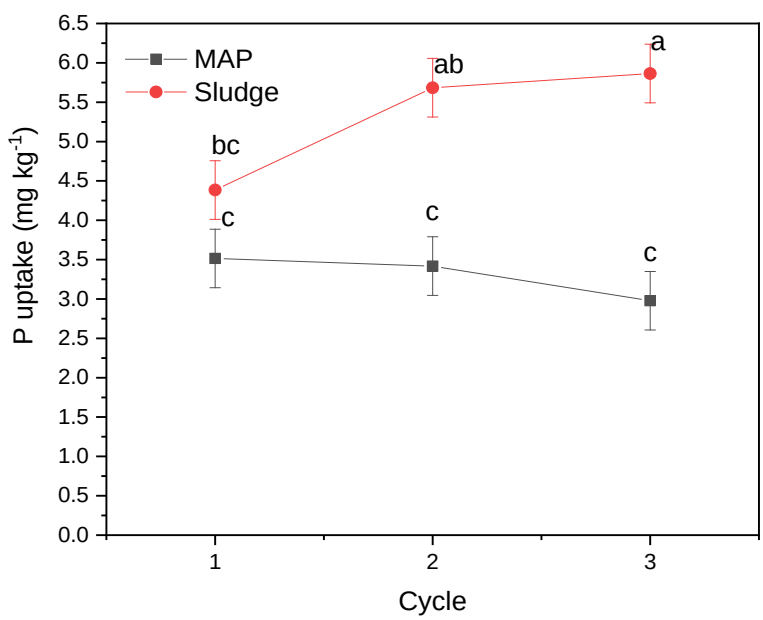

Figure 4. 1: Phosphorus uptake response to cycle and P source interaction over 3 harvest cycles

There was also a significant P source effect on cumulative P uptake (Table 4.5). Averaged over P sources for above and below ground P uptake, alum-P treated pots had significantly higher P uptake than MAP. Cumulative P uptake in MAP was also significantly greater than the control. Cumulative above and below ground P uptake were significantly affected by application rate, with an increase in P uptake seen up to the application rate of 19.4 mg P kg^{-1}. Further increase in application rate had no significant effect on P uptake. This result is consistent with that reported by Kering et al. (2012) which indicated that the effect of P fertilizer on switchgrass showed no further effect on P uptake above application rate of 15 kg P ha^{-1} of triple superphosphate in both Ardmore and Waurika locations (both soils were low Olsen-P soils with 3.1 mg P kg^{-1} and 3.4 mg P kg^{-1} and pH of 6.1 and 5.9, respectively).

Generally, all alum-P sludge amended pots had an average of about 56% increase in P uptake relative to pots amended with MAP over all cycles. The highest uptake of P from alum-P sludge was different for each harvest. Switchgrass in alum-P sludge pots had 24.7%, 66.3% and 96.9% greater P uptake than MAP in the first, second and third cycle of harvest, respectively. The P uptake was significantly greater from alum-P sludge, suggesting that it is a suitable source of P for growth of switchgrass when compared to MAP. The ability of switchgrass to thrive even in low P conditions while scavenging for nutrients is revealed (Popp et al. 2018; Kering et al. 2012) as pots with alum-P sludge actually out-performed MAP amended pots in P uptake. In addition, alum-P sludge amended pots had P uptake 2 to 4 times more than pots without any treatment while there was 1.5 times increase in P uptake in alum-P sludge compared to MAP. Bah et al. (2006) reported a 3 to 4 times increase in P uptake for Setaria plants grown with green manure when compared to

rock phosphate and this was attributed to the mobilization of soil P due to decomposition products of the manure (pH of 4.8 and Olsen-P of 10.9 mg P kg^{-1}) (Bah et al. 2006).

There was a slow release of P from alum-P sludge as suggested by the gradual increase in P uptake relative to the cycle (Figure 4.1). Factors not considered in this study that may affect nutrient uptake of switchgrass include timing of the harvest (Brodowska et al. 2018), also, the length and diameter of the root in addition to the soil P availability, which is dependent on the concentration of phosphate ions in soil solution and soil-P buffer capacity (Syers et al. 2008; Sattari et al. 2012).

4.3.2 Soil TP and Olsen P concentrations

Soil total P concentration at the end of the experiment differed significantly among P sources ($p=0.001$; Table 4.5). Alum-P sludge pots showed a significantly higher TP value compared to MAP and control. This was most likely due to the fact that the sludge was added based on Olsen-P content, resulting in the addition of much higher TP compared to MAP.

Olsen P concentration after the three cycles did not differ significantly among P sources ($p = 0.65$; Table 4.5).

Table 4. 5: Cumulative effect of rate of alum-P sludge and MAP on switchgrass*

Effect	Total Biomass Yield *g kg^{-1} soil*	Total-P Uptake *(mg kg^{-1} soil)*	Total-Al Uptake *(mg Al kg^{-1} soil)*	Root-P Uptake *(mg kg^{-1} soil)*	Root-Al Uptake *(mg Al kg^{-1} soil)*	Soil Olsen-P *(mg kg^{-1} soil)*	Soil TP *(mg kg^{-1} soil)*
P source							
Control	18.55a	13.51c	68.56a	6.35c	30.03a	7.48a	278.65b
MAP	25.17a	20.11b	101.24a	10.31b	49.24a	13.33a	292.26b
Sludge	25.28a	31.43a	107.43a	15.40a	37.22a	14.91a	414.23a
Rate							
0	18.55a	13.51c	68.56a	6.35b	30.03a	7.48a	278.65a
9.7	24.62a	20.52b	105.21a	9.35b	33.91a	12.28a	320.16a
19.4	26.44a	26.45a	124.64a	13.97a	56.75a	12.08a	374.47a
29.1	25.36a	27.34a	97.79a	14.08a	46.15a	16.37a	356.56a
38.8	24.76a	27.01a	94.66a	13.79a	38.96a	17.24a	345.57a
P value							
P source	0.96	<0.0001	0.72	<0.0001	0.12	0.65	0.001
Rate	0.95	0.007	0.63	0.004	0.22	0.62	0.62
P source × Rate	0.60	0.64	0.90	0.53	0.29	0.91	0.59

* Means within a column followed by the same letter are not significantly different from each other at $p \leq 0.05$

As reported by Olsen and Sommers (1982), plant productivity requires at least 10 mg kg^{-1} soil concentration as measured by the Olsen-P test; both MAP and alum-P sludge amended pots had adequate levels of available P to support plant growth. Note that differences in Olsen-P were only accounted for in this analysis at the end of the third cycle.

4.3.3 Biomass yield

Analysis of variance showed that there was a significant difference in biomass yield among growth cycles averaged across treatments ($p < 0.0001$; Table 4.4). Biomass yield (calculated as the mass of yield/weight of soil in pot) was significantly greater in cycles 2 and 3 than in cycle 1, but there was no significant difference between cycles 2 and 3. Since switchgrass is a perennial crop, the first year of growth is mostly characterized by a low biomass yield (Giannoulis et al. 2016). Increase in yield in cycles 2 and 3 relative to cycle 1 could be as a result of better development of the switchgrass roots and their ability to scavenge for P.

Dry matter yield was not significantly different between sludge and MAP amended soils. However, the concentration of P (P concentration data not presented) in the harvested biomass was higher for alum-P amended soil than for MAP amended soil.

According to Kering et al. 2012, biomass yield for switchgrass at amendment rates (0, 15, 30, 45 kg P ha^{-1}) showed no significant difference except for the highest application rate of 45 kg P ha^{-1} which was 17% higher in yield. This analysis was done on a thermic udic Argiustolls (pH = 5.9 and Olsen-P = 3.4) with the application of triple superphosphate from 2008 to 2012. The non-response to application rate was attributed to precipitation issues during its vegetative season (Kering et al. 2012).

Sanderson et al. (2001) reported an increase in switchgrass yield with increasing N application rates (0, 50, 100, 150 and 200 kg N ha^{-1}) of dairy manure in an acidic thermic udic Paleustalf

(Olsen-P of 8.5 mg kg^{-1} soil). The differences in biomass yield were attributed to the volatilization of ammonia from lagoon effluent and solid manure and also the slow mineralization of N in solid manure (Sanderson et al. 2001).

With similar biomass mean for MAP and alum-P sludge at the same application rate, it can be seen that there was no effect of P source on switchgrass yield, thus, using the right application rate of alum-P sludge can sustain switchgrass and prevent overapplication (Kering et al. 2012) although harvest timing and type of switchgrass cultivar used have been pointed out as some of the factors that affect yield (Lee et al. 2012; Lee et al. 2009; Giannoulis et al. 2016; Mitchell et al. 2013). The slow rate of P release from alum-P sludge never posed a concern for its utilization in biomass production and was more efficient as cropping continues.

4.3.4 Aluminum uptake

Aluminum uptake in all cycles did not differ significantly among amendments and rates. However, results show higher Al concentrations in biomass grown in alum-P sludge-amended soil than MAP-amended and control soils (Table 4.5). Although studies have shown that switchgrass can take up heavy metals such as cadmium, chromium, and zinc (Chen et al. 2012; Sanderson et al. 2001; McLaughlin et al. 1999), it is capable of also taking up Al as seen in this study. Some other studies reported that in acidic soils, visible Al effect on the growth of switchgrass was observed at Al concentration above 5.0 mM (Clark 2002; Koslowsky and Boener 1989). At 2.4 mg Al kg^{-1} soil, a visible response to Al toxicity was noticed in certain varieties of wheat in an acidic soil, hence the more acidic the soil, the more the vulnerability of the plant to Al uptake (Barszczak and Bilski 1983; Kluczka et al. 2017). In this work, however, switchgrass did not show any visible defects in growth nor in nutrient uptake and this may be due to the short exposure time before each harvest and the soil pH of 8.3. In addition, for the above ground biomass, the highest Al uptake in

biomass yield was at the 19.4 mg P kg^{-1} soil application rate while the least uptake was in the control. Soil pH is the major factor that controls Al uptake based on solubility, mobility, bioavailability and even toxicity in any soil (Dong et al. 1999; Rahman et al. 2018).

Root uptake at the end of the three cycles did not differ significantly with application rate and P source, except for the control, the results were not significantly different for both above and below ground biomass (Table 4.5). Aluminum accumulation was largely confined to the roots (Table 4.5). Although the roots were washed before analysis, it is possible that small amounts of soil were not washed off the roots and this might have increased the Al content. This difference in average uptake in roots and shoots was seen in all rates, which corroborates the report that only minute amounts get to the leaves (Mossor-Pietraszewska, 2001; Steiner et al. 2012). Possibilities are that the roots would excrete organic acids which are able to react with Al to form aluminum-organic acid complexes in the soil (Ma 2000). Abuscular mychorrhizal fungal (AMF) roots have been reported to secrete organic acids to protect the plant against toxic elements (Gupta et al. 2013; Rahman et al. 2018; Clark et al. 1999). In acidic soils, excess Al prevents root development and damages its growth while fixing P (Zheng, 2010; Rahim et al., 2018).

