EVALUATION AND DEVELOPMENT OF LIME-BASED PRODUCTS TO REDUCE PHOSPHORUS LOSS FROM AGRICULTURAL SOILS

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ABSTRACT

Phosphorus loss from agricultural fields is one of the main contributors to the rapid eutrophication of lakes and rivers. Application of soil amendments may be an effective measure in reducing phosphorus loss from agricultural fields. Lime-based products, as high calcium-containing materials, could be promising soil amendments in retaining phosphorus in the soil. However, limited study has been conducted on lime as a phosphorus-immobilizing amendment in neutral and alkaline soils. There exists an urgent need for cost-effective novel materials to mitigate phosphorus loss. Therefore, the main goal of this research was to evaluate the effectiveness of existing lime-based products on reducing phosphorus concentration in the leachate from common agricultural soils without interfering with crop growth as well as to develop a novel, cost-effective lime-based product to increase soil phosphorus adsorption capacity in the soil. This principle goal was achieved through 5 main objectives by both laboratory and lysimeter experiments as described below.

Based on a laboratory study with repacked soil columns amended with various application doses of four different lime products (high calcium hydrated lime, dolomite hydrated lime, lime kiln dust #1 and #2), high calcium hydrated lime and lime kiln dust #2 were able to reduce phosphorus concentration in the leachate from clay loam soil columns to less than 0.03 mg L^{-1} at the lowest application dose of 1% by air-dried soil mass.

In order to study the interactions between lime amendment and phosphorus leaching in different soil types with alkaline pH, intact soil columns with three different soil textures of sandy loam, loam and clay loam were studied and compared to laboratory repacked columns. The results showed that hydrated lime applied to the top 5 cm of soil could significantly reduce soluble reactive concentrations in the leachates from sandy loam and loam soil columns in both intact and repacked columns, while soluble reactive phosphorus concentrations in the clay loam soil leachates did not show a significant change. Total dissolved phosphorus was reduced in limed loam and limed clay loam leachates in indoor intact and repacked columns.

In order to study the effect of lime application on phosphorus leaching and soybean growth at field-scale under natural conditions, lysimeters packed with sandy soils of neutral pH were used. The results showed that lime could significantly reduce soluble reactive phosphorus in the leachate collected from lysimeters (at two depths of 7 and 30 cm) by 50% without having negative impacts on soybean growth. Soybean yield was increased by 10% with lime treatment.

Adsorption/desorption studies were conducted on the four different soil types (sandy, sandy loam, loam, and clay loam) amended with high calcium hydrated lime and lime kiln dust. The results demonstrated that soils amended with both hydrated lime and lime kiln dust significantly increased the Freundlich adsorption coefficient by 3.2, 2.4, 2.0, and 1.6 times in loam, sandy, sandy loam, and clay loam soils, respectively. Although the hydrated lime showed higher potential to increase the maximum adsorption capacity in comparison to lime kiln dust, they both exhibited similar performance in lower phosphorus concentration ranges found in the soil solution.

Given the potential of lime kiln dust, and being inexpensive, this product was selected to be modified through a simple iron-coating procedure to further increase its adsorption capacity and to develop a neutral pH product. The novel iron-coated lime kiln dust had a pH of 7.65 and an increased Brunauer-Emmet-Teller surface area of 35 m^2 g^{-1}. Both image and chemical analysis confirmed the presence of iron loads on the lime kiln dust (16% of total mass). The clay loam amended with the new iron-coated lime kiln dust had phosphorus adsorption of 450 mg kg^{-1} (at 1mM P), a 30% increase compared to that of the non-amended clay loam, while the Langmuir phosphorus adsorption affinity was increased by 4 times in the clay loam amended with the iron-coated lime kiln dust.

Given the simple development procedure, high efficiency, and low-cost final product, the iron-coated lime kiln dust could be a promising soil amendment to increase soil phosphorus adsorption to eventually mitigate rapid eutrophication of downstream water bodies.

RESUMÉ

ÉVALUATION ET DÉVELOPPMENT DES PRODUITS À BASE DE CHAUX POUR RÉDUIRE LA PERTE DE PHOSPHORE DES SOLS AGRICOLES

La perte de phosphore des terres agricoles est l'une des origines principales de l'eutrophisation rapide des cours d'eau. L'application d'amendements au sol pourrait efficacement réduire la perte de phosphore. Des produits à base de chaux pourraient servir en tant que des matériaux fixant le phosphore. Cependant, ils existent des recherches limitées sur cette sujet surtout concernant des sols neutres et alcalins et pareillement, il y a une grande demande pour des nouveaux produits rentables immobilisant le phosphore.

Par conséquent, cette étude vise à évaluer des produits à base de chaux pour réduire la concentration de phosphore dans le lixiviat des sols agricoles et également développer un original produit rentable augmentant la capacité du sol pour adsorber plus du phosphore. Ce but principal était réalisé à travers 5 objectifs par une combinaison des expérimentés en laboratoire ainsi que sur le terrain.

La chaux hydratée riche en calcium et la poussière de four à chaux ont réduit la concentration de phosphore à moins de 0.03 mg L^{-1} dans le lixiviat des colonnes de sol en laboratoire. La dose d'application optimale a été trouvé égal à 1% en poids du sol.

Afin d'étudier les interactions entre l'amendement de chaux et la perte de phosphore dans les textures de sol variés et alcalins, des colonnes de sol intacts ayant trois textures de sol de limon sableux, limon et limon argileux ont été étudiées et comparées avec les colonnes en laboratoires. L'application de la chaux hydratée à la surface de sol (5 cm) peut réduire la concentration de phosphore réactif soluble dans les lixiviats des colonnes intactes limon sableux et limon ainsi que dans les colonnes en laboratoires. La concentration de phosphore réactif soluble n'a pas été touché

par la chaux en case des colonnes de sol limon argileux. La concentration de phosphore soluble total a été réduite dans les colonnes intactes intérieures et en laboratoires des sols limon et limon argileux.

Pour étudier l'effet de l'application de chaux sur la perte de phosphore et le rendement du soja sous les conditions naturelles, les lysimètres sableux à pH neutre ont été utilisés. Les résultats ont indiqué la capabilité de la chaux à réduire le phosphore réactif soluble dans la solution de sol jusqu'à 50% sans imposer des effets négatifs sur la croissance du soja. Le rendement du soja était augmenté par 10% grâce à l'application de la chaux.

Les études de sorption ont été effectuées sur 4 sols distincts mélangés avec la chaux hydratée riche en calcium ainsi que la poussière de four à chaux. Le coefficient d'adsorption de Freundlich a été augmenté par 3.2, 2,4, 2.0 et 1.6 fois dans les sols limon, sableux, limon sableux et limon argileux, respectivement, par rapport aux sols non modifiés. Bien que la chaux hydratée ait démontré plus de potentiel pour augmenter la capacité maximum d'adsorption de Langmuir, la poussière de four à chaux a montré une efficacité similaire par rapport à la chaux hydratée aux niveaux de concentrations faibles de phosphore (0- 0.2 mg L^{-1}).

La poussière de four à chaux a été sélectionnée pour être modifier grâce aux résultats prometteuses ainsi que à son bas prix. Une nouvelle poussière de four à chaux couverte par fer a été développée. Le nouveau produit avait un pH neutre de 7.65. Sa surface analysée par BET était 30 m^2 g^{-1} qui est un accroissement de 30 fois en comparaison avec la chaux non modifiée. Il y avait 16% de fer présent sur le produit modifié confirmé par analyse d'image et chimique. L'ajout du nouvel amendement au sol limon argileux à 1% (w/w) a abouti à l'adsorption de phosphore de 450 mg kg^{-1}, une augmentation de 30% par rapport au sol non modifié.

La poussière de four à chaux couverte par le fer pourrait être un nouvel amendement immobilisant le phosphore qui offre une solution prometteuse pour atténuer l’eutrophisation rapide des cours d’eaux précieuses.

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DEDICATION

This thesis is dedicated to my father, Prof. Saeid Eslamian, who was my inspiration and motivation to pursue a doctorate degree.

THESIS FORMAT AND CONTRIBUTION OF AUTHORS

This thesis was prepared by the candidate in the manuscript-based format in accordance with McGill university guidelines for the preparation of a Ph.D. thesis. The thesis consists of five manuscripts accepted, under review or to be submitted to recognized peer-reviewed journals. The candidate, Faezeh Eslamian, is the first author of all five manuscripts. Faezeh Eslamian was fully responsible and involved during all stages of the research, including literature review, concept development, experimental design, project implementation, laboratory and field sampling and analysis, material and supplies management, data interpretation, statistical analysis as well as manuscript preparation. The co-authors of all five manuscripts include Dr. Zhiming Qi, Dr. Shiv Prasher, Kevin Kelly Varges, Cheng Qian, Mike Tate, Nikolas Romaniuk, Dr. Tiequan Zhang.

Dr. Zhiming Qi, as the thesis supervisor provided scientific guidance and supervision throughout this thesis as well as assistance in editing and review of all manuscripts. Dr. Prasher had a scientific and technical advisory role in two manuscripts. Kevin Kelly Varges assisted in concept development and interpretation of the data of one manuscript. Cheng Qian had a laboratory assistance role in one manuscript. Mike Tate helped with the editing of all manuscripts, while Nikolas Romaniuk and Dr. Tiequan Zhang assisted in editing one manuscript each.

The five publications related to this thesis are as follows:

- **Eslamian F.**, Qi Z., Tate M., Zhang T., Prasher S.O. 2018. Phosphorus loss mitigation in leachate and surface runoff from clay loam soil using four lime-based materials. Water Air Soil Pollution. 229:97. https://doi.org/10.1007/s11270-018-3750-0.

- **Eslamian, F.**, Qi, Z., Tate, M. and Romaniuk, N. Lime application to reduce phosphorus release in different textured intact and small repacked columns, Journal of Soil and Sediments. Under Review.

- **Eslamian, F.**, Qi, Z., Prasher, S.O. and Tate, M. The effect of lime on phosphorus leaching and soybean growth in sandy lysimeters. To be submitted.
- **Eslamian, F.**, Qi, Z., Qian, C. and Tate M. Lime amendments to enhance phosphorus adsorption capacity in alkaline soils to mitigate eutrophication. Journal of Environmental Science and Pollution Research. Under review.
- **Eslamian, F.**, Kelly Varges, K., Qi, Z. and Tate M. Development of an iron-coated lime kiln dust to increase soil phosphorus adsorption capacity. To be submitted.

Conference presentations related to this thesis are as follows:

- **Eslamian, F.** and Qi, Z**.** Application of dolomite hydrated lime as an amendment to reduce phosphorus loss in Pike River Watershed. Canadian Society for Bioengineering (CSBE) Conference, Halifax, Canada. 14-17 July 2016. (Poster Presentation-2nd prize winner)
- **Eslamian, F.** and Qi, Z. Phosphorus leaching as influenced by lime application in undisturbed soil columns with different soil textures. American Society for Agricultural and Biosystems Engineering (ASABE) annual meeting, Boston, USA. July 7-10, 2019. (Oral presentation)
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CHAPTER ONE: INTRODUCTION

1-1 Problem Statement

Eutrophication is defined as the over-enrichment of nutrients especially phosphorus (P) and Nitrogen (N), and it is associated with rapid algal growth, state of hypoxia, fish mortality as well as negative impacts on the ecosystem (Rabalais et al., 2001; Chen et al., 2007; Schindler et al., 2012; Environment Canada, 2016; Lake Champlain Basin Program, 2016; Bol et al., 2018).

Traditionally nitrate was considered the primary limiting nutrient. However, recent research has demonstrated that P is currently the limiting nutrient for aquatic life and freshwater quality. Phosphorus loss from point sources such as industrial effluent and municipal sewage or non-point sources such as agricultural runoff or leaching can contribute to accelerated eutrophication of lakes and rivers (Sims et al., 1998; Lalley et al., 2016). Non-point sources such as agricultural activities account for considerable amounts of P loads into Canadian waters as well as around the world (Sharpley et al. 2013; Jarvie et al. 2013, 2017; Kleinman et al., 2015; King et al., 2015; Ortiz-Reyes and Anex, 2018; Sachdeva et al., 2019). The over-application of fertilizer and manure in excess of plant requirements and only based on soil N requirements has led to excessive accumulation of P in soils (Gburek et al. 2000; Li et al. 2013). This surplus P can leach beyond the topsoil or runoff into downstream water bodies and consequently cause rapid algal growth (Tian et al. 2017).

Approximately 150 lakes have been affected by “cyanobacteria bloom” in Quebec alone (MSSS 2007). The annual average P concentration in the Missisquoi Bay of Lake Champlain, located in southern Quebec, was reported as 0.06 mg L^{-1} in 2016 being two times more than the Quebec water quality standard for P at 0.03 mg L^{-1} (Lake Champlain Basin Program, 2016). In 2014, P concentration in the Saint Lawrence River was reported twice as high as the water quality guideline (Environment Canada, 2016). In Lake Erie, which is the shallowest of the Great Lakes, high levels of P were reported (Michalak et al., 2013; Environment Canada 2017). In Lake Winnipeg, high P concentrations related to rapid algal growth were observed (Environment Canada, 2018).

A critical water quality guideline of 0.03 mg L^{-1} was set by the provinces of Quebec, Ontario, and Vermont to avoid further eutrophication of surface water in the area (Environment Canada, 2004). There is still much uncertainty involving nutrient management and eutrophication prevention. Watershed management practices have been employed during the past decades to reduce P loss from agricultural fields (Jarvie et al., 2013). However, these traditional practices have been unsuccessful in reaching the target P concentration and meeting water quality guidelines (Kleinman et al., 2015). In Lake Erie, which is the shallowest of the Great Lakes, total and particulate P loadings were considerably reduced through nutrient management practices such as P-based fertilizer application. However, dissolved P forms have been significantly increasing throughout the years (Kleinman et al., 2015). Conservative agricultural practices aimed at reducing particulate P loss led to an increased soluble reactive P transport into Lake Erie (Javie et al., 2017). Effective P loss reducing strategies and novel materials are required to mitigate this issue. Application of soil amendments to reduce P desorption from agricultural soils could be an effective measure alongside preventive agricultural practices. Lime as a high calcium material and its by-products can serve as potential P-immobilizing material to decrease P desorption from agricultural soils. There is a high need for cost-effective novel materials to increase soil P adsorption capacity to retain this surplus P in the soil to prevent further eutrophication. While lime is solely applied to agricultural soils to neutralize acidity, there is limited research on its role as a P-immobilizing material, especially in neutral or alkaline soils. A novel lime-based amendment to increase soil P adsorption capacity has not been previously developed.

1-2 Research objectives

The main objectives of this Ph.D. study were as follows:

- Evaluation of existing lime-based products as soil amendments to reduce P in leaching from agricultural soils
- Development of a novel lime-based product to increase soil P adsorption capacity

The two main objectives were accomplished through the following sub-objectives:

- Find the minimum application dose of four lime-based products to reduce P concentrations in leachates from laboratory repacked clay loam columns to meet Quebec P water quality guidelines.
- Evaluate the potential of the four lime-based products on reducing P concentrations in the runoff in an indoor rainfall simulator experiment at the studied minimum dose.
- Study the effect of lime application on P concentration in the leachate from intact soil columns of three different soil textures with alkaline pH.
- Compare the performance of lime application on P leaching in intact soil columns under natural conditions with that of the laboratory repacked columns for the three soil textures
- Investigate the effect of lime application in reducing P release from sandy lysimeters under natural conditions
- Evaluate the effect of lime application on soybean yield in sandy lysimeters during a full growing season under natural weather conditions

- Compare the effect of fall versus spring lime application on P release from sandy lysimeters
- Study the potential of hydrated lime and lime kiln dust in increasing soil P adsorption capacity in four different soil types with neutral to alkaline pH
- Develop and characterize a novel, cost-effective iron-coated lime kiln dust with increased P adsorption capacity and neutral pH
- Compare the efficiency of the new iron-coated lime kiln dust in increasing soil P adsorption capacity with that of non-amended soil and soils amended with the unmodified lime kiln dust

1-3 Thesis Outline

This thesis is presented in 10 chapters. Chapter 1 includes a general introduction to the problem to be resolved and the objectives of this research. Chapter 2 gives a comprehensive literature review of this research topic and finds the knowledge gap. Chapter 3 deals with finding the minimum application dose for the studied lime products to reduce phosphate concentration to below the standards. Chapter 4 studies the interaction between lime and P in three different soil textures with alkaline pH. Chapter 5 discusses the potential of lime in reducing P loss without having negative impacts on soybean growth. Chapter 6 compares the performance of hydrated lime and the lime kiln dust in increasing soil P adsorption capacity. Chapter 7 deals with the development of the novel iron-coated lime kiln dust and its performance. A general summary and conclusion are presented in Chapter 8, while contributions to knowledge and recommendations for future research are presented in Chapter 9. Finally, all cited references are listed in Chapter 10.

CHAPTER TWO: LITERATURE REVIEW

2.1 Phosphorus

2.1.1 Phosphorus forms in soil

Phosphorus (P) is a chemical element with an atomic number of 15 and an atomic weight of 31. Phosphorus is the second essential nutrient for plant growth. Phosphorus is never found as a free element on earth since it is highly reactive.

Phosphorus can be found in both organic and inorganic forms in soil. Inorganic P has simpler forms. Orthophosphate (PO_4^{3-}) is the main part of inorganic P. The term orthophosphate can be used for any other hydrated or substituted form of this ion, such as HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, or $CaPO_4^-$ (Reynolds and Davies, 2001; Darch et al., 2014). Inorganic P is more readily available to plants than organic P (Nachimuthu et al. 2009). Organic P often needs to be hydrolyzed to inorganic P first, prior to plant uptake. The main sources of inorganic P in the soil are primary minerals, atmospheric deposition, and mineral fertilizers. Organic P includes more complex compounds that contain carbon (C)–hydrogen (H) bonds, in addition to P (Darch et al., 2014). The most important group of organic P compounds are labile monoesters. Monoesters contain a phosphorus-oxygen-carbon (P-O-C) chain. Since labile monoesters have weak sorption to the soil, this results in a greater tendency for mobility (Darch et al., 2014). Therefore, labile P is of great concern in leaching from soils with the over-application of manure.

The relationship between different measures of P is described in Equation 2-1:

$$TP = TDP + PP \qquad \text{(Equation 2-1)}$$

Where TP is Total phosphorus, TDP is Total dissolved P, and PP is particulate P. Particulate phosphorus is the form of P adsorbed on the soil particles while dissolved P is soluble in the soil solution. Soluble reactive phosphorus (SRP), alternatively called dissolved reactive phosphorus (DRP), is the major sub-category of TDP accounting for its inorganic portion. Soluble reactive phosphorus is mainly composed of orthophosphate. The difference between TDP and SRP is due to some dissolved organic phosphate complexes or condensed phosphates, being multiple orthophosphates condensed together, having a covalent bond between O and P (Water analysis, 2013). Soluble reactive P is the most available form of P for plant uptake, which can cause more significant algal bloom issues in waters compared to PP, which is a less available form (Fozzard et al., 1999). Therefore, SRP can be considered as the most critical part of P targeted for P reduction in leaching to mitigate eutrophication. However, under high flow conditions, PP can play a major role (Lake Champlain Basin Program, 2016). Different studies report various forms of P as a P-indicator since there has been no universal agreement on this case. However, most studies have indicated that SRP can be an important form of P since it is the most readily available form and especially related to algal growth and can increase eutrophication.

Orthophosphate in the soil solution is found as either $H_2PO_4^-$ or HPO_4^{3-} depending on the soil pH. In more acidic conditions, orthophosphate is mostly found as $H_2PO_4^-$, whereas, in more alkaline conditions, the HPO_4^{3-} form will be dominant (Sposito, 1989).

In acid soils, P is fixed in the soil by forming compounds with Fe and Al through precipitation and sorption reactions (Borling et al., 2001). In alkaline soils, P is considered to form compounds with Ca or Mg. However, there is limited research on P transport in alkaline soils. Phosphate ions are attracted to positively charged sites of the soil surface. Therefore, pH can be a determining factor in the availability and transport mechanism of P in soil.