4.3.5 Phosphorus recovery efficiency (PRE)

The treatment by rate interaction was significant ($p = 0.03$; Table 4.4) for PRE. Orthogonal polynomial contrasts indicated a significant linear response to P application rate, which was dependent on P source. For sludge, PRE decreased linearly ($P < 0.0001$) with an increase in P rate, while for MAP, regression analysis indicated no significant trend ($P = 0.93$). Alum-P sludge showed the highest recovery efficiency of 28.2% at the 9.7 mg P kg^{-1} soil rate while higher rates showed no significant effect relative with efficiencies of 16%, 11%, 7% for 19.4, 29.1 and 38.8 mg P kg^{-1} soil, respectively (Fig. 4.2). MAP on the other hand, showed no significant P rate effect

on the PRE with the highest recovery at 4.1% for application rate 19.4 mg P kg^{-1} soil. Other MAP rates showed 4.0%, 3.9% and 3.5% at 29.1, 38.8 and 9.7 mg P kg^{-1} soil. Based on the regression equation (Fig. 4.2), PRE decreased by 0.7% for every mg kg^{-1} increase in sludge P rate. The lack of a significant rate effect on PRE in MAP treated soil may be due to the fact that the lowest application rate was sufficient to support growth of switchgrass (Muir et al. 2001). It is also possible that the calcareous nature of the soil could have limited the optimum usage of available MAP in the soil (Yossif and Gezgin 2019) hence binding available P over time. In their greenhouse experiment on maize, Sá et al. (2017) documented that the MAP application rates had no significant difference on PRE over a period of four successive maize cultivations (Sá et al. 2017).

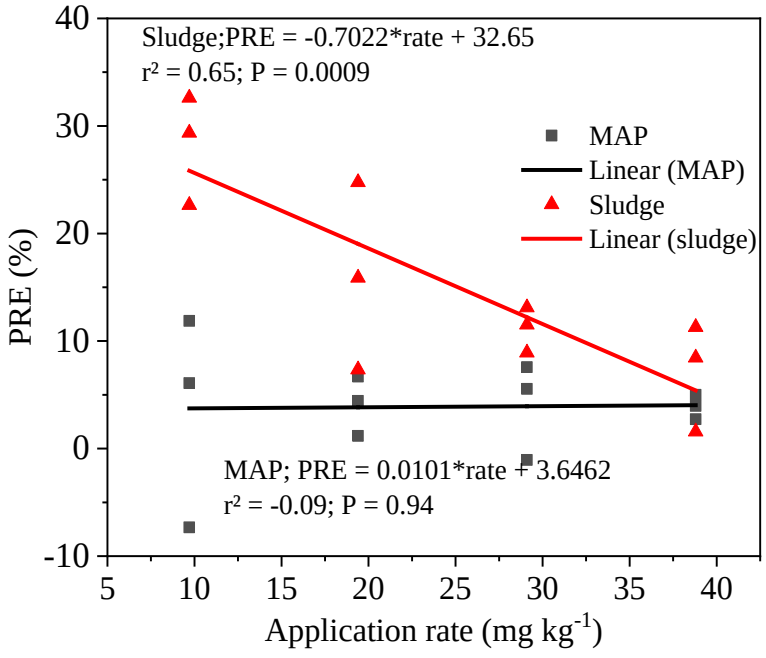

Figure 4. 2: Phosphorus recovery efficiency as affected by the rate by P source interaction for switchgrass

PRE in cycles 2 and 3 were significantly greater than cycle 1 indicating that uptake of P increased with each harvesting cycle (Table 4.4). Alum-P sludge showed a better recovery effect (75% more

P than in MAP) on P; however, recovery efficiency for alum-P sludge decreased at higher application rates. On the basis of the information gathered in this study, the best recovery efficiency was achieved by the application of optimal P application rate of 9.7 mg P kg^{-1} soil for alum-P sludge. This optimum rate of application would help prevent over-application and also protect surface water. This rate effect corroborates the results reported by Barbieri et al, 2014 where higher application rates of diammonium phosphate resulted in decreased PRE for wheat in loamy soil with pH between 6.0 - 6.3 and Olsen-P range of 8.9 - 13.9 (Barbieri et al. 2014).

4.4 Conclusion

For alum-P sludge treated soils, over 30% increase in biomass P uptake was observed at all rates from the first to the third harvest. P uptake from alum-P sludge increased numerically from cycle 1 to cycle 3. Remarkably, P uptake for MAP showed no statistical difference from the first harvest cycle till the last cycle due to depletion of readily available P. The results clearly suggest a gradual availability of P over time for alum-P sludge compared to MAP. With no biomass difference among treatments, alum-P sludge produced greater P uptake than MAP for each harvest from a source that is perceived as an almost unavailable source of P (alum-P sludge); however, this analysis indicates adequate availability. P uptake was accompanied by some uptake of Al in plant biomass. Alum-P sludge had an overall PRE of 75% more P compared to MAP. With the optimal application rate for switchgrass identified as 9.7 mg P kg^{-1} soil, alum-P sludge can be applied directly to grow switchgrass as this would prevent overapplication of nutrients and generate the much-needed biomass for biofuels. Total P application from sludge was much higher than that from MAP since sludge rate was based on plant-available P content of the sludge as represented by bicarbonate-extractable P. The large total P addition from sludge application may be an

environmental concern over time, due to the increased potential for P runoff as more P becomes available.

4.5 References

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CHAPTER 5

ALUMINUM PHOSPHATE SLUDGE AS A P SOURCE FOR MAIZE PRODUCTION IN A LOW-P SOIL

5.0 Abstract

With increasing food demand as a consequence of the growing world population, there is a corresponding demand for additional sources of phosphorus (P). Alum-phosphate (alum-P) sludge is a by-product of wastewater treatment and can be a good source of P. In this study, the response of maize (*Zea mays* L.) to alum-P sludge was tested. Maize was chosen as the test crop due to its prevalent use as human and animal food and as a source of biofuel. The objective of the study was to investigate alum-P sludge as a source of P compared to a commercial fertilizer (monoammonium phosphate, MAP). A growth chamber assay was conducted over four cropping cycles (45 d each). The application rate was 9.7, 19.4, 29.1 and 38.8 mg P kg^{-1} dry soil. Amendments were applied once at the start of the first cropping cycle. Plants were harvested after each cycle and pots were re-seeded. Dry matter yield (DMY), total P uptake, Al-P uptake, soil total P and Olsen-P concentrations, pH, and EC were measured.

DMY was significantly greater in pots amended with alum-P sludge than in pots treated with MAP. There was a significant rate by cropping cycle interaction effect on DMY with the differences among rates in cycle 1 different from those in cycle 4. Phosphorus uptake depended on cropping cycle, P source and P application rate. With sludge uptake higher than MAP in all cycles, the highest P uptake was observed at the highest application rate except for cycle 2 where this was observed at the rate 29.1 mg kg^{-1}. For MAP, Phosphorus recovery efficiency (PRE) at the highest rate was significantly greater than that at the lowest rate whereas PRE in cycle 1 was significantly higher than that in cycle 4. In the first two cycles, aluminum uptake was negligible in both MAP and alum-P sludge treatments; however, in cycles 3 and 4, there was significantly more Al in maize

from sludge amended pots. Our results show that Al-P sludge was as effective as MAP in supplying enough P for biomass yield. We, therefore, conclude that alum-P sludge could be an alternative source of P, especially for growing maize as feedstock for bioenergy.

5.1 Introduction

To sustain future economic growth, fertilizer usage will continue to increase due to increasing population and corresponding food demand (Schroder et al., 2011). With several speculations of pure phosphate rock extinction, there may be a looming crisis in the nearest future (Liu et al., 2020). Improved agronomic practices and soil fertilization are expedient to alleviate P pressured demands. With over-reliance on mineral fertilizers, the agronomic sector face a near global-P challenge and increasing environmental concerns as global P usage efficiency is reported to be not more than 25% on average in the first year of application (MacDonald et al., 2011; Dhillon et al., 2017; Syers et al., 2008; Sattari et al. 2012). In the face of this scarcity, with the agricultural sector accounting for about 90% of P demand (Maghsoodi et al., 2020; Childers et al., 2011), focus on P recovery from alum-P sludge should be prioritized.

P is abundantly found in wastewater sludge, and depending on the treatment method applied, it could be chemically or biologically bound (Ojo and Ifelebuegu, 2018). With the abundance of chemical sludge (aluminum phosphate) in Manitoba Canada, aluminum-phosphate (Al-P) sludge is mostly landfilled. This disposal method is quite expensive (Keeley et al., 2012; Babatunde and Zhao, 2007). P recovery from chemical sludge is one of the ways to ensure a cleaner and more sustainable environment as well as ensure that all sludge P are put to beneficial use (Tolofari et al., 2021; Alvarenga et al., 2016; Mazen et al., 2010).

As a widely studied crop, maize is mostly known for its feed generation for humans and animals. It is the third-ranking cereal and a very critical staple for the world's growing population

(FAOSTAT 2010; Ranum et al., 2014). In recent times, it is a widely sought-after feed for ethanol production. Maize generates more ethanol due to cellulose conversion technology (Schwietzkey et al., 2009). With an increasing demand for maize in bioethanol production, there will be intensifying competition and a surge in demand for all first users (man and animal). Maize cultivation and production should be intensified to secure its availability through a rising global demand scenario. Rosegrant et al. (2009) reports a shortage in current production compared to demand, which is most likely to double by 2050 in developing countries (Shiferaw et al., 2011). A significant challenge to achieving this surplus production is hinged on the reports of depleted P reserves (Cordell et al., 2009), with fertilization cost seen as a major contributor making maize less affordable (Omenda et al., 2021; Pereira et al., 2020; Metson et al., 2016). P usage for maize is crucial at the initial growing season and can primarily affect yield and uptake (Cadot et al., 2018; Lino et al., 2018; Grant et al., 2001). Root development and distribution relative to the P in soil solution determine the extent of P uptake by maize (Klamer et al., 2019; Mollier and Pellerin, 1999). With a higher initial P concentration in soil solution, plants have a better initial root development and subsequent yield increase (Dhillon et al., 2017; Wu et al., 2015).

Therefore, reuse options for alum-P sludge are viable to enhance the reduction of GHG emissions; this can be achieved by the cropping of maize solely to produce ethanol as a biofuel (Tolofari et al., 2021; Maghsoodi et al., 2020). This would improve cost competition against inorganic fertilizers, better the environment and prevent groundwater contamination (Hoekman et al., 2018; Chiodo et al., 2018).