2.1.2 Phosphorus cycle

The P cycle is the interactions between various forms of P through different physical, chemical, and biological processes. This interaction will determine the different forms of P, their availability is soil, and their transport in leaching or surface runoff (Ritter and Shirmohammadi, 2001). The major P transformation processes in soil include adsorption/desorption, precipitation/dissolution, mineralization/immobilization, and weathering. Desorption, dissolution, mineralization, and weathering are processes that release P and contribute to the soluble P, whereas adsorption, immobilization, and precipitation are mechanisms through which P is fixed in the soil and thereby, less available to the plant as well as leaching. Figure 2-1 illustrates the input and output to the soil solution in addition to interactions between these processes in soil.

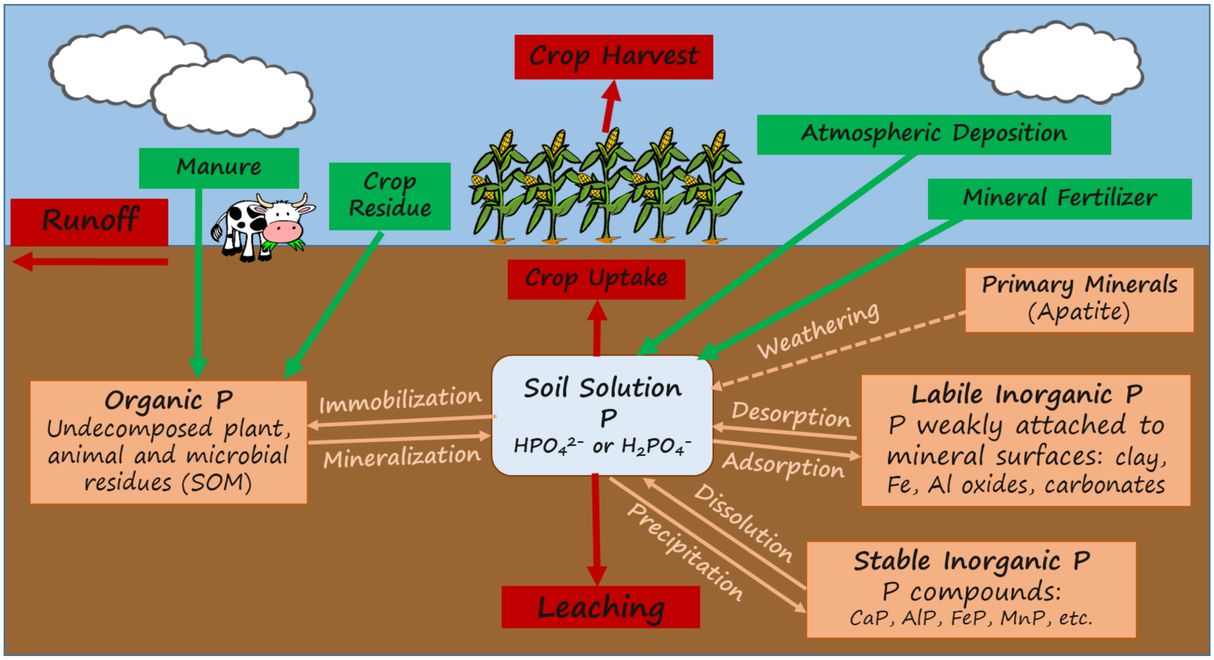

Figure 2-1: Phosphorus cycle in soil solution

The main source of P in the lithosphere is formed from primary minerals such as apatite. This source of P can be transformed into orthophosphate through weathering. Labile organic P is weakly attached to mineral surfaces such as clays, iron or aluminum oxides and carbonates, which can contribute to the soil solution through the process of desorption and adsorption being the reverse process. Stable inorganic P includes stable phosphate compounds such as calcium phosphate compounds. This pool of P can contribute to the soil solution through dissolution (the reverse is precipitation). The organic P pool consists of undecomposed plants, animals, and microbial residues. This P pool is the least available form of P, which can be slowly transformed into a more available form through mineralization with immobilization being the reverse process.

Phosphorus can be added into the soil solution through atmospheric deposition, mineral fertilizer, manure, or crop residue. While atmospheric deposition and mineral fertilizer contribute directly to the soil solution, P added in the form of manure or crop residue will contribute to the organic P pool, which can be slowly broken down to orthophosphate through mineralization. Phosphorus can be lost from the soil solution through leaching, runoff or crop uptake.

2.1.3 Phosphorus leaching

Agricultural fields are one of the main non-point sources of P loss into water bodies (Jarvie et al. 2013; King et al. 2015). Phosphorus can be lost from agricultural fields in various forms through runoff and/or leaching. In Quebec, Goulet et al. (2006) have reported that 95% of the TP and 91% of dissolved P loss occurs in tile drainage (Lake Champlain Basin Program, 2016). Phosphorus concentrations measured in tile drainage from agricultural fields have been highly variable. This could be partly due to soil properties, agricultural management (tillage, fertilization, and crop rotation), and climate. However, a significant amount of P loss is found in tile drainage. This P, which has reached below the root zone, has exceeded the required levels by plant and will consequently enter the surface water bodies and induce eutrophication.

The primary factors which influence P transport through subsurface drainage are as follows: Soil properties, management practices, drainage depth and spacing, hydrology, and climate (King et al., 2015). Soil properties, including soil texture, initial P content, and P sorption capacity, greatly influence the amount of P loss and its transport pathway and mechanism.

The variability of P load based on seasons has been inconsistent in reports (Lake Champlain Basin Program, 2016). However, studies have suggested that under storm events, the P loss is expected to increase. In this case, the soil matrix will be the major pathway for P transport rather than soil macropores (Heathwaite and Dils, 2000; Vidon and Cuadra, 2001; King et al., 2014; Van Esbroeck, 2015). Simard (2005) reported that, in Quebec, the highest P loads in tile drainage occur in spring and fall. Goulet et al. (2006) also found that the spring snowmelt and fall rainfall after crop harvest (non-growing season) account for most of the annual total P load loss.

Several studies carried out on agricultural fields in Quebec (with different soil textures) revealed that the TP load in tile drainage was considerably higher than that of the allowable limits with TP concentrations ranging from 0.03 to 1.1 mg L^{-1} (Beauchemin et al. 1998; Beauchemin et al. 2003; Enright and Madramootoo, 2004; Lake Champlain Basin Program, 2016). Field research in Quebec has reported an estimated TP load approximately ranging from 0.5 to 1.2 kg ha^{-1} yr^{-1} (Eastman et al., 2010; Jamieson et al., 2003; Simard, 2005; Goulet et al., 2006; Enright and Madramootoo, 2004). Therefore, phosphorus leaching from subsurface drainage can be one of the main pathways for P loss in the subsurface drained field, especially in Quebec.

2.2 Soil

2.2.1 Soil texture

Soil properties, especially soil texture, greatly influence the form, amount, and transport mechanism of P loss. Soil texture is related to the percentage of sand, silt, and clay in the soil. Soil texture determines many soil characteristics, including nutrient availability and sorption capacity. Soil texture can affect phosphorus availability due to its influence on soil physicochemical properties, adsorption-desorption mechanisms, and soil microbial activity (Suner and Galatini, 2015). The relationship between extractable soil P and the total dissolved P concentration in leaching and runoff will vary with soil type and texture (Sharpley, 1995). Phosphorus can be adsorbed onto clay or soil organic matter surfaces as well as forming a compound with Ca, Al, or Fe. Soil P and P sorption indices vary with soil type and depth (Pizeghello et al., 2016). Phosphorus leaching has been strongly correlated to soil texture (Leinweber et al., 1999).

Soil texture seems to have an important influence on the form of P loss. Phosphorus losses majorly occur as PP in clay loam soils, while DP plays an important role in sandy loam (Eastman et al., 2010). Clay soil shows a higher potential for binding P in soil than do sandy soils (Andersson et al., 2013). A mineralogical test on a common Swedish clay soil revealed that P seems to become bound to Ca complexes in the finer fraction of the clay soil and this increases with depth (Ulén and Snäll, 2007). The subsoil properties play a more important role in P leaching as compared to the topsoil (Djodjic et al., 2004). Andersson et al. (2013) indicated that there was no significant difference in the volume of leachate influenced by soil type, while P concentration of the leachates differed significantly in response to soil type. Chemical soil properties in sandy soils are predictors of P leaching, whereas in clay soils with macropores, transport mechanisms dominate P leaching behaviors (Andersson et al., 2013). The presence of macropores leads to a quick transport of P through the soil owing to more available water pathways and, therefore, shorter contact time with the matrix will reduce the opportunity for P sorption and lead to release of more P (Djodjic et al., 2004).

2.2.2 Soil phosphorus content

Soil initial phosphorus content is another factor influencing the risk and extent of P loss from soil. Soil initial phosphorus is highly related to and affected by soil texture. Phosphorus is mainly fixed in the soil either attached to Al or Fe oxides in non-calcareous soil. However, in calcareous or alkaline soils, P can be mainly attached to Ca or Mg cations. Soil P saturation index (PSI) is widely used to assess the risk of P desorption from the soil. Phosphorus saturation index or degree of soil P saturation is calculated with equation 2-2, where M3*P*, M3*Al,* and M3*Fe* represent the Mehlich-3 extractable P, Al and Fe in the soil (mg kg^{-1}), respectively (Jiao et al. 2004).

$$PSI = {}^{M3P}\!/_{(M3Al + M3Fe)} \qquad \text{(Equation 2-2)}$$

Soil saturation index should be used in addition to soil P tests (e.g., Mehlich-3) when considering a large range of soil types and pHs (Beauchemin and Simard, 1999). In Quebec, a critical PSI of 20 % is recommended, above which P levels will be higher than crop requirement, and the risk of P leaching will increase (Conseil des Productions Végétales du Québec, 1996).

The correlation between PSI and P solubility is less predictable in neutral and alkaline soils with higher clay content (Beauchemin and Simard, 1999). Heckrath et al. (1995) suggested that in calcareous clay loam, soil Olsen P concentrations higher than 60 mg kg^{-1} will result in weaker retention of P in the soil matrix. Based on the PSI for heavy soils (>30% clay), the recommended amount of phosphorus for corn is 70 kg ha^{-1} (CRAAQ, 2003). Furthermore, it has been suggested that for PSI of 0.089-0.131 (Beauchemin et al., 2003), the phosphorus concentration in the leachate will be higher than the Quebec water quality standard of 0.03 mg P L^{-1} (Medalie, 2014).