Alum-P sludge is rich in organic carbon and major nutrients such as N, P and K, which are beneficial to crops (Kluzcka et al., 2017; Kim et al., 2002). The use of alum-P sludge for growing crops is a cost-effective way of recovering P as well as a means to improve overall soil properties

that facilitate plant growth (Kim et al., 2002). This amendment can fill some gaps in the P industry and also foster growth in the agricultural industry. The risk of Al toxicity has been highlighted as a limitation to the use of alum-P sludge (Kluzcka et al., 2017; Kim et al., 2002); however, creating the right balance in terms of soil conditions and application rate could allow for the safe use of alum-P sludge as a nutrient source for crop plants. The reuse of alum-P sludge as a P recovery option is a crucial step in addressing some of the challenges with the forecasted depletion of global P reserves and to reduce the dependence on inorganic fertilizers. Phosphorus availability in alum-P sludge could be dependent on the organic matter content and pH of the soil (Chowdhury et al., 2020; Tolofari et al., 2021).

The objective of this study was, therefore, to investigate the effectiveness of alum-P sludge as a source of P compared to a commercial fertilizer (monoammonium phosphate) at 9.7, 19.4, 29.1 and 38.8 mg P kg^{-1} dry soil. We hypothesize that (i) P uptake by maize is greater in MAP-amended soil than in soil amended with alum-P sludge, (ii) maize biomass yield increases with P application rate and (iii) maize biomass yield decreases as the number of cropping cycles increases.

5.2 Materials and Method

5.2.1 Phosphorus sources

Dewatered sludge with 18% solids content was sourced from Headingley wastewater treatment plant in Manitoba, Canada (49°52' 25.4" N; 97°26'16.1" W), while monoammonium phosphate (MAP, 11-52-0; a soluble inorganic commercial fertilizer containing 11% nitrogen and 52% phosphate) was obtained from a local distributor in Canada. Application of P to potted soil was based on the available P concentration in the alum-P sludge to enable comparison between sludge and MAP treatments. Since a large percentage of total P in the sludge is organic and unlikely to be readily available for plant uptake, applying P on the basis of bicarbonate-extractable P (Olsen-P;

Olsen et al., 1954) content in alum-P sludge was more appropriate. Application of sludge based on available P (Olsen-P) should be carefully considered as a part of the non-labile P pool could mineralize during the cropping period. Thus, sludge application based solely on available P could lead to the addition of excess available P than intended (Tolofari et al., 2021). Chemical properties of the Headingly sludge have previously been reported (Tolofari et al., 2021) with a moisture content of 82% and total P (TP) concentration of 64,221 mg kg^{-1}.

5.2.2 Soil

Topsoil (0-15 cm) from Roseisle, Manitoba, Canada (49°33.577' N; 98°24.824' W) was used for this study. The soil was a well-drained Entisol (dark-grey Gleyed Regosolic sand) with an initial pH of 8.2 and a Olsen P concentration of 3 mg kg^{-1} (Tolofari et al., 2021).

Chemical properties of the soil have been previously published (Tolofari et al., 2021) and are summarized in Table 5.1.

Table 5. 1: Chemical properties of the soil

Properties	Roseisle
Nitrate (mg kg^{-1})	33.6
Olsen P (mg kg^{-1})	3
Potassium (mg kg^{-1})	46
Organic C (g kg^{-1})	25
Carbonates (CCE) (g kg^{-1})	12
Soil pH	8.2
Cation exchangeable capacity $cmol_c$ kg^{-1}	25.1
Sulfur (mg kg^{-1})	26.9
Baron (mg kg^{-1})	2

Zinc (mg kg^{-1})	0.44
Iron (mg kg^{-1})	32.3
Manganese (mg kg^{-1})	1.7
Copper (mg kg^{-1})	0.2
Magnesium (mg kg^{-1})	912
Calcium (mg kg^{-1})	3402
Sodium (mg kg^{-1})	86
Electrical conductivity (dS m^{-1})	0.25

5.2.3 Experimental set-up

The investigation was conducted in a growth chamber where the temperature regime was maintained at 25/15°C for day/night respectively, with a relative humidity of 60%, and a proportionate photoperiod of 16 h. The experimental design was completely randomized; the set-up was with a factorial treatment structure involving two P sources (MAP and alum-P sludge), four P application rates (9.7, 19.4, 27.1 and 38.8 mg P kg^{-1} dry soil) and four cropping cycles. Sludge P application was based on Olsen P concentration. The sludge application rates were 12, 24, 36 and 48 g kg^{-1} dry soil to achieve the above stated P application rates. All treatments, including the control, were replicated three times. On a dry weight basis, P application rates corresponded to 9.8, 19.7, 29.5 and 40 kg ha^{-1} P. Typical agronomic rates for corn in Manitoba are within the range 20 to 25 kg ha^{-1} P (Manitoba Agriculture, 2007).

The soil was meticulously mixed and passed through a 4 mm sieve to remove stones and roots, after which it was air-dried and properly stored for analysis. Approximately 1.5 kg of air-dried soil sample was put into each 14.9 cm diameter by 16.5 cm height plastic pots. Reverse osmosis (RO)

water and a full-strength nutrient solution without P (Zvomuya et al., 2006) were added to all pots to bring the soil moisture content to field capacity. The pots were then stored in a growth room for 24 h prior to the commencement of planting.

Three maize seeds were planted into each pot; the seedlings were later thinned down to one 5 d after germination. The pots received two applications of essential macronutrient solutions (P excluded) in each growth cycle (Zvomuya et al., 2006). All pots were weighed and watered every other day to replace moisture lost via evapotranspiration. A total of four cropping (seeding to harvest) cycles were completed, with each cycle lasting 45 d in duration. Plants were harvested on Day 45 by clipping at 2 cm height above the surface of the soil. The contents of each pot were emptied into a clean tray and thoroughly mixed. A 20-g soil subsample was collected at the end of every growth cycle for analysis. Plant roots were recovered, cut into small pieces, and mixed with the soil, which was re-potted for the next cropping cycle. The soil was stored in the growth room for 5 d before planting. Harvested biomass was weighed and oven-dried for 72 h at approximately 60°C. Oven-dried biomass samples were later weighed, chopped into tiny pieces, and fine-ground in a mill grinder (< 0.2mm, Model 8000D Spex Sample Prep, Metuchen, NJ). At the completion of the fourth cycle, plant roots were retrieved, washed with RO water, dried, and ground for analysis.

5.2.4 Laboratory analysis

Preliminary analysis before bioassay, the plant available (Olsen) P was analyzed for the soil using the ascorbic acid-molybdate method (Murphy and Riley, 1962) with a Skalar SAN++ segmented flow analyzer (Skalar Analytical B.V., Breda, Netherlands)] after extraction with 0.5 M concentration of $NaHCO_3$ at pH 8.5 (Olsen et al., 1954); concentration of nitrate (using Cd reduction method; Mulvaney, 1996); pH of the soil and electrical conductivity (1:1 soil to water

suspension); exchangeable K, Mg, Ca, and other cations [using atomic absorption spectroscopy after extraction of 5 g of soil with 33 mL of 1 M concentration NH_4OAc at a pH of 7 (Hendershot et al., 2008)]; concentration of aluminum (Al) in the soil was measured with an inductively coupled plasma optical spectrophotometer (ICP-OES, Thermo Electron ICAP 6300 Radial) after the digestion of the samples in block digester using sulfuric acid (99.7% H_2SO_4) and hydrogen peroxide (30% H_2O_2) (Parkinson and Allen, 1975); cation exchange capacity (sum of exchangeable Na, K, Ca and Mg) (Hendershot et al., 2008); concentration of soil organic matter (SOM) [using loss on ignition method (Nelson and Sommers, 1996)]; and carbonates were analyzed using the pressure calcimeter method (Loeppert and Suarez, 1996), represented as calcium carbonate equivalent (CCE). Soil organic carbon (SOC) concentration was obtained by multiplying SOM by 0.58.

Total P (TP) and aluminum (Al) concentrations in the plant tissue were measured with an inductively coupled plasma optical spectrophotometer (ICP-OES, Thermo Electron ICAP 6300 Radial) after the digestion of the plant tissue samples in a block digester using sulfuric acid (99.7% H_2SO_4) and hydrogen peroxide (30% H_2O_2) (Parkinson and Allen, 1975). Concentration of Olsen-P in the soil was determined by the $NaHCO_3$ (99.7%) extraction method (Olsen et al. 1954; Olsen and Sommers 1982) at pH 8.5. Phosphorus concentration in the extract was determined colorimetrically using the ascorbic acid-molybdate method (Murphy and Riley, 1962).

5.2.5 Statistical analysis

To determine treatment and interaction effects, analysis of variance (ANOVA) was carried out on P concentration in the soil, dry matter yield, P uptake and PRE data using PROC GLIMMIX for repeated measures (with cycle as the repeated measures factor) in SAS 9.4 (SAS Institute, 2013). PRE was computed as [(P uptake in each amended pot – P uptake in control pot)/ P application

rate] for each harvest. Phosphorus source and P rate were modeled as fixed effects. Data for all variables were normally-distributed, except for Olsen P data which were analyzed as a lognormal distribution and PRE as a beta distribution. Treatment means were compared using the Tukey multiple comparison procedure at $\alpha = 0.05$.

5.3 Results and Discussions

5.3.1 Dry matter yield (DMY)

We observed a significant effect of P source on maize DMY (Table 5.2). Averaged across all rates and cycles, pots amended with sludge had a significantly higher DMY than MAP amended treatments. Ramphisa and Davenport (2020) reported a different result as no significant effect of P source (MAP and organic manure) was observed on corn yield in their study. The authors attributed the lack of P source effect on maize yield to the short time (2 years) of the study. The same was true for the study on maize using alum sludge where there was no recorded significant DMY although this was attributed to the type of seed used (Lin and Green, 1990). The higher yield observed in our study for sludge amended soils could be due to the increase in inorganic P from sludge total P, as organic P can be transformed to inorganic P with time (Shen et al., 2011). Another reason could be that the sludge addition increased the organic matter content present in the soil coupled with the plant residue/root incorporated after each cycle. This could have increased microbial activities hence the overall increase of DMY (Gatiboni et al., 2008).

Regardless of the amendment applied, the rate effect on DMY varied with the cropping cycle (Table 5.2; Fig. 5.1). For cycle 1, as the rate increased from 9.7 to 19.4 mg P kg^{-1} soil, we observed a significant increase in DMY. Between 19.4 and 29.1 mg P kg^{-1} soil, there was no significant difference between DMY. However, a significant increase in DMY was identified between 29.1 mg P kg^{-1} soil and 38.8 mg P kg^{-1} soil. For cycles 2 and 3, DMY was similar across all rates, no

significant effect of rate on DMY. For cycle 4, DMY was similar for rates 9.7, 19.4 and 29.1 mg P kg^{-1} soil. DMY was significantly higher at 38.8 mg P kg^{-1} soil in contrast to the lowest rate, 9.7 mg P kg^{-1} soil. However, the DMY at 38.8 mg P kg^{-1} soil was similar to DMY at 19.4 and 29.1 mg P kg^{-1} soil. Similar to what was observed in cycle 1, Lino et al. (2018) observed an increasing rate effect on corn yield. Ortas and Islam (2018) observed a non-linear increase in corn yield with respect to increasing P application rate. They attributed the increased yield to higher soil P availability due to mycorrhizal root interactions and mineralization of soil organic material (Ortas and Islam, 2018). For our study, a low-P soil was used; however, since some P was supplied in the first cycle, it could be that this increased the available P pool thus removing any rate effect in cycles 2 and 3 (Lopes et al., 2007). The increase in DMY for the highest rate in cycle 4 could be because of an interaction effect between soil processes and mineralization of incorporated roots (Ortas and Islam, 2018, Martinazzo et al., 2007; Santos et al., 2008).