2.3 Practices to reduce phosphorus loss

Phosphorus loads from agricultural lands are considered the major non-point source of P into surface waters. Several management practices such as nutrient management, water table management, and wetlands have been suggested to improve the quality of the leachate from tile drainage (Fraser and Fleming, 2001). Preventive management practices include changes in tillage, cropping systems, and fertilizer application guidelines. The latter has great influence on P since it is the direct source of additional P into the soil. Therefore, the type of P source (inorganic vs. organic) in the fertilizer or manure, its application rate, timing, and placement can play a major role in the potential future P loss (King et al., 2015). Phosphorus fertilizer application guidelines need to be respected and should be based on PSI. While preventive agricultural management practices are essential in the long-term, they cannot alleviate the already existing high phosphorus content in soils and water bodies. The best management practices such as chemical adsorption, wetland treatment, and water table management are considered essential in reducing P loss from tile drainage (Kleinman, 2015). King et al. (2015) categorized these management practices into three groups as follows: disconnecting the drainage flow from surface waters, reduction in the drainage flow volume (controlled drainage) and incorporating treatment practices such as filters to remove P from the drainage outflow.

Most studies in the area of P-reducing practices include performing treatment techniques on the outflow of the drainage prior to entering the surface bodies. In Delaware, Bryant et al. (2012) reported a removal efficiency of 65-73% for TDP from the ditch flow using flue gas desulfurization gypsum. In Oklahoma, Penn et al. (2012) suggested the use of steel slag can remove 25% of DP in urban stormwater. Steel stag was also investigated by McDowell et al. (2008) in New Zealand, where they reported a removal efficiency of 70% in P load. CaO was also applied at the outflow of drainage in a study in Lithuania, and a 64.4% decrease in the phosphate concentration in comparison with the control was observed (Saulys and Bastiene, 2008). Aluminum and Fe-based by-products have been investigated and proven effective as ditch filters to remove P from tile drainage water (Stoner et al. 2012; Schneider 2013). Some minerals such as iron oxide, shale, and limestone were used as filters for agricultural runoff (Agyin-Birikorang et al. 2007; Agrawal et al., 2011; Buda et al., 2012). Another filtering technique is the use of commercial adsorbents such as activated carbon, activated alumina, or zeolite. King et al. (2010) showed an average 50% reduction in SRP by using the preceding materials in an outflow filter on a laboratory scale. Furthermore, natural and constructed wetlands have been reported successful to some extent in adsorbing P from drainage outflow as they also act as bio-filters (Vohla et al., 2011; Tanner and Sukias, 2011). However, these measures have not been studied extensively on large scale and are often expensive since they call for constant long-term maintenance, replacement, and operation costs.

Phosphorus is not toxic, therefore, it does not require pre-treatment before entering water bodies in normal conditions. Phosphorus can be problematic in high concentrations to the downstream water bodies but not for soil. Therefore, an effective measure could be retaining the P in the soil and reducing P loss through P-immobilizing materials. This practice would not require changing existing tile drainage systems installed in the field. This research intends to explore the concept of using P-sorbing materials as soil amendments to retain P in the soil and reduce P loss through leaching. The advantage of these materials is that they offer P fixation at the source. Furthermore, P is often fixed in the soil through a reversible process (either adsorption or precipitation), which could be later reversed when the crop becomes nutrient deficient. The use of P-sorbing materials as best management practices to reduce P loss is an emerging field of study, but limited research has been conducted.

Soil amendments are materials added to soil to improve soil properties. Phosphorus-sorbing amendments increase the phosphorus sorption capacity of the soil. An increase in a soil phosphorus sorption capacity will lead to less P release from the soil, and less P will leach into downstream water bodies. These materials are often Fe, Al, or Ca-based products as P is often bound to these metal oxides in the soil. These Ca, Mg, or Fe based soil amendments can be a source of nutrients for the plant as well (Leader et al., 2008).

Zvomuya et al. (2006) studied five P-immobilizing amendments at laboratory scale to reduce P loss from soil irrigated with wastewater. They examined alum $[(Al_2(SO4)_3.14H_2O]$, ferric chloride, calcium carbonate, water treatment residual (which includes $Ca(OH)_2$ and $NaAlO_2$), and sugar beet lime. Alum was reported the most effective being able to reduce the water-extractable P to 20 mg kg^{-1} at an application rate of 3.9 g kg^{-1}. Furthermore, alum was added to lysimeters, and resulted in a 27 and 25% reduction in TP and SRP in the leachate, respectively (Zvomuya et al., 2006). Leader et al. (2008) evaluated various by-products as P-sorbing soil amendments. The results showed that some Ca and Fe-based residues collected from drinking water treatment plants, a commercial Al, a humate product, and coated sand were able to remove considerable amounts of P from soil solutions (Leader et al. 2008). Laboratory incubation studies on acidic and neutral soils amended with gypsum as well as water treatment residues reported a decrease in the water-extractable P in these soil solutions (Callahan et al., 2002). Eduah et al. (2019) studied the effect of corn cob and rice husk biochar as soil amendments on P sorption in two acid and one neutral soil. The biochar was applied at a rate of 1% by soil weight. The results showed that both types of biochar were able to increase soil P retention capacity in the neutral soil while it led to a decrease in P retention in acid soils.

The primary P-sorbing chemicals are Ca, Fe, and Al-based materials. Lime as a high calcium-containing material could be a promising soil amendment to immobilize P in soil and increase soil P sorption capacity. Therefore, the potential of lime-based products in retaining P in the soil will be further discussed.

2.4 Lime

2.4.1 Lime chemistry

Lime is a calcium-containing inorganic material in which carbonate, oxide, and hydroxides are predominant. Lime can exist in three basic forms in a simple cycle: limestone ($CaCO_3$), Quicklime (CaO), and hydrated or slaked lime ($Ca(OH)_2$).

Limestone is a naturally occurring mineral that consists primarily of carbonate calcium and is extracted from mines. Limestone is classified based on its origin, chemical composition, and geological formation. Limestone deposits are widely found around the world (Oates, 1998). Calcium is extracted from early igneous rocks by weather erosion and corrosion by acidic gases. Carbon dioxide is 0.03% by volume of the atmosphere and is dissolved in both sea and freshwater. A combination of dissolved Ca ions and CO_2 results in sedimentary deposition of carbonate calcium, which is subsequently transformed into limestone rock (Oates, 1998). The sedimentation of carbonate calcium occurs by two mechanisms: organic and inorganic. The organic mechanism involves a wide variety of micro-organisms while the inorganic mechanism includes direct precipitation of carbonate. Most commercially viable deposits of carbonate are formed by organic mechanisms (Oates, 1998).

Quicklime is formed by thermal dissociation of limestone. In other words, if carbonate calcium is heated to approximately 1000 ºC, calcium oxide (quicklime) will be produced (Equation 2-3):

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(Equation 2-3)}$$

The quicklime (or pure lime) is highly unstable and can quickly react with H_2O. The handling and storage of this form of lime are difficult and dangerous. If not stored properly, quicklime can cool off and convert back to calcium carbonate.

When quicklime is slaked with water, slaked lime ($Ca(OH)_2$) is produced (Equation 2-4):

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(Equation 2-4)}$$

When just enough water is added to CaO to convert to $Ca(OH)_2$ but still remain in powder form (dry slaking), the product is called hydrated lime.

2.4.2 Lime application

Lime is largely used in construction industries as a building material and to stabilize soil foundation. Furthermore, lime is used in wastewater treatment systems as part of the precipitation process. In Sweden, lime is used for soil structuring and stabilization (SBA, 2015). Lime was reported effective in reducing P leaching losses from clayey soils through improvements in soil structure in Sweden (Svanbäck et al., 2014). Lime used for soil stabilization and improvement of the soil structure can demonstrate many advantages including clay flocculation, decreased plasticity, and reduced tendency to expand with added moisture. When quicklime (CaO) or hydrated lime [$Ca(OH)_2$] is mixed with clay soils, it results in improved soil stability, porosity, and aggregate strength. This is due to several reactions that take place, including cation exchange, flocculation, cementing, and pozzolanic reactions (Kavak and Baykal, 2012). It is suggested that lime stabilization associated with slow pozzolanic reactions may have a continuous long-term effect of up to 10 years (Kavak and Baykal, 2012). Cementing can potentially decrease the dissolution of soil aggregates in water and, therefore, reduce P leaching (Ulén and Etana, 2014).

In agriculture, lime is primarily used to raise soil pH (Zimdahl, 2015). Lime is often applied to acidic soils to increase soil alkalinity and to promote crop growth by reducing toxicity and increasing nutrient availability (Adams, 1984). Furthermore, a study has shown that liming can improve crop yield by amending the soil structure (Bolenius, 2014). This result could be in effect for a long period (up to 13 years). The improved crop yield could be due to better gas exchange and more stable aggregates favoring root growth (Bolenius, 2014).

2.4.3 Phosphorus and lime in soil

Liming can have different effects on various forms of P depending on its application rate, soil type, pH, and PSI in the soil. Liming can affect phosphorus solubility in soil through three processes: 1) precipitation which is the formation of calcium phosphate compounds, 2) adsorption by adhering onto clay minerals or metal oxides and 3) mineralization or immobilization of soil organic phosphorus through the enhancement of microbial activity influenced by the lime and soil organic matter interactions (Haynes 1982).

The effect of lime on phosphorus availability is rather complex and unpredictable. Lime changes cation exchange composition and ion strength of soil solution. Both these factors change soil surface potential and its pH dependence (Barrow, 1984). The response is also influenced by soil type.

Lime application to acidic soils can increase P availability and reduce Al toxicity up to a pH of 6-6.5 (Haynes 1982). In this case, P speciation such as HPO_4^{2-} ion becomes more available and ready for adsorption. However, the increase in pH can increase the negatively charged surfaces, and thereby, reduce the chances for P adsorption (Barrow, 1984). In neutral to alkaline soils, higher soil pH along with the increase in the Ca ions can lead to precipitation of calcium phosphate compounds and, therefore, decrease phosphorus availability (Haynes, 1982). Calcium can also act as a cation bridge on the soil surface, binding more phosphate on to the soil (He et al., 1992). Also, liming can increase phosphorus availability by contributing to the mineralization of soil organic phosphorus (Haynes, 1982).