Sludge, which is rich in organic matter and major nutrients, can improve soil physical and chemical properties which are important for plant growth (Rodríguez-Berbel et al., 2022), and therefore yield. The increase in DMY must have been improved by soil properties such as cation exchange capacity (CEC), organic carbon, carbonates etc. The addition of alum-P sludge to the soil resulted in an increase in SOM, which then improved the fertility and properties of the soil (Chowdhury et al., 2020). For example, Chowdhury et al. (2020) explained that CEC above 10 $cmol_c$ kg^{-1} soil would improve plant growth as well increase biomass yield. This would also improve uptake of micronutrients and prevent deficiency. The presence of organic carbon improves the availability of nutrients by the continuous decomposition and breaking down of bound nutrients into readily usable forms which would improve crop growth and invariably the dry matter yield of the plant.

Organic matter decomposition facilitates nutrient availability and uptake by roots, thus increasing DMY (Chowdhury et al., 2020; King et al., 2020).

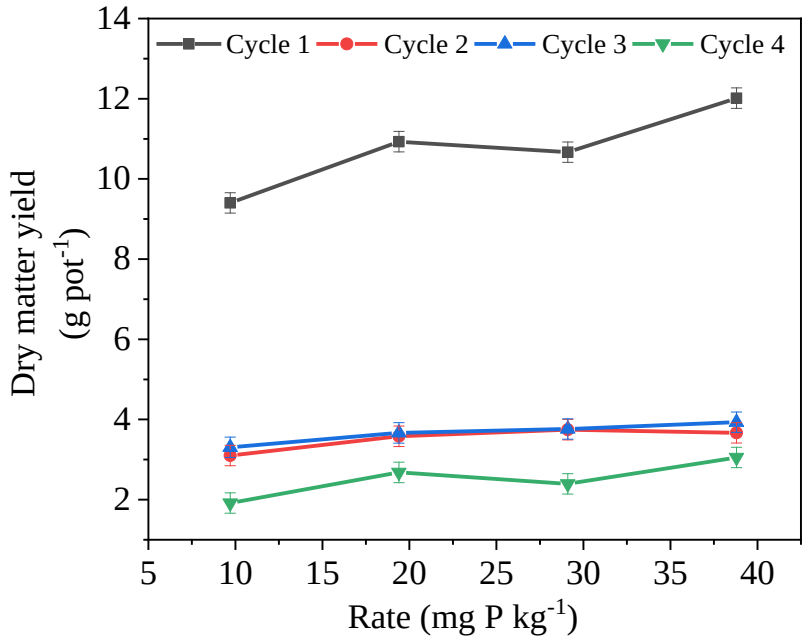

Figure 5. 1: Effect of the cropping cycle by application rate (mg P kg^{-1} soil) interaction on maize dry matter yield.

Table 5. 2: DMY, phosphorus uptake, PRE, aluminum uptake, pH, and EC as affected by sludge and MAP Application†.

Effect	DMY	P uptake	PRE	Al uptake	pH	EC	Olsen P	Soil TP
	g kg^{-1}	mg P kg^{-1}	%	mg Al kg^{-1}		µS cm^{-1}	mg P kg^{-1}	mg P kg^{-1}
Cycle (C)								
1	10.8	11.1a	23.6	0.1b	7.9a	562c	13.4ab	563a
2	3.5	4.8c	11.4	0.0b	7.0c	664bc	22.4a	510b
3	3.7	7.1b	17.0	4.9b	7.1c	1133b	12.4ab	405c
4	2.5	4.0c	8.2	13.3a	7.6b	1915a	10.0b	424c
P-source (P)								
Control	1.6c	2.6c		2.2b	8.1a	253c	10.2	456b
Sludge	6.05a	9.7a	30	6.0a	7.6b	888b	14.1	510a
MAP	4.3b	3.8b	3	3.1b	7.2c	1249a	13.3	440b
Rate (R, mg P kg^{-1})								
0	1.68	2.6d		2.2	8.05a	253	10.2	456
9.7	4.4	4.8c	14.5	4.7	7.3c	1079	11.1	446
19.4	5.2	6.5b	16.4	5.4	7.3c	1231	12.0	486
29.1	5.1	7.3b	13.6	4.3	7.4bc	1046	14.6	478
38.8	5.7	8.4a	13.9	3.9	7.5b	918	18.0	491
		P-value						
C	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
P	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0003	0.57	<0.0001
R	<0.0001	<0.0001	0.68	0.59	0.007	0.009	0.007	0.06
P × C	0.38	<0.0001	<0.0001	0.001	<0.0001	0.33	0.49	0.14
P × R	0.30	<0.0001	0.01	0.18	0.89	0.27	0.80	0.13
R × C	0.04	0.01	0.28	0.88	0.09	0.35	0.91	0.10
P × R × C	0.62	0.002	0.35	0.20	0.97	0.17	0.86	0.13

†Means followed by different letters within a column are significantly different at $p \leq 0.05$

5.3.2 Phosphorus uptake

Phosphorus uptake showed a significant amendment by rate by cycle interaction ($p < 0.002$) (Table 5.2, Fig. 5.2). For cycle 1, as the rate increased from 9.7 mg P kg^{-1} soil to 38.8 mg P kg^{-1} soil, we observed a significant increment in P uptake by maize in both MAP and sludge amended soils. Interestingly, P uptake by maize was significantly higher in sludge amended soils than in MAP at

all application rates. For both P sources, the highest P uptake by maize occurred at the highest application rate. This report corroborates what Pizzeghello et al. (2019) and Yossif and Gezgin (2019) observed. The authors reported an increased P uptake as the application rate of MAP/single superphosphate and MAP/DAP increased (Pizzeghello et al., 2019; Yossif & Gezgin, 2019). Silva et al. (2012) also reported that the highest P uptake was at the highest P application rate.

For cycle 2, P uptake in sludge amended pots was significantly higher at each rate compared to MAP amended pots, this observation is similar to cycle 1. As the rate increased for MAP, there was no significant increase in P uptake. For sludge amended soils, there was no significant difference in P uptake at these application rates (9.7, 19.4, and 38.8 mg P kg^{-1} soil). The highest P uptake from sludge amended soils occurred at rate of 29.1 mg P kg^{-1} soil and was significantly higher than P uptake in pots amended with rate 9.7 mg P kg^{-1} soil. However, in cycle 3, there was a significant increase in P uptake between rate 9.7 and 38.8 mg P kg^{-1} soil for sludge amended soils. As the application rate increased, no significant increase in P uptake from MAP amended soils was observed for cycle 3. For cycle 4, similar to what we observed in cycle 3, there was no significant increase in P uptake with increasing P rate in MAP amended soils. However, P uptake increased between rate 9.7 and 29.1 mg P kg^{-1} soil. P uptake in pots amended at rate 29.1 mg P kg^{-1} soil was not significantly different to P uptake at 38.8 mg P kg^{-1} soil, for sludge amended soils.

For MAP and sludge amended soils, the highest P uptake was observed for cycle 1. This was not surprising for MAP as it is an inorganic source of P, and all its P is in the readily available form. Readily available P in MAP may have been precipitated by calcium and magnesium in the soil, thus reducing its availability to plants (Tolofari et al., 2021). Sludge, being an organic source of nutrients has both organic and inorganic pools of P, with the organic pool being a long-term source of available P with a gradual release pattern for other growth cycles (Ahmed et al., 2010; Kiehl,

2008). This provides an explanation of the differing trends we observed in the different cycles as the organic P becomes more available. In cycles 1, 2 and 3, at each P rate, P uptake in sludge amended soils was significantly greater than MAP amended pots. However, in cycle 4, at 9.7 mg P kg^{-1} soil amendment application rate, there was no observed significant difference in P uptake between sludge and MAP amended pots. At other rates, the trend was similar to those observed in previous cycles where P uptake for sludge treatments was higher. The similar P uptake in cycle 4 for both MAP and sludge at the lowest rate (9.7 mg kg^{-1} soil) could be explained by the complete mineralization of all the organic P in the sludge as a consequence of the lower P supplied at this rate (9.7 mg kg^{-1} soil) (Santos et al., 2008; Martinazzo et al., 2007). It is also possible that newly developing roots do not have good contact with soil solution, hence reducing P uptake from the pot (Rehim et al., 2016).

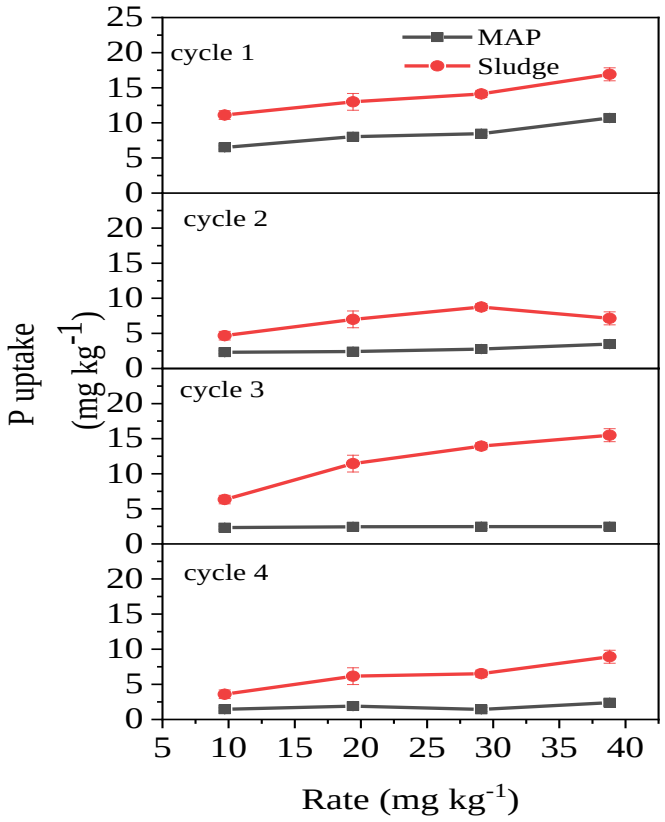

Figure 5. 2: Effect of application rate (mg P kg^{-1} soil) on cropping cycle and P source interaction on P-uptake by maize

5.3.3 Phosphorus recovery efficiency

There was a significant P source by cycle interaction and P source by application rate interaction. For sludge, there was no significant effect of rate on PRE, while for MAP, there was a numerical increase in PRE with increasing P application rate (Fig. 5.3). PRE for MAP amended soils was significantly higher at 38.8 mg kg^{-1} soil compared to 9.7 mg kg^{-1} soil. Similar to our alum-P sludge treatment, Sa et al. (2017) reported no significant change in PRE across all rates of P application for both organic and inorganic P sources (50-400 mg P kg^{-1} soil). The authors also observed no

significant difference between PRE of MAP and organomineral phosphate fertilizer (Sa et al., 2017). This was not the case in our study as at every application rate, sludge had a significantly greater PRE than MAP. Although, Sa et al. (2017) expected differences due to the different formulations of the fertilizers and the uniqueness of the contact surfaces, which could affect P availability, they observed none. They however concluded that the recovery efficiency with the high DMY makes poultry litter a competitive source of P. In our study, the higher PRE for sludge compared to MAP might be due to an increase in the bioavailability of the P in Alum-P sludge when in contact with the calcareous soil (Von Wandruszka, 2006). Since P in MAP is in the readily available form, its P bioavailability in calcareous soils could be limited due to the formation of less soluble forms through its interaction with Ca and Mg hence leading to precipitation (Weeks and Hettiarachchi 2019; Naeem et al., 2013; Syers et al., 2008).

Tolofari et al. (2021) reported that PRE for sludge amended pots had shown the highest recovery efficiency at the lowest P application rate (9.7 mg kg^{-1}). At the other P rates in their study, no significant difference in PRE at was observed (Tolofari et al., 2021); this is similar to our observation. Yossif and Gezgin (2019), who worked on maize, observed that P recovery for calcareous soils is low, with the highest recovery observed at 30 mg kg^{-1} P_2O_5 (13.77%) and the least recovery at 90 mg kg^{-1} P_2O_5 (9.36%). Low PRE observed at higher P application rates could mean that maize used just a small fraction of the applied rate (Rehim et al., 2012a).

There was also a significant P source by cycle interaction (Fig. 5.4). In all cycles, PRE of sludge was significantly higher than MAP. For MAP, PRE decreased with cycle. This is mostly due to the possible fixation of available P due to the calcareous nature of the soil, and this is also aggravated by the one-time P source addition which was prior to the first cycle. In contrast, no increasing or decreasing trend was observed for sludge amended soils in all four cycles. The

varying PRE for sludge is similar to the trend we observed for P uptake and could be attributed to the slow release of available P from the organic P pool in sludge (Iyamuremye et al., 1996). The lowest P uptake was observed in cycle 4, which explains the PRE in cycle 4. Tolofari et al. (2021) observed an increase in PRE with cycle which was dissimilar to our study, as we observed decreasing PRE with cycle (for MAP) and no trend for sludge. This difference could be due to the effect of the plant/organic residue which was re-introduced into the pots, and which must have increased biological activities in the soil (Smith et al., 1993; Nziguheba et al., 1998).

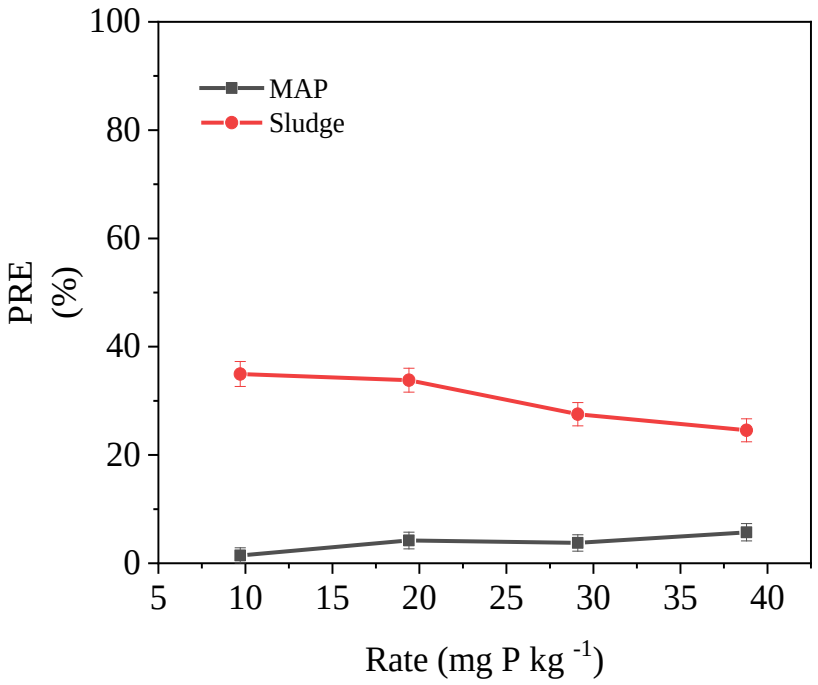

Figure 5. 3: P source against P application rate (mg P kg^{-1} soil) interaction on PRE

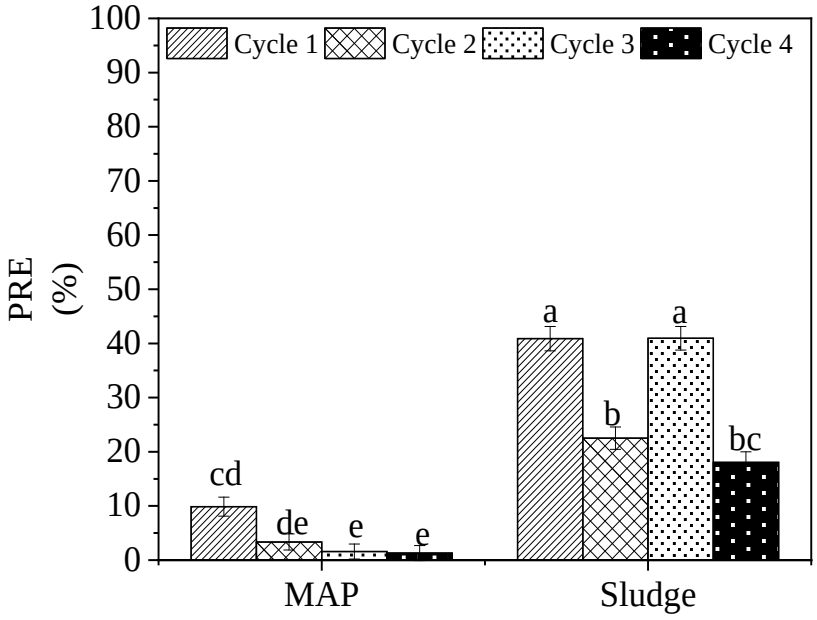

Figure 5. 4: P source x cycle interaction on PRE

5.3.4 Aluminum uptake

There was a significant P source × cycle interaction on aluminum uptake, indicating that aluminum uptake in each cycle was dependent on the P source (Fig. 5.5). In cycle 1 and 2, Al uptake by MAP and sludge was similar (Fig 5.5). It is important to state that the Al uptake was very close to zero in cycle 1 and 2 (Table 5.2). In cycles 3 and 4, there was significantly more Al uptake in sludge amended soils compared to MAP amended soils, with the uptake in cycle 4, higher than uptake in cycle 3. This suggests an effect of time as well as P source on Al release from soil. Unfortunately, Al in soil was not quantified at the start of the study. The Al in sludge could have contributed to the increased Al uptake from sludge amended pots. The mineralization of organic

matter may have caused an increase in the uptake of Al by the plants (Meriño-Gergichevich et al., 2010; Hede et al., 2001).

Maize is reportedly a very sensitive crop to Al and high levels of Al limits biomass production and P uptake, even at very low Al application rates and short exposure intervals (Giannakaola et al., 2008; Yossif and Gezgin, 2019; Tandzi et al., 2018). The effect of Al in alkaline and acidic soils negatively impact root growth, however acidic soils have much more severe impact on root reduction (Stass et al., 2006; Lidon & Barreiro, 2002). In this work, the effect of Al was not noticeable as Al uptake did not occur in the first two cycles. This could be due to the pH of the soil which was at 8.2 at the start of the experiment. Mimmo et al. 2009 explained that prominent levels of Al in soil may affect nutrient uptake; however, their experiment on beans showed that P uptake was not significantly limited by Al in soil even at a pH of 4.50. Although the species of Al in the soil were not assessed, Al can be organically bound, exchangeable or in crystalline form (Kluckza et al., 2017). The Al species expected at the pH in our study are $Al(OH)_3$, $Al(OH)^{2+}$ and $Al(OH)_2^+$(Meriño-Gergichevich et al., 2010). Understanding the speciation of Al in the soil explains a lot about their interaction. In this study however, Al uptake occurred even in the control which could be due to the solubility of Al in the soil. Kluckza et al. (2017) explained that increase in Al around neutral pH is mostly due to exchangeable Al in the soil and Al bound to organic matter.

The duration of Al species incubation in the soil can also affect its bioavailability (Iqbal, 2012).

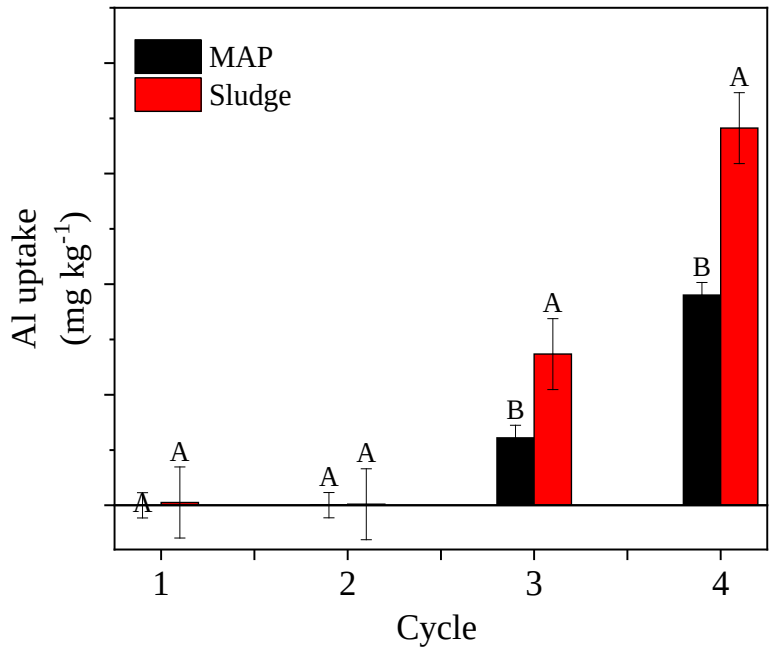

Figure 5. 5: Effect of P source by cycle on aluminum uptake (mg Al kg^{-1} soil)

5.3.5 pH

There was a significant P source × cycle interaction for soil pH (Fig. 5.6, Table 5.2). In cycles 1 and 2, the pH did not differ significantly between sludge and MAP. It is noteworthy that, in cycle 1, the pH of both MAP and sludge amended soils were in the alkaline range, while in cycle 2, the pH of both P source treated soils were near neutral indicating a reduction in pH in cycle 2 (Fig. 5.6). In cycle 3 however, the pH for MAP amended soils was in the acidic range (6.3) and was significantly lower than pH for sludge amended soils (7.8). This reduced pH in MAP amended pots in the third cycle may be due to the excretion of organic acids by the roots in the soil. Since available P may have been diminished, organic acid excreted by roots may be able to solubilize P from metal P salts and make it available for utilization (Hinako et al., 2021). In cycle 4, there was no significant difference between pH of MAP and sludge amended soils (Table 5.2). Calba et al.