Given the complexity of phosphorus and lime interaction in soil, varying responses have been reported on the effect of liming on phosphorus availability in soil (Haynes, 1982; Tunesi et al., 1999; Curtin and Syers, 2001; Kavak and Baykal, 2012; Ulén and Etana, 2014; Andersson et al., 2016; Blomquist et al., 2017; Simonsson et al., 2018). Lime was reported to be effective in reducing P leaching losses through improvements in soil structure in Sweden (Svanbäck et al., 2014; Ulén and Etana, 2014; Andersson et al., 2016). Structure liming was found effective in mitigating P leaching from two agricultural fields in Sweden with both high clay percentage and P content (Ulén and Etana, 2014). Quicklime was added to the subsoil of three Swedish agricultural soils, and the results showed that quicklime has the potential to reduce P leaching from clay soil columns (Andersson et al., 2016). The application of CaO or hydrated lime on clay topsoil is recommended by Swedish officials to improve soil structure (SBA, 2015). Liming has been reported to decrease, increase, or have no effect on P availability in the soil for different conditions. The availability of P to plants is controlled by adsorption and desorption processes. These processes are influenced by the changes in pH and the increase in Ca ions due to lime application (Curtin and Syers, 2001). Liming can increase P adsorption proportional to each soil's P retention capacity (Curtin and Syers 2001). It is reported that for soils with initial Olsen P values of 5 to 30 mg P kg^{-1}, liming would decrease Olsen P by 2 to 5 mg kg^{-1} per unit increase in soil pH. However, the response of the water-extractable P to liming was not consistent for different soils. Laboratory desorption experiments showed that liming increased the solubility of the fertilizer added P in different soil textures ranging from silt loam to silty clay with an initial pH of 5.0-6.0 (Simonsson et al., 2018). Lime application to three acid soils in Brazil showed no effect on P adsorption. However, solution P was reduced for two soils with high exchangeable aluminum content (Anjos and Rowell, 1987). Sorption could be the main mechanism through which P availability in soil solution is affected by lime-based products.

2.5 Adsorption

2.5.1 Phosphorus adsorption

Phosphate specific adsorption is formed as inner-sphere surface complexes and as ligand exchange (Sposito, 1989). In adsorption, phosphate anions in solution and the soil metal complexes form covalent bonds, while displacing OH^- groups on the surface of the soil particle. Phosphate in soil solution can also be adsorbed onto clay surfaces that have hydroxyl surfaces. The reactions at the soil solution and soil surface interface influence adsorption and desorption of soil phosphorus. Since P adsorption on the soil is suggested to be an inner sphere bond where phosphate replaces anion ligand such as OH^-, P adsorption should thereby increase soil pH by releasing OH^-. The sorption of P is found to be very complex, since some of the sorbed phosphates might take the reversible path (desorption) while some are strongly fixed in the soil and not subject to exchange (Griffith et al., 1973). At relatively low phosphate concentrations, adsorption is expected to be the dominant process while at higher concentrations, precipitation is expected to take place as the dominant P-fixing process (Holford et al., 1974; Jiao et al. 2007).

2.5.2 Adsorption isotherms

Adsorption isotherms are empirical descriptive models that are plotted as adsorbed P (mg kg^{-1}) against P in solution (mg L^{-1}). The amount of adsorbed P is calculated as the difference between the initial P concentration in the solution (added P) and P concentration in the solution at equilibrium per adsorbent in the solution. Some adsorption models can present further information about the adsorption process through the model constants. The limitation of these models is that they are only valid under a certain condition for which they are described (e.g., specific pH).

The Freundlich model assumes adsorption to be a multi-layer process where the amount of adsorbed solute per unit adsorbent mass continuously increases (Chung et al., 2015). The Freundlich isotherm model (Freundlich, 1926) is described by Equation 2-5:

$$Q = K_F {C_e}^{1/n} \qquad \text{(Equation 2-5)}$$

Where Q is the amount of P adsorbed per unit weight of soil (mg kg^{-1}), C_e is the P concentration in the solution at equilibrium. K_F is the Freundlich sorption coefficient, which is related to the adsorption capacity, and n shows the intensity of sorption, which varies with the soil heterogeneity.

The Langmuir model assumes the adsorption process to take place on a mono-layer. Therefore, maximum adsorption capacity is defined for this model (Chung et al., 2015). The Langmuir adsorption isotherm model (Langmuir, 1918) is described as Equation 2-6:

$$Q = Q_{max} \frac{K_L C_e}{1+K_L C_e} \qquad \text{(Equation 2-6)}$$

Where Q is the amount of P adsorbed per unit weight of soil, Q_{max} is the maximum adsorption capacity, K_L is the adsorption constant, which may be related to the binding strength of P on soil surfaces and C_e is the concentration of P in the solution at equilibrium.

2.6 Knowledge gap

Application of P-sorbing materials to mitigate P loss is a new and promising management practice. However, limited research exists on this topic, and most research is conducted at a laboratory scale and limited only to one type of soil (acidic or neutral). There exists a great need for cost-effective P-sorbing materials for retaining more P in the soil to prevent accelerated eutrophication.

Lime, as a high calcium-based product, can potentially increase soil P sorption capacity. However, most research on lime is limited to lime application as an adsorbent in water treatment and solutions, as a filter at drainage outlet or as a pH-adjusting material. Lime being accessible and familiar to farmers, could be a promising soil amendment to mitigate P loss if its potential is fully investigated. Most studies on lime are conducted on acidic soils, whereas soil P response to lime in neutral and alkaline pH conditions is more complicated. In order to suggest a global use of a soil amendment, its efficiency needs to be evaluated for different soil types, especially in alkaline conditions and preferably field-scale experiments. Lime by-products have the potential to be modified to attain a cost-effective global soil amendment to immobilize more P in the soil by increasing P sorption capacity in the soil, and thereby, alleviating the rapid eutrophication of freshwater bodies.

Connecting to Chapter 3:

There is a urgent need for phosphorus-immobilizing materials to retain more phosphorus in phosphorus-rich soils and to prevent excessive phosphorus release. In chapter three, as the first step in our study, four different lime products, both high quality and by-products, were evaluated in laboratory soil columns for an alkaline, high phosphorus-containing clay loam soil to find the minimum application dose to reduce phosphorus concentration in the leachates and runoff to meet water quality guidelines. This manuscript was published in the Journal of Water, Air, and Soil pollution in 2018. The co-authors to this paper are as follows: Dr. Zhiming Qi, my supervisor, Michael Tate, marketing manager at Graymont, Dr. Tiequan Zhang, a research scientist at Agriculture and Agri-food Canada and Dr. Shiv O. Prasher, professor in Bioresource Engineering at McGill. For consistency, the formatting of the manuscript is slightly modified. The references are presented at the end of the thesis.

CHAPTER 3: PHOSPHORUS LOSS MITIGATION IN LEACHATE AND SURFACE RUNOFF FROM CLAY LOAM SOIL USING FOUR LIME-BASED MATERIALS

3.1 Abstract

The increased eutrophication phenomenon in Quebec lakes calls for an urgent phosphorus-reducing strategy to meet the Quebec water quality standard of 0.03 mg L^{-1} for phosphorus (P). The objective of this research was to evaluate the application of four lime-based products in reducing P losses through subsurface leachate and surface runoff as well as to determine their minimum effective application dose. Two sets of experiments were conducted: laboratory leaching study and runoff study with a rainfall simulator, using a clay loam soil collected from the Pike River watershed. The former followed a flow method with a full factorial design in three replicates. Soil columns were amended with different application dosages of lime ranging from 0 to 2% by air-dried soil mass. The results showed that all four lime-based products could be promising amendments in reducing P losses in the leachate. According to statistical analysis of variance, high calcium hydrated lime and lime kiln dust #2 were found to be the most effective with an minimum application dosage of 1% while reducing dissolved phosphorus concentrations in leachate from 0.057 to 0.009 and 0.023 mg L^{-1}, respectively. For the runoff study, a rainfall simulator with a maximum rainfall intensity of 2 cm h^{-1} was built. High calcium hydrated lime and lime kiln dust #2 were able to reduce total dissolved phosphorus to 0.034 and 0.037 mg L^{-1}, respectively. However, particulate phosphorus was significantly increased at the studied application rate. The results from this study can offer a promising measure in reducing dissolved phosphorus in groundwater while providing a solution to the existing environmental issue of eutrophication.

Keywords: Phosphorus; Lime; Leaching; Surface Runoff; Eutrophication.

3.2 Introduction

The increased eutrophication phenomenon in the lakes in Quebec is primarily associated with P losses from agricultural lands through subsurface drainage and surface runoff (Michaud, 2002; Jamieson et al., 2003; Eastman et al., 2010). Terrestrial P legacy includes the effect of nutrient management, where soil P levels exceed the amount required by crops (Sharpley et al., 2013). Nutrient mismanagement has led to P buildup in soils with agricultural land use and has changed the fate and transport of P from soil to surface waters (Sharpley et al., 2013). In Lake Champlain's Missisquoi Bay, 75% of the P load is due to non-point source pollution from cultivated farmlands (Hegman et al., 1999). During the last two decades, 156 lakes have been affected by the cyanobacteria bloom in Quebec (MSSS, 2007). Missisquoi Bay located 60 km to the south of Montreal, Canada, is one of the many examples. This bay has undergone eutrophication due to loads of P for two decades (Gombault et al., 2015), while Missisquoi Bay is a source of drinking water and home to many aquatic organisms (Union Quebequois pour la conservation de la nature 2005). In 2007, an agreement was set between the state of Vermont and Quebec to reduce the P load into the bay and to reach a goal of 0.025 mg L^{-1} by 2016 (Medalie, 2014). Despite the efforts, the annual average P concentration in the Missisquoi Bay was reported as 0.06 mg L^{-1} in 2015 which is still twice as high as the goal set by Missisquoi Bay phosphorus agreement and the Quebec water quality standard for P at 0.03 mg L^{-1} (Lake Champlain Basin Program, 2015). Furthermore, along the St. Lawrence River, P levels exceeded the water quality guidelines more than 50% of the time during 2010-2012 (Environment and Climate Change Canada, 2016). Therefore, a stricter P-reducing strategy is required to meet the water quality goals set for Missisquoi Bay, St. Lawrence River, and other problematic surface water bodies.