(2006) reported a reduction in soil pH of about 0.23 units upon continuous maize cropping using organic and inorganic fertilizer in acidic soil of pH 4.8. Similar to Calba et al. (2006), we observed a decreasing trend for MAP until cycle 3, however there was an increase in pH in cycle 4. This alkalinity reduction could mostly be due to the buffering capacity of the soil (Keramati., 2010).

Generally, at the soil pH in cycles 3 and 4, we would not expect high Al exchange in the soil. The increased uptake of Al in the 3rd and 4th cycles for alum-P pots could be part of the effect of incubation duration and an effect of organic matter mineralization due to the incorporation of roots into the pots after each cycle (Grzyb et al., 2020; Hadas et al., 2004). Schwesig et al. (2003) highlighted that the mineralization of organic matter in the soil would result in increased concentrations of free Al^{3+} in soil solution.

There was also a significant rate effect on soil pH (Fig. 5.7). Across all cycles and both P sources, there was a numerical increase in pH with amendment rate. Soil pH was not significantly different between rates 9.7 and 29.1 mg kg^{-1}, however, pH in soil amendment with the highest P rate (38.8 mg kg^{-1}) was significantly higher than pH in pots amended at P rates of 9.7 and 19.4 mg kg^{-1}. Contrary to our finding, Arvas et al., 2011 reported that the lowest pH values were identified in pots of the highest application rate of sewage sludge; this they attributed to the effect of root biomass in the soil. Ahmad et al. (2019) observed the highest values in units with the highest DAP application rates while single superphosphate showed a slight decrease in pH.

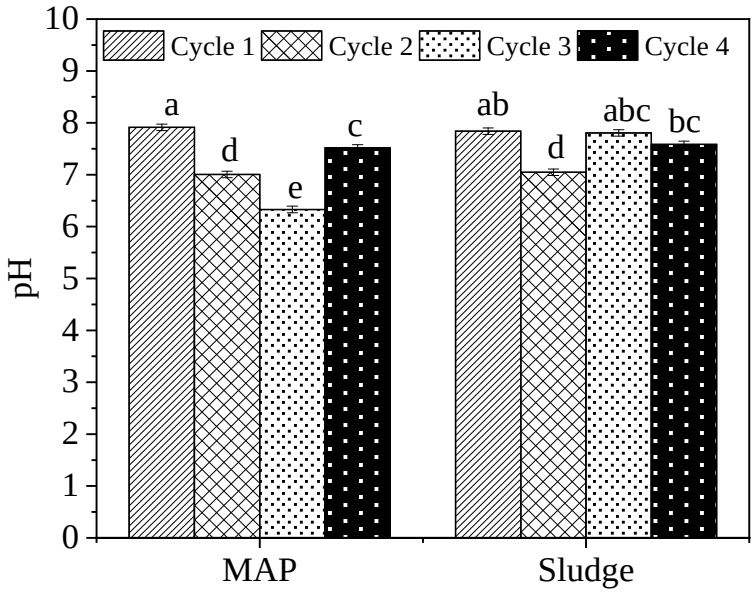

Figure 5. 6: P source against cycle interaction on soil pH

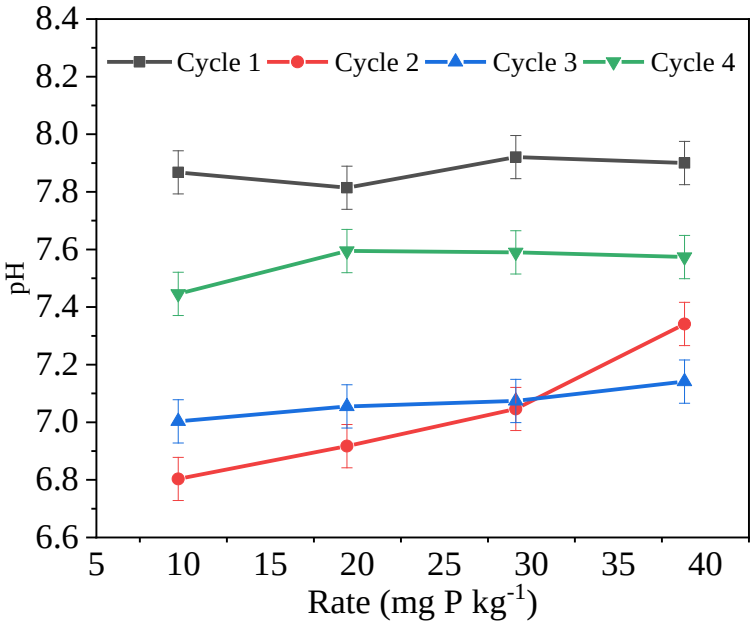

Figure 5. 7: P application rate by cycle interaction on soil pH

5.3.6 Olsen P and TP

There was a significant effect of P rate on soil Olsen P (Table 5.2). As expected, there was a numerical increase in soil Olsen P as the amendment rate increased. At the lower P application rates, there was no significant difference in soil Olsen P between P sources. The highest Olsen P recorded in our study was at the highest P application rate. Wen et al. (2016) and Zhan et al. (2016) indicated that the increase in Olsen-P at higher rates was as a result of increased decomposition of organic matter in the soil. Rehim et al. (2016) also found a similar increase in Olsen-P with respect to increasing rate of P application while lower Olsen-P values could be attributed to efficient P usage by the crops.

There was also a significant cycle effect on soil Olsen P. The highest soil Olsen P was observed in cycle 2, and this was significantly greater than Olsen P in other cycles. Overall decrease in Olsen-P could have resulted in declining PRE trend observed for MAP.

For soil total P, there was a significant cycle and P source effect. Total P decreased with cycle until cycle 3, and no significant change was observed in cycle 4. TP trend was cycle 1> cycle 2 > cycle 3= cycle 4. This was as expected as it clearly shows that accumulated soil P was being utilized for subsequent crop growth (Zhang et al., 2020). TP measured in sludge amended pots was significantly greater than in MAP-amended pots. This was not surprising as sludge properties showed that it contained a large amount of total P (Tolofari et al., 2021).

5.4 Conclusion

Our results demonstrate the effectiveness of P uptake from alum-P sludge using maize as a test crop in a growth room. Maize yield significantly increased with the application of alum-P sludge compared to MAP; however, there was a general decrease in biomass yield as the number of

cropping cycles increased. PRE significantly increased with alum-P sludge application relative to conventional fertilizer. In addition, as the application rate increased, there was no significant difference in PRE for the different application rates of alum-P sludge. Generally, as the cropping cycle increased, P uptake decreased alongside TP and soil Olsen-P concentrations. Also in most cases, at all cycle and in all rates, P uptake from alum-P sludge amended soil differed significantly from MAP amended soil.

Overall, alum-P sludge could be an alternative source of P in a world with an ever-increasing P demand, thus reducing the demand for inorganic fertilizers such as MAP. This can promote the dedicated use of alum-P sludge to produce feedstock for biofuel, leading to diversified P usage. Based on the sludge application rates in this study, the lowest application rate of 9.7 mg P kg^{-1} soil showed adequate PRE that is comparable to higher rates and hence may be the most suitable for future use to prevent overapplication. Although the one-time application of alum-P sludge is beneficial to subsequent crops, we recommend that care should be taken in the use of alum-P sludge as application based on available P may lead to P accumulation and pose a potential risk to the environment.

5.5 References

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CHAPTER 6

ENGINEERING SIGNIFICANCE

6.0 Main Findings

Wastewater treatment plants (WWTPs) are closely intertwined with global nutrient cycles because of the amount of nitrogen (N) and phosphorus (P) they hold (Daigger, 2009). Although significant data on actual wastewater volumes and sludge generated are not found in literatures, pockets of information exist. For instance, Statistics Canada estimated that in 2017 alone, the volume of municipal wastewater was about 5,900 million cubic meters with about 4% of this volume as untreated (Statistics Canada, 2019) whereas the treated portions were 26%, 48% and 24% in primary, secondary and tertiary treatment systems. While the use of metal salts can be applied in any of the dedicated treatment portions, in 2006 alone, 276 ktons of alum salt (aluminum sulphate) was produced in Canada with over 80% utilized in water and wastewater treatment (Environment Canada, 2010). Estimating based on sludge handling data between 2014 and 2016 for wastewater treatment plants having hydraulic capacity above 1,000 $m^3 d^{-1}$, it was quantitatively assessed that over 660,000 tons dry sludge was generated yearly in Canada (CCME, 2012a; Jin et al., 2018). If we estimate a 10% landfilling of the total dry sludge generated as alum sludge, it implies a 66,000 tons of alum sludge. With a maximum total phosphorus (TP) of 2.3% sludge mass, total estimated P in the landfill site would be 1,518 tons P (Jin et al, 2018; Stehouver et al., 2010) which is equivalent to 23 kg P ton^{-1} sludge. With the price of commercial fertilizer (monoammonium phosphate) been as high over 1,000 Canadian dollars ton^{-1} in April 2022 (Ontario Farm Input Monitoring Project, 2022), every recovered and reused P would reduce the effect of these skyrocketing prices on users.

The recovery of P is a very urgent task as P reserves are finite in nature and scarce while the world's population on the other hand keeps increasing (Khiewwijit et al., 2016). Aside that, the removal and recovery of P from wastewater protects the environment from pollution (Cordell et al., 2009). Alum salt is widely employed in WWTPs of small communities in Canada due to its abundant nature, low cost implications and avoidance of challenges associated with unstable microbes (Stratful et al. 1999; Morse et al. 1998). However, alum-P sludge disposal comes with high costs of haulage and landfilling (Kirchmann et al. 2017).

With a projected 4% per year increase in global fertilizer demand, P recovery from alum-P sludge could influence the trajectory of demand for commercial fertilizer (Elser and Bennett 2011).

Although a major concern to land application is the addition of aluminum to the soil and also P overapplication, this thesis has considered some of these concerns and they are explained below. The recovery of P from alum-P sludge was the major focus of this study with chemical dissolution of alum-P sludge identified as one of the ways to accumulate, reuse and recycle P using NaOH. The time-dependent behaviour of dewatered (DW) and waste activated sludge (WAS) were investigated under the influence of different concentrations of NaOH in Chapter 3. Chapter 4 examined P recovery from alum-P sludge through a bioavailability study using switchgrass (SG) as the test crop. SG was the choice crop due to its perennial nature, huge biomass yield and usefulness in biofuel production.

Chapter 5 reports a study where alum-P sludge was used as the source of P for maize in a low-P soil. Maize as a choice crop was studied due to the important yet competitive role it plays in the survival of man and livestock as well as its contributions to the biofuel world. The following were findings to help with the reuse of chemical sludge as a by-product from mostly small communities with conventional wastewater treatment methods.

6.1 Statistical Modeling of Phosphorus Solubilization from Chemical Sludge and Evaluation of Optimal Sodium Hydroxide Dose

Main findings and contributions:

It was demonstrated from our in-house solubilization analysis that solubilization of P solution can be done using NaOH. The supernatant can be recycled to coagulate more P in wastewater solution as well as to generate struvite for agricultural purposes. The optimal dose of NaOH as well as the modeling approach illustrated in this study could be tested for other types of sludge. We identified that P solubilization was very fast with the application of low dosage of NaOH; maximum P solubilization was achieved within the first 20 min of reaction time for instant NaOH application. After this equilibrium point, no significant increase was observed in orthophosphate concentration. Successive NaOH application however, increased the amount of orthophosphate but this was not significantly different from that observed at 20 min. Regardless of the method of application, P concentration at the end of 100 min was the same for both methods. The application of alkali caused a disintegration of floc materials in the sludge with soluble P peaking at 1 M NaOH. These results are important as they highlight the impact of reaction time, sludge P concentration and alkali strength in the solubilization of P from sludge.

Linear correlations for P remaining in sludge after solubilization in relation to the concentration of NaOH used were also developed.

These results are important as they could be used to predict the amount of P remaining in sludge and give an estimate of the amount of NaOH needed to solubilize a certain concentration of P in sludge. For our study, it could be concluded that there is a limitation to NaOH solubilization as the remaining P in sludge could not be recovered using this method. Solubilized P in the supernatant could be treated to generate struvite which is a proven slow-release fertilizer. Aluminum in the supernatant can be recycled to serve as a precipitant for P in wastewater.

6.2 Bioavailability Study of Phosphorus in Alum-Phosphorus Sludge using Switchgrass

Main findings and contributions:

This study aimed at identifying the bioavailability of P from alum-P sludge when cultivated with switchgrass (SG) for 3 cycles with each cycle spanning a 45-day period. Our analysis revealed that the use of alum-P sludge as a P source for SG growth is quite comparable to MAP (monoammonium phosphate). Alum-P amended soils had greater biomass yield compared to control pots. Biomass yields from both sludge and MAP treated pots were similar hence the ability of alum-P to promote crop growth just like MAP. In alum-P sludge amended pots, P uptake increased with cycle, which was attributed to the perennial nature and root system of SG which can penetrate deep into the soil. We also identified that alum-P sludge displayed characteristics of a slow-release fertilizer as we observed an increased biomass yield with each new season.

The phosphorus recovery efficiency (PRE) was highest for alum-P sludge in cycle 3 where all roots had stabilized and could sufficiently support above ground growth. Note that perennial grasses do better in subsequent years after proper root establishment. Application rates above 9.7 mg^{-1} kg P made no difference in PRE for alum-P sludge. This application rate identification is very useful as it would help to prevent over-application, surface run-off and ground water contamination. The amount of biomass generated could support the generation of biofuel as well as serve as feed for animals. This offers an opportunity to reduce the land-use competition between food and hay as it can utilize low-quality land. Cropping SG using alum-P sludge would reduce dependence on MAP and still produce better biomass yield over MAP. This would also drive down the cost of inorganic fertilizer and our overdependence on inorganic fertilizer. It could also improve the quality of prairie lands and reduce soil erosion due to its fibrous and dense root system. We identified that SG could extract Al from alum-P sludge, however, the extent of Al uptake should not affect the usability of SG as a source of biofuel or feed. The amount of Al extracted as

a result of the addition of alum-P sludge application is relatively little when compared to the naturally abounding Al in soil. From our findings, there were no significant differences in Al uptake among control pots, alum-P sludge and MAP amended pots. Hence Al in the sludge had no visible effect on the grown switchgrass.

6.3 Aluminum Phosphate Sludge as an Alternative P Source for Maize Production in a Low Olsen-P Soil

Main findings and contributions:

This research showed some of the limitations associated with inorganic fertilizer when compared to alum-P sludge as seen with maize in a low Olsen-P calcareous soil. PRE for sludge amended soil showed no significant rate variation while MAP increased with rate. This means that the smallest application rate is sufficient to support comparable biomass yield like MAP. The rate of application of alum-P sludge may become a concern if not properly managed. Interestingly, biomass yield and P uptake all showed improved output with alum-P sludge than MAP. Yield, however, decreased with cropping cycle for both MAP and alum-P sludge. The use of alum-P as an alternative source of P supply could be beneficial when the right rates are considered. Increase in Al uptake was seen in the third cycle which could connote that cropping for just 2 cycles should be sufficient to prevent Al uptake. This is an important consideration, especially if maize grown on alum-P amended soils is to be explored as an animal feed option. Overall, the application of alum-P sludge is beneficial and produces results that are better when compared with the use of MAP/inorganic fertilizer.

Generally, the use of alum-P sludge could be an alternative source of P in a world with an ever-increasing P demand for inorganic fertilizers such as MAP. The promotion of alum-P sludge usage solely for the production of feedstock for biofuel would lead to a diversified P usage. Although

one time application of alum-P sludge is beneficial to subsequent crops, we recommend that care should be taken in the use of alum-P sludge as application based on available P may lead to P accumulation and pose a potential risk to the environment.

6.4 Cost Savings in this Work

Although P recovery in the form of struvite and other established methods have been properly documented, the use of chemical sludge as a source of P is deeply frowned at. Recent studies are emerging which showcase the benefits of careful and well-planned application of chemical sludge to farmlands for crop growth. Here we have shown that P can be solubilized using NaOH and this would be at optimal recovery within the first 30 min of the process. The model developed can identify the amount/strength of NaOH required to achieve this and this depends on the initial P concentration in the sludge. This is a cost-effective solubilization of P as NaOH is readily available and affordable since sludge handling and disposal cost has been estimated to be around 30 - 60% of the wastewater treatment plant management cost in general (Chakraborty et al., 2020; Jin et al., 2018; CCME, 2012b). Zhao et al. (2021) reports that cost of sludge disposal could be as high as 41.5 - 69.1 million CAD and as low as 3.9 million CAD yearly for some countries. With the commercial value of 1kg of NaOH roughly estimated to be about 0.43 - 0.51 CAD (export.rumarket), we estimate that chemical need would be about 1 kg of NaOH for 5 kg of sludge. For the previously estimated 66,000 tons dry alum sludge, chemical cost is estimated to be roughly 5.94 million CAD making solubilization cheaper on a scale of sludge handling, transportation and disposal. The chemical sludge-alkaline mixture must be separated into supernatant and insoluble part before any further processing can take place. This solubilized P in the supernatant can then be precipitated out using magnesium and ammonia as struvite, this option must also be properly analysed for its cost-benefit compared to the purchase of commercial fertilizer since the

supernatant from alkali solubilization may have some specific chemical needs as well as other demands to enhance struvite formation. There is also the cost associated with introducing an additional alkali-sludge equipment into an already existing wastewater treatment plant. Capital expenditure of the equipment for batch solubilization plus the cost of immediate integration must be part of this integral assessment for benefit analysis.

Growth room experiments have shown that chemical sludge is beneficial as not only are the P, N and other nutrients utilized, but the presence of organic matter also improves and stabilizes the soil. Alum-P sludge showed that it could compete with MAP and perform better. The use of alum-P sludge on agricultural lands or as an organic amendment would reduce the over-dependence on inorganic P. However, alum-P sludge usage can be focused on biofuel needs and livestock feed.

Concerns over shortage of facilities, contamination of groundwater/surface water and landfilling cost can be overwhelming however, the concept of using sludge as a source of P when applied at a justifiable rate cannot be overlooked as the world envisaged P shortage looms while sludge remains an abundant sink of beneficial nutrient.

There may be an overwhelming notion of aluminum introduction into the soil through the use of chemical sludge however, from the experiments done, it could be seen that the soil is mostly abundant in aluminum and its uptake by plant was identified in all pots (control and P treated pots). The introduction of pathogens into the soil could be a major challenge (Reilly, 2001) as there are concerns of plant, water and land contamination. More research, regular testing, and a continuous engagement as well as risk assessments with all stakeholders and government agencies is required going forward.

Secondly, the overapplication of nutrients like nitrogen in various forms as found in the sludge could be one of the major challenges of chemical sludge application based on bicarbonate P

content. Proper analysis of the organic nitrogen, ammonia, and all other forms of nitrogen in the sludge is a critical step to ensuring overdosing of nutrient is prevented.

The phosphorus recovery efficiency identified over all cycles for sludge amended pots summed up to be over 100% over the course of the experiment, this may have been because of other forms of P in the sludge that were not accounted for in the initial sludge analysis. It may be worthwhile reassessing the bicarbonate P, organic P and total P in the soil after every recovery for accuracy in recovery analysis as well as in the initial sludge.

Assessment on different soil types would help to broaden the usability of chemical sludge as a source of P since only one soil type (sandy soil) and pH (8.2) was tested in this work.

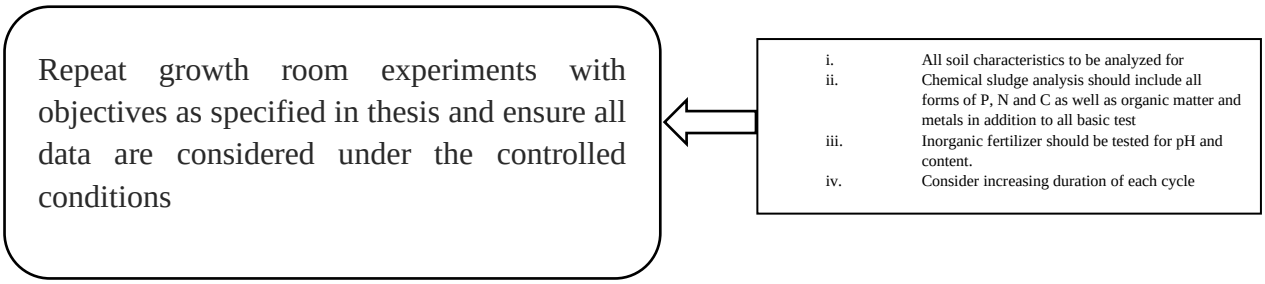
Furthermore, only one type of chemical sludge was tested in these growth room experiments, whereas, there are a range of chemical sludges with different pH and a range of soil characteristics which may influence the results reported in the work. For example, with ferric sludge, results may show dissimilar P sensitivity compared to what has been identified in this work in acidic soils.

For a 3 ppm Olsen-P soil (soil layer 0-15cm) soil in Manitoba, the P application rate of 4.45 Mg sludge ha^{-1} soil is needed to supply the required P application rate of 20 kg P ha^{-1} dry soil (Manitoba Agriculture, 2007) for maize cropping based on the experimented alum-P sludge. To verify and validate this application rate, it is necessary to recreate this experimental work with a complete sludge and soil analysis. The results should then be followed by a predictive simulation model for upscaling.