Structure liming was considered effective in mitigating P leaching from two agricultural fields in Sweden with both high clay percentage and P content (Ulén and Etana ,2014; Svanbäck et al., 2014; Blomquist et al., 2017). Quicklime was added to the subsoil of three Swedish agricultural soils, and the results showed that quicklime has the potential to affect P leaching from clay soil columns (Andersson et al., 2016; SBA, 2015). When quicklime (CaO) is mixed with clay soils, it results in improved soil stability, porosity, and aggregate strength. This is due to several reactions that can take place, including cation exchange, flocculation, cementing, and pozzolanic reactions (Kavak and Baykal, 2012). It is suggested that lime stabilization associated with slow pozzolanic reactions may have a continuous long-term effect of up to 10 years (Kavak and Baykal, 2012). Cementing can potentially decrease the dissolution of soil aggregates in water and, therefore, reduce P leaching (Ulén and Etana, 2014).

Furthermore, a study has shown that liming can improve crop yield by amending the soil structure where the results could be in effect for a long period (up to 13 years). The improved crop yield could be due to better gas exchange and more stable aggregates favoring root growth (Bolenius, 2014). In 2017, Blomquist et al. applied two types of structure lime (slaked lime as well as a mix of carbonate calcium and slaked lime) at various rates to clay textured fields. The results revealed that the products were able to significantly enhance soil aggregate stability (Blomquist et al., 2017). Increased soil stability could lead to reduced P losses from the soil. However, the effect of structure lime application on crop yield was not consistent for all the studied treatments over the four-year study period, resulting in varying positive and negative responses (Blomquist et al. 2017).

Clay soil shows a higher potential for binding P than sandy soils (Andersson et al., 2013). A mineralogical test on a common Swedish clay soil revealed that P seems to become bound to Ca complexes in the finer fraction of the clay soil, and this increases with depth (Ulén and Snäll, 2007). The subsoil properties play a more important role in P leaching as compared to the topsoil (Djodjic et al., 2004). Peltovuori (2006) found in his study that the maximum P sorption capacity occurs in the 30-70 cm soil depth. Soil chemical properties in sandy soil can predict P leaching, whereas transport mechanisms in clay soil with macropores dominate P leaching behaviors (Andersson et al., 2013). The presence of macropores leads to a quick transport of P through the soil owing to more available water pathways, therefore, shorter contact time with the soil matrix will cause less opportunity for P sorption and larger P release (Djodjic et al. 2004). CaO was also applied at the outflow of drainage in a study in Lithuania, and a 64.4% decrease in the phosphate concentration in comparison with the control was observed (Saulys and Bastiene 2008).

The main goals of this research were to 1) evaluate the efficiency of four different lime-based products in reducing P losses through surface runoff and subsurface leaching in a laboratory scale and 2) to find the minimum application dosage to meet the Quebec water quality standard for P. The four lime-based products include dolomitic hydrated lime, high calcium hydrated lime, and two types of high calcium lime kiln dust. The first two products are more accessible forms of lime (compared to CaO) commonly produced by large lime companies in North America, and the last two are by-products that could potentially serve as low-cost alternatives to quicklime or hydrated lime. For this study, two sets of experiments on the fate and transport of phosphorus in soils were conducted: one runoff study with a rainfall simulator and a laboratory leaching study. The results of this study can introduce a low-cost and environmentally friendly approach to minimize P-pollution in surface waters.

3-3 Materials & Methods

3-3-1 Lime

Four lime-based products, namely dolomite hydrated lime (DHL), high calcium hydrated lime (HCHL), high calcium lime kiln dust #1 (LKD1) and high calcium lime kiln dust K#2 (LKD2) produced by Graymont were examined in this study. DHL is a fine white powder formed by hydrating dolomitic quicklime (CaO-MgO) at atmospheric pressure forming $Ca(OH)_2$-MgO. HCHL is also a fine dry white powder, produced by combining quicklime with a sufficient amount of water converting calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) (Lewis, 2005). LKD is a dark grayish powder and a by-product of the high calcium lime producing process. It is composed mainly of calcium carbonate and calcium oxide. Table 3-1 summarizes the chemical and physical properties of the four studied lime products.

The total calcium content as calcium oxide for DHL, HCHL, LKD1, and LKD2 is 47.0, 73.4, 56.2, and 67.6%, respectively, while their average bulk densities are 0.533, 0.462, 1.235 and 1.188 g cm^{-3}, respectively. Besides the total calcium content, LKD1 and LKD2 essentially differ in their percentage of available lime as calcium oxide (23 vs. 41%, respectively) and silica content (12 vs. 3.8%, respectively). Also, LKD2 has a finer texture than LKD1. The percentage passing a 0.075 mm (N 200) sieve is 85, 97, 60, and 90% for DHL, HCHL, LKD1, and LKD2, respectively, with HCHL having the finest texture and LKD1 having the lowest.

Table 3-1: Chemical and physical properties of the four lime products

Chemical Properties (%) [1]	Dolomite Hydrated Lime (DHL)	High Calcium Hydrated Lime (HCHL)	High Calcium Lime Kiln Dust #1 (LKD1)	High Calcium Lime Kiln Dust #2 (LKD2)
Available lime index as calcium oxide (CaO)	-	70.3	23.0	41.0
Available lime index as calcium hydroxide ($Ca(OH)_2$)	62.1	92.8	-	-
Total calcium as calcium oxide (CaO)	47.0	73.4	56.2	67.6
Calcium carbonate ($CaCO_3$)	3.5	2.3	37.9	32.5
Magnesium oxide (MgO)	33.9	0.8	0.9	0.8
Silica (SiO_2)	0.4	1.2	12.0	3.8
Ferric oxide (Fe_2O_3)	0.2	0.2	1.9	0.6
Alumina (Al_2O_3)	0.1	0.4	5.1	1.6
Total sulfur (S)	0.06	0.17	2.3	4.5
Total carbon (C)	-	-	6.3	3.9
Moisture (H_2O)	0.8	0.7	-	-
Physical Properties				
Bulk density (ASTM 110), $g\ cm^{-3}$	0.533	0.462	1.235	1.187
Solubility in water (0 ºC), $g\ L^{-1}$	1.0	1.85	1.31	1.31
pH (Saturated solution at 25 ºC)	12.45	12.45	12.45	12.45
Size Distribution				
Smallest 100% passing sieve, (mm)	1.25	0.600	2.00	2.00
Percent passing 0.075 mm (N 200) Sieve, (%)	85	97	60	90

[1] Chemical properties measured using ASTM C25, C 1271, and C 1301 methods by Graymont.

3-3-2 Soil

The required soil was collected from an agricultural field in the vicinity of the Missisquoi Bay located in southern Quebec, Canada (45º 07’ 44” N; 73º 03’ 04” W). This site has a clay loam soil texture with a sub-angular blocky structure and belongs to the Brown Podzolic soil classification (OMAFRA, 1987; AAFC, 1948). The parent material is loam to clay-loam till derived from underlying calcareous rocks (AAFC, 1948). The soil was reported to have poor internal drainage with reoccurring deep vertical cracks when exposed to alternating wetting and drying conditions

(Eastman et al., 2010). Soil samples were collected from ten random locations from two different soil depths of topsoil (0-30 cm) and subsoil (30-50 cm). Soil samples were then air-dried, crushed, and passed through a 2 mm sieve. Soil texture was determined by the particle size distribution test (hydrometer method). All elements (P, Ca, Mg, Al, and K) were measured on the soil Mehlich-3 extracts (Mehlich, 1984). Phosphorus was measured by colorimetry using the Lachat instrument (QuikChem FIA$^+$ -8000 series, Hach Company, Loveland, CO), while cations were measured by atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential). Organic matter percentage was measured by loss on ignition, and soil pH was measured in water at soil to water ratio of 1:2. The experiment setup for both the laboratory leachate study and runoff study with rainfall simulator is shown in Figure 3-1 and will be discussed in the following sections.

3-3-3 Laboratory leaching study

The leaching study was carried out using a column miscible displacement method (MacDonald et al., 2004). For this purpose, a programmable vacuum extractor (SampleTek, model 24VE) was used to facilitate the leaching and sampling process (Fig. 3-1 left). This experiment followed a full factorial design with two factors, including product type (4 levels) and application dosage (6 levels) with three replicates. The six lime application dosages included 0, 0.5, 1, 1.25, 1.5, and 2 by percent mass of air-dried soil where 1% application rate is the equivalent of 7 t ha^{-1} of product applied to the plowing depth of the clay loam soil (bulk density of 1.41 g cm^{-3}). The vacuum extractor was placed in a cold room to conduct the experiment in a temperature-controlled environment. The average fall temperature of 11ºC for southern Quebec was used since the application time of the lime products was assumed to be in fall after harvest. Fifty grams of soil (equivalent to 7 cm) were mixed with various percentage dosages of the four lime-based products and packed into a 13 cm long syringe barrel (60 mL). Based on the total calcium content of the products (Table 3-1), 1% application dosage (0.5 g) of DHL, HCHL, LKD1, and LKD is equivalent to 0.235, 0.367, 0.281 and 0.338 g of calcium. High-density polyethylene frits were placed on both ends of the soil, confining the soil in the syringes (MacDonald et al., 2004). Twenty four hours after the initial mixing, soil columns were leached at a constant rate (1 mL h^{-1}) with 25 mL of double deionized water per day for ten consecutive days to ensure that equilibrium has been reached.