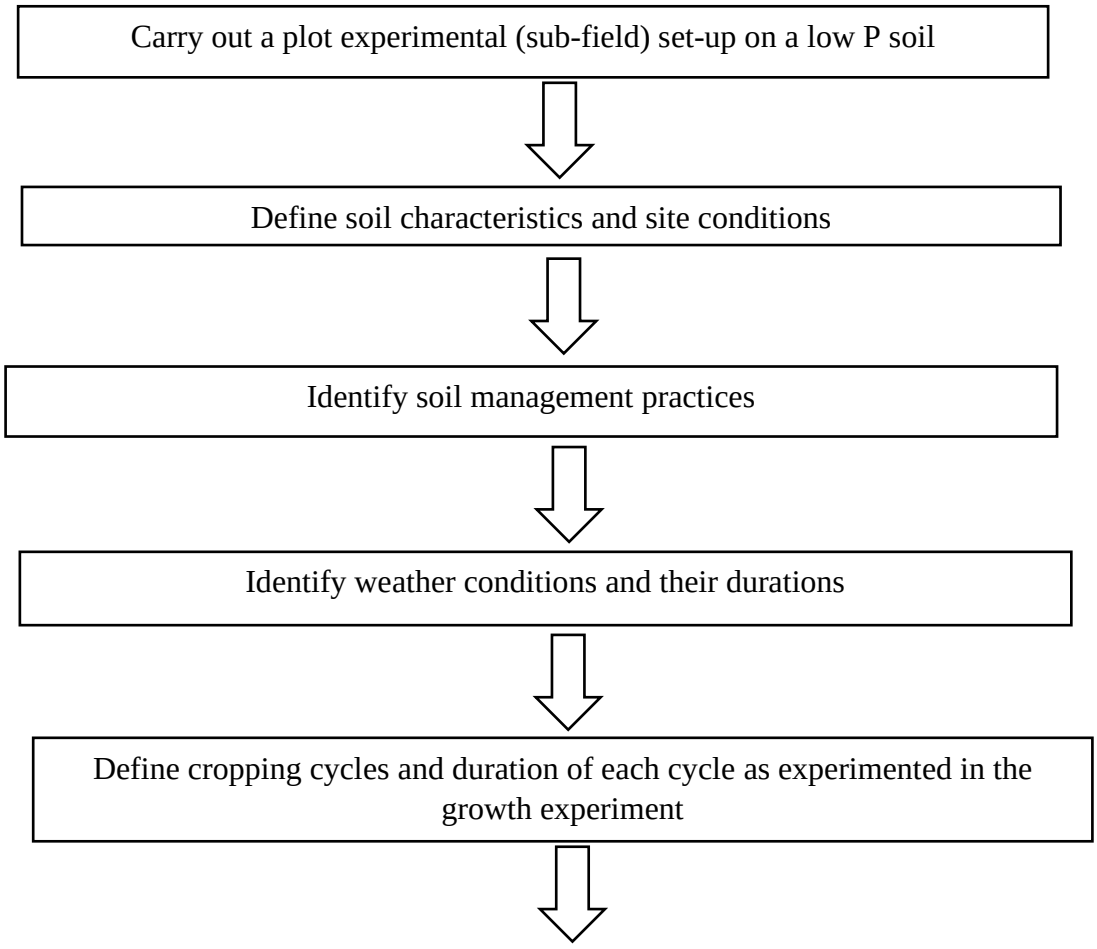
In upscaling of this bench experiment, a roadmap to ensure a clear outlook on the application of chemical sludge under the effect of climatic changes and other environmental factors is looked at. A crop model simulation (for example Agricultural Production Systems Simulators: APSIM) (Wang et al., 2014; Manivasagam & Rozenstein 2020) could be used to identify performance effect

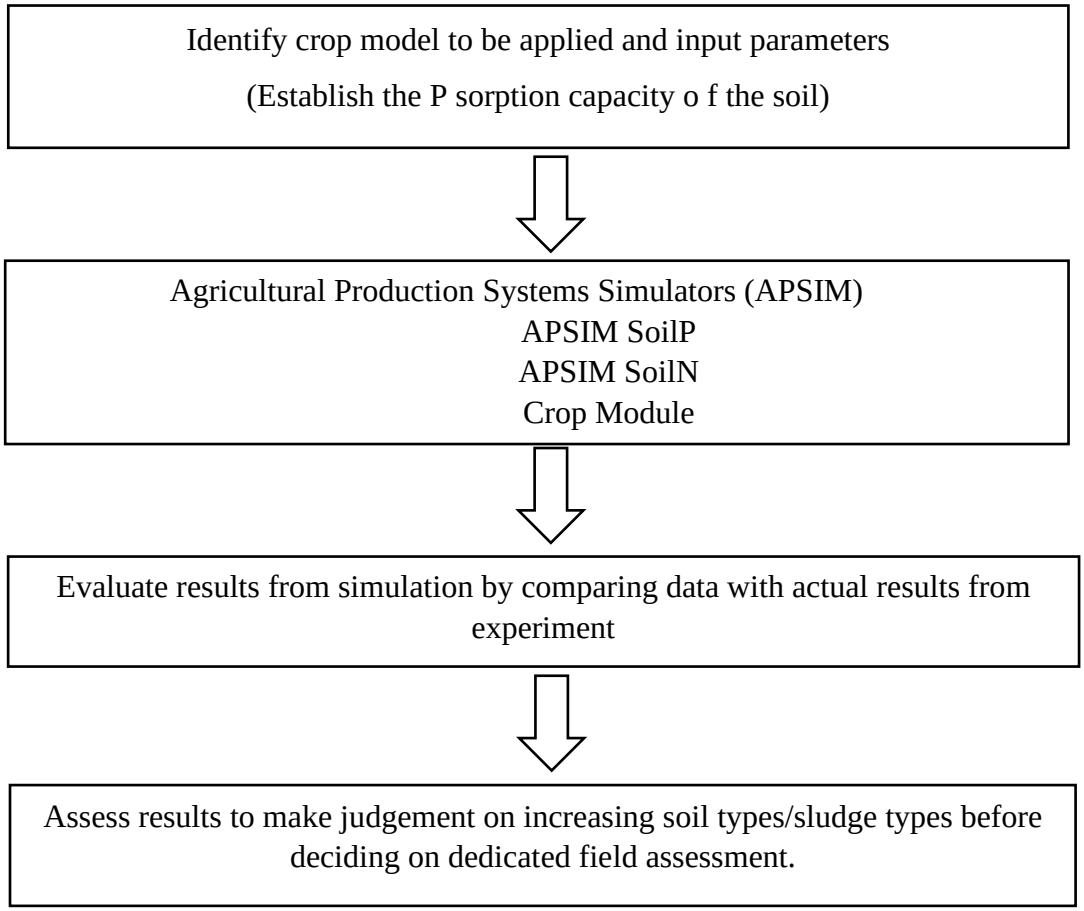
over time for maize and switchgrass based on P application rates. This gives an understanding that parameters such as weather variation, soil morphology and biological parameters may influence the results compared to results from growth room. The flowchart below itemizes the next steps needed to ensure the bench experiments are available for better acceptance and scale-up.

1. Immediate steps to be taken:



2. For scale-up of the bench experiments:




Identify crop model to be applied and input parameters
(Establish the P sorption capacity o f the soil)
Agricultural Production Systems Simulators (APSIM)
APSIM SoilP
APSIM SoilN
Crop Module
Evaluate results from simulation by comparing data with actual results from experiment
Assess results to make judgement on increasing soil types/sludge types before deciding on dedicated field assessment.

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CHAPTER 7

RECOMMENDATIONS FOR FUTURE WORK

7.0 Overview

The studies conducted herein provide information on P in alum-P sludge and how it can be influenced by alkali solubilization (chapter 3) and plants in a low-P soil (chapters 4 and 5). It is of great importance that there is a growing interest in the reuse of alum-P sludge as a means of P recovery to curb challenges around P availability, reduce disposal cost and promote environmental sanity especially groundwater quality.

Recommendations from this work include the following:

1. Sludge P is beneficial and as competitive as MAP as demonstrated in this study. Government should encourage more research to enable applicability of chemical sludge as a source of P since reintroducing sludge to soil has shown potential to be one of the most beneficial ways of nutrient recycling.
2. Due to the beneficial contributions of sludge P to crops and soil, government should encourage and assign dedicated lands for cropping of SG and maize with chemical sludge application as the P source. We also recommend that landfilled sites should be cropped, and biomass generated used solely for biofuel production. This will generate income for farmers, reduce land use competition for food and hay. Most importantly, it would impact positively on biomass generation for biofuels while reducing inorganic fertilizer demand.
3. P from chemical sludge can lead to overapplication due to mineralization of organic to inorganic forms of P therefore, annual soil monitoring should be done even at low application rates. A study to understand the impact of bacterial community around alum-P

amended soils (physicochemical, biological and biochemical impacts) should be carried out as it would expose the importance of root fungus and how it may have impacted P uptake and mineralization since the roots were reintroduced into the soil after each cropping cycle.

4. Plants were grown in a controlled environment, and this must have eliminated a lot of variabilities from factors such as light, temperature, humidity, and water. This constant environmental condition may not depict the fluctuations that may alter the dynamics of growth and nutrient uptake from the soil in the open. However, a repeat pot experiment is required with a complete parametric analysis for both soil and sludge (all forms of nutrients to be identified). Furthermore, a field assessment is necessary to validate data based on uptake and yield using alum-P sludge. Pot experiments may also have limited the ability of the plant roots to explore for nutrients in the soil. P uptake may vary greatly when this is carried out in the field as roots may interact with different pH at different soil levels. Simulation tools would help with upscaling analysis using field parameters for predicting P outcome. APSIM should be considered for initial scale-up.
5. There is no evidence from this research that the addition of alum-P sludge caused high level of Al uptake and influences Al in soil since soil is already very abundant in Al (Oberg and Mason-Renton, 2018). However, we recommend a replicate pilot experiment for maize to analyze for Al uptake in cycles 1 and 2. Results from this analysis could impact the usage of biomass as a source of animal feed if Al quantity in biomass remains negligible or just for biofuel. In subsequent cropping years where Al may be released, SG should be grown.

6. This study was done on an alkaline soil (pH 8.2). It would be interesting to evaluate the P release nature in different soil types with different pH ranges when soils are fertilized with alum-P sludge.
7. Pretreatment/solubilization of chemical sludge would promote nutrient (P) recovery in the form of struvite. Studies on NaOH solubilization of chemical sludge with different total solid content to validate the predicted recovery model should be done. This would also satisfy the concerns over the optimal reaction time for maximum solubility and NaOH dosage requirements. Further studies should focus on treating the recovered P solution to generate struvite.

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