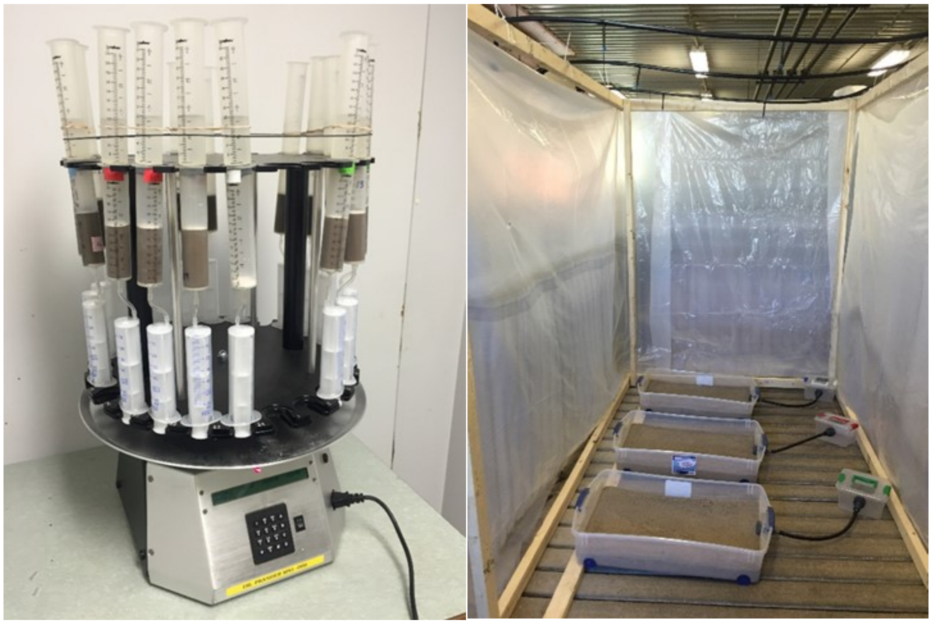

Figure 3-1: Experiment setup: laboratory leachate study (left); Runoff study with rainfall simulator (right)

Leachate samples were collected daily for the ten consecutive days and measured for electrical conductivity (EC), pH, P, Ca, and Mg content. Since the soil was confined by polyethylene frits, particulate phosphorus (PP) in the leachate samples were considered to be negligible. Therefore, the phosphate measurement on the collected leachate samples accounts for total dissolved phosphorus (TDP), which was measured by colorimetry on the Lachat Instrument auto-analyzer.

Total dissolved P is a more available form for plant uptake, which can cause greater algal bloom issues in waters compared to PP, which is a less available form (Fozzard et al. 1999). However, under high flow conditions, PP can play a significant role (Lake Champlain Basin Program 2016). Dissolved reactive P includes orthophosphates ($H_2PO_4^-$ and HPO_4^{3-}), which are the readily available P for plant uptake and is the most considerable portion of the TDP (Reynolds and Davies 2001).

Furthermore, at the end of 10 days, soils were extracted from the columns, air-dried and prepared for the Mehlich-3 extraction method (Mehlich 1984) to measure the extractable P, Ca, Mg, K, and Al in the soil. Phosphorus was measured with Lachat Instrument (QuikChem FIA$^+$ -8000 series), Ca, Mg, K, and Al with atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential), pH with pH meter (Fisher Scientific, AR10 model) and EC with conductivity meter (Radiometer Copenhagen, CDM 83).

It should be noted that the ideal dry mixing of the soil in the laboratory, neglects the effect of soil macropores and soil heterogeneity which can both significantly alter the results due to the change in soil structure. However, this method allows us to study the effect of one variable (lime addition) while other factors are constant.

3-3-4 Runoff study with a rainfall simulator

In order to examine the efficiency of the lime-based products on reducing the phosphorus concentration in the runoff, a 1.5 × 2.5 × 2 m rainfall simulator was constructed using wood with sprinklers and placed in an indoor controlled environment. Full-circle pattern micro-sprinklers with a 50 cm radius range were selected for this project. Three rows of micro-sprinklers attached to polyethylene tubes were installed on the wooden frame to simulate rainfall (Figure 3-1 right). The simulator provided a maximum rainfall intensity of 2 cm h^{-1}. Three 90 ×45 × 15 cm commercial rectangular containers were used for this experiment (figure 3-1 right). The containers were later modified to create an outlet for collecting and conducting the running water into a storing container. Ten-centimeter-deep soil was added to the containers in three replicates and mixed with the four lime products individually at their optimum application dosage acquired from the leaching study. Twenty four hours later, the containers were then placed inside the rainfall simulator with a slight slope for a one-hour rainfall event (2 cm h^{-1} intensity). After the one-hour rainfall, three spatially random soil samples were collected from each container. Also, three runoff samples were taken from the runoff storage container. Soil samples were later air-dried and prepared for the Mehlich-3 extraction (Mehlich, 1984). The runoff samples were kept in a cold room (5ºC) until analysis (less than 48 hours). Runoff samples were filtered within 24 h and directly analyzed for the dissolved reactive P (orthophosphate) content using the Lachat instrument, while persulfate digestion was conducted on both filtered and unfiltered samples for the measurement of the TDP and TP content, respectively. Particulate P was calculated as the difference between TP and TDP. pH and EC were also measured for all runoff samples.

3-3-5 Statistical analysis

The mean values of the steady-state (day 10) P concentrations were compared using one-way Analysis of variance (ANOVA) and post hoc tests (Tukey, LSD, and Duncan) in SPSS statistics software (IBM corporation 2016, version 24) to find the minimum effective dosage of the lime-based products capable of reducing P concentration in leachate to below 0.03 mg L^{-1}. Also, the univariate general linear model (GLM) was used to analyze the simultaneous effect of our two factors (product type and dose) on P concentration. ANOVA and post hoc tests in SPSS statistics software were also used for the runoff study to compare the significance of the four different lime-based products in reducing phosphorus concentration in the runoff.

3-4 Results & Discussions

3-4-1 Soil properties

The soil texture was found to be clay loam (40 % clay, 38% silt, and 22% sand) for both topsoil and subsoil, with the pH of 7.9 and 8.2, respectively. The average total phosphorus content for topsoil and subsoil was measured as 70.0 and 47.3 mg kg^{-1} (148.05 and 100 kg ha^{-1}), respectively. In heavy soils (>30% clay), the recommended amount of P for corn, based on the phosphorus saturation index (PSI) is 70 kg ha^{-1} (CRAAQ, 2003). Therefore, the soil phosphorus content in this field exceeds the recommended level (> 70 kg/ha). Furthermore, it has been suggested that for the PSI of 0.089-0.131 (Beauchemin et al., 2003), the phosphorus content in the leachate will be higher than the Quebec water quality standard for P at 0.03 mg/L (Medalie, 2014). The PSI for this soil was found at 0.101 and 0.104 for topsoil and subsoil, respectively, which is could indicate a risk of higher P loss. Therefore, this verifies the P leaching issue in this area. Also, the initial soil test results showed that the bulk density of the subsoil is greater than the topsoil (1.41 > 1.32 g cm^{-3}), indicating that the subsoil is more compacted.

3-4-2 Laboratory leaching study

Figure 3-2 shows the variation in the TDP content of leachate samples in the ten days of leaching for different application dosages (0, 0.5, 1, 1.25, 1.5, and 2%) of DHL, HCHL, LKD1, and LKD2.

Phosphorus concentration in the leachate varied with time until it reached an equilibrium except for low dosages (e.g., 0.5%) where P continuously increased with time. The control soil with 0% application dosage was measured to have a mean TDP concentration of 0.057 mg L^{-1} in its leachate, which exceeds the Quebec water quality standard of 0.03 mg L^{-1}.

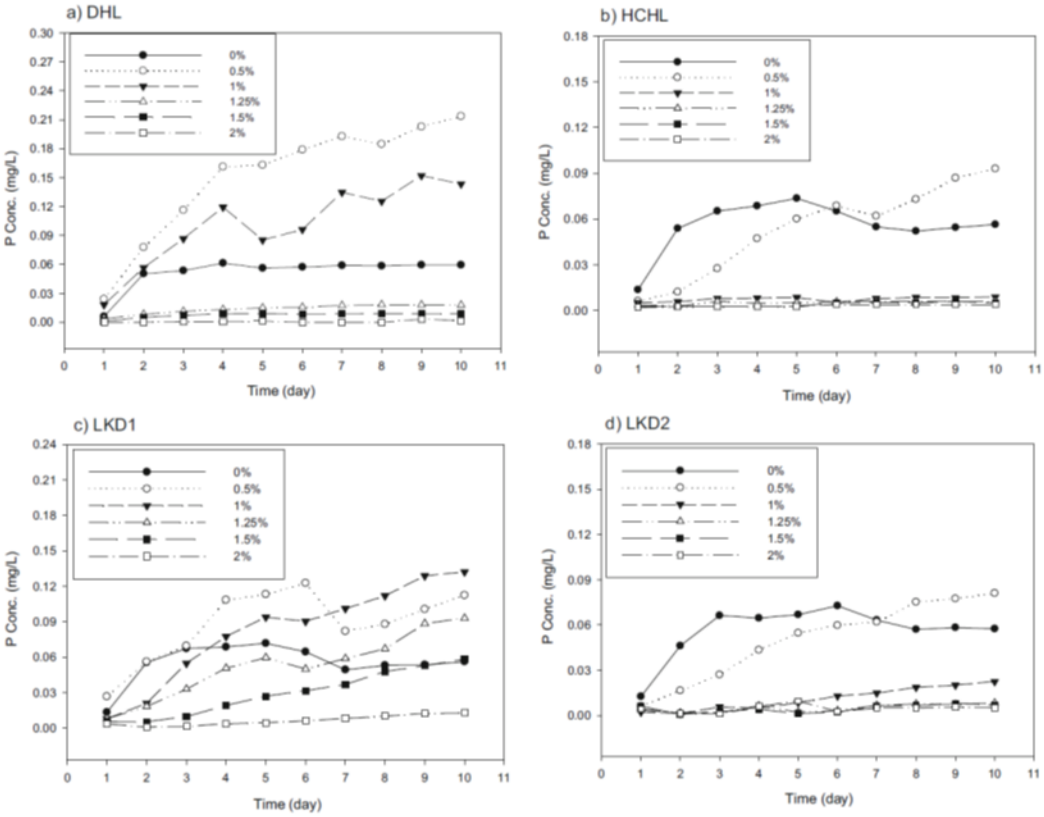

Figure 3-2 Phosphorus content (TDP) of the leachate sample in 10 days for different application dosages of a) dolomite hydrated lime (DHL); b) high calcium hydrated lime (HCHL); c) high calcium lime kiln dust #1 (LKD1); d) high calcium lime kiln dust #2 (LKD2)

The DHL application dosage of 1.25% of the soil was successfully able to reduce P concentration to 0.018 mg/L on the tenth day, meeting the guideline (Fig. 3-2a). Higher application dosages such as 1.5 and 2% were also capable of reducing P loss to as low as 0.009 and 0.002 mg L^{-1}, respectively. However, ANOVA of the effect of application dose on P revealed that there was no significant difference between the 2, 1.5, and 1.25% levels for DHL ($p<0.05$). Taking cost-effectiveness into account, an application dosage of 1.25% was selected as the recommended application dosage for DHL. Lower application dosages of 0.5 and 1% were not effective in reducing P loss as they showed an inverse relationship of increasing P loss to as high as 0.2 mg L^{-1}. This phenomenon can be explained as follows: lime materials react with soil moisture and release Ca or Mg (in the case of dolomitic lime) cations (Saulys and Bastiene 2008). These released cations will be attracted onto negatively charged clay surfaces and form clay flocculation leading to a more porous soil structure. Furthermore, the released Ca and Mg cations can react with phosphate anions, forming phosphate compounds (Saulys and Bastiene 2008). The addition of lime and the change in pH decreases the availability of soluble Ca-P compounds ($CaHPO_4$) while increasing the insoluble P compounds as $Ca_3(PO_4)_2$. At lower doses, the released Ca and Mg cations from DHL have led to an increase in pH resulting in P release (Goldberg and Sposito 1984; Devau et al. 2009). However, the Ca and Mg content are not sufficient to promote precipitation and form P compounds. They might have only been attracted to clay surfaces, forming floccules and thereby increasing phosphate in leaching (Devau et al. 2009; Tunesi et al. 1999). Therefore, the application dosage of lime is a significant factor in the fate of P in the soil and leachate.

Similarly, it was found that HCHL application doses of 1% and higher were able to significantly reduce P to a value of less than 0.03 mg L^{-1} (Figure 3-2b). Therefore, a 1% dosage, which is the first dosage to have reached an acceptable level of 0.009 mg $L^{-1,}$ is the recommended application dosage for HCHL. The Duncan test on the effect of HCHL dose on P concentration showed that there is no significant difference regarding P among HCHL application doses of 1, 1.25, 1.5, and 2% indicating that by increasing the application dosage beyond 1% no significant decrease is observed in the P concentration.

Figure 3-2c demonstrates that for LKD1, only the highest dosage of 2% reduced P loss to 0.013 mg L^{-1}. The Duncan test also showed that there was no significant difference between dosage levels of 0.5, 1, and 1.25% in terms of P while dosages of 1.5 and 0% showed similar results ($p<0.05$). By increasing the application dosages from 0 to 1%, P increases from 0.056 to 0.132 mg L^{-1}, then, P decreases, reaching back to the initial P with the LKD1 application dosage of 1.5%. Finally, P is reduced to the desired level of 0.013 mg L^{-1} (<0.03 mg L^{-1}) at a 2% LKD1 dosage. Therefore, dosages 0.5, 1, 1.25, and 1.5% may be deemed insufficient to reduce P loss. Again, the lower dosages not only were unable to reduce P loss but also increased the P concentration up to 0.132 mg $L^{-1,}$ which is approximately twice as much as the initial P concentration. LKD1 has a lower available lime index and total Ca compared to HCHL, therefore, at these dosages (0.5, 1, 1.25 and 1.5%) the amount of Ca cations contributed by LKD1 is not sufficient to bind with phosphates, to form an insoluble form and reduce the P solubility. Despite having a higher calcium content than that of DHL, LKD1 has shown a lower performance. This could be explained with the finer texture and the higher magnesium oxide content of DHL (Table 3-1). Application dose of 2% LKD1 was the minimum effective dose, which is high and not cost-effective despite being a low-cost product (Table 3-2).

Figure 3-2d indicates that 1% LKD2 is the minimum application dosage reaching a reduced concentration of 0.023 mg/L (< 0.03 mg L^{-1}). The Duncan test results demonstrated that there is no significant difference between dosage levels of 1.25, 1.5, and 2% LKD2 regarding P content while the lower application dosage of 0.5% LKD2 significantly increased P concentration in leachate to 0.081 mg L^{-1} similar to that of HCHL ($p <0.05$). It can be concluded that LKD2 performed significantly better compared to LKD1 owing to its higher calcium content (56.2% in

LKD1 vs. 67.6% in LKD2) and finer texture, which leads to an increased performance and reaction with the available clay in the soil due to a higher contact area.

Table 3-2: Comparison of the optimum condition of the four examined lime by-products

Product	***Recommended dosage*** *(%)*	***In Leachate*** *(mg L^{-1})*			***In Soil*** [£] *(mg kg^{-1})*					**pH**[€]
		TDP	**Ca**	**Mg**	**P**	**Ca**	**Mg**	**K**	**Al**	
Control	-	0.057	30.81	6.69	41.2	4677.9	439.3	193.8	769.8	8.2
Dolomite Hydrated Lime (DHL)	1.25	0.018	44.57	0.02	48.8	5828.4	2191.4	194.6	602.8	9.49
High Calcium Hydrated Lime (HCHL)	1	0.009	77.33	0.05	45.9	7950.0	464.0	175.9	789.7	9.00
High Calcium Lime Kiln Dust #1 (LKD1)	2	0.013	55.07	0.03	43.4	7453.1	478.1	181.7	730.4	8.71
High Calcium Lime Kiln Dust #2 (LKD2)	1	0.023	34.30	0.05	46.7	6886.6	478.2	186.5	688.9	8.69

[£] Mehlich-3 extractable P, Ca, Mg, K and Al in soil

[€] pH measured in the soil solution (soil to water ratio of 1:2)

According to the Duncan test in ANOVA, pH in the leachate samples does not significantly change with time ($p<0.05$). However, pH does significantly increase by increasing the application dosage of the four lime products (Figure 3-3). The pH of the leachates collected from lime-treated soil columns is high since this leachate is collected directly after in contact with limed soil. However, in the field application, lime is only applied to the top 5 cm and, later, it is buffered by the soil. The pH of the soil samples at the recommended dosage is shown in Table 3-2.

The EC of the leachate samples was high on the first day, while it suddenly dropped on the second and third days and eventually reached a constant state after ten days (Figure 3-4). This drop might be due to Ca leaching out on the first day before the formation of Ca-P compounds. After 3-4 days, Ca and P form insoluble compounds (Shashkova et al., 2000). The EC was measured daily to ensure the leachate solution has reached equilibrium on the 10th day. Samples containing larger application dosages (e.g., 1.5 and 2%) showed a higher EC trend, in general, since they contain higher concentrations of ions.

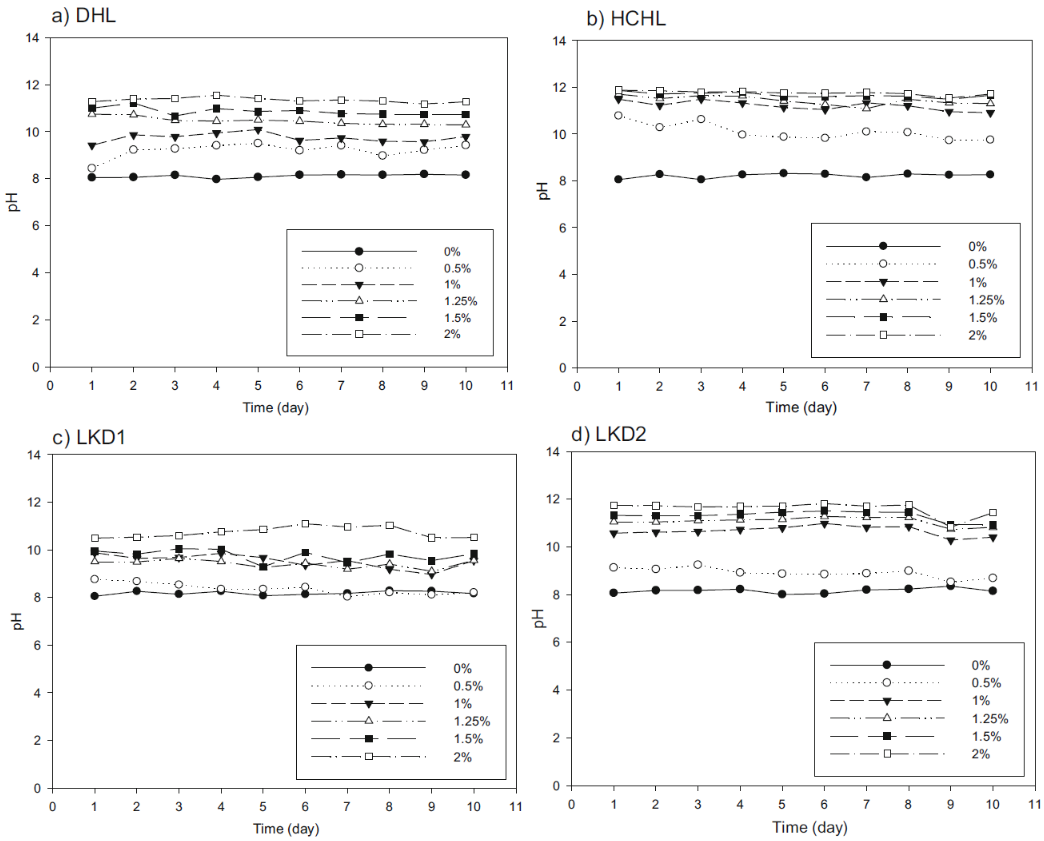

Figure 3-3: The variations in pH of the leachate samples in 10 days for different application dosages of a) Dolomite Hydrated Lime (DHL); b) High Calcium Hydrated Lime (HCHL); c) High Calcium Lime Kiln Dust #1 (LKD1); d) High Calcium Lime Kiln Dust # 2 (LKD2)

Figure 3-5 illustrates the effect of lime application dose on Ca, Mg, P concentrations as well as pH in the leachate samples for the four products (DHL, HCHL, LKD1, and LKD2). The graph shows that P loss increases for lower dosages (less than the optimum dose), while it considerably decreases at the recommended dosages and higher. Furthermore, the increase in application dosage increases the Ca content of leachate samples since Ca is the main element in lime-based products. Whereas, Mg content decreases in the leachate samples and approaches zero by increasing the application dosage. This could be due to the formation of magnesium-phosphate compounds, which are insoluble.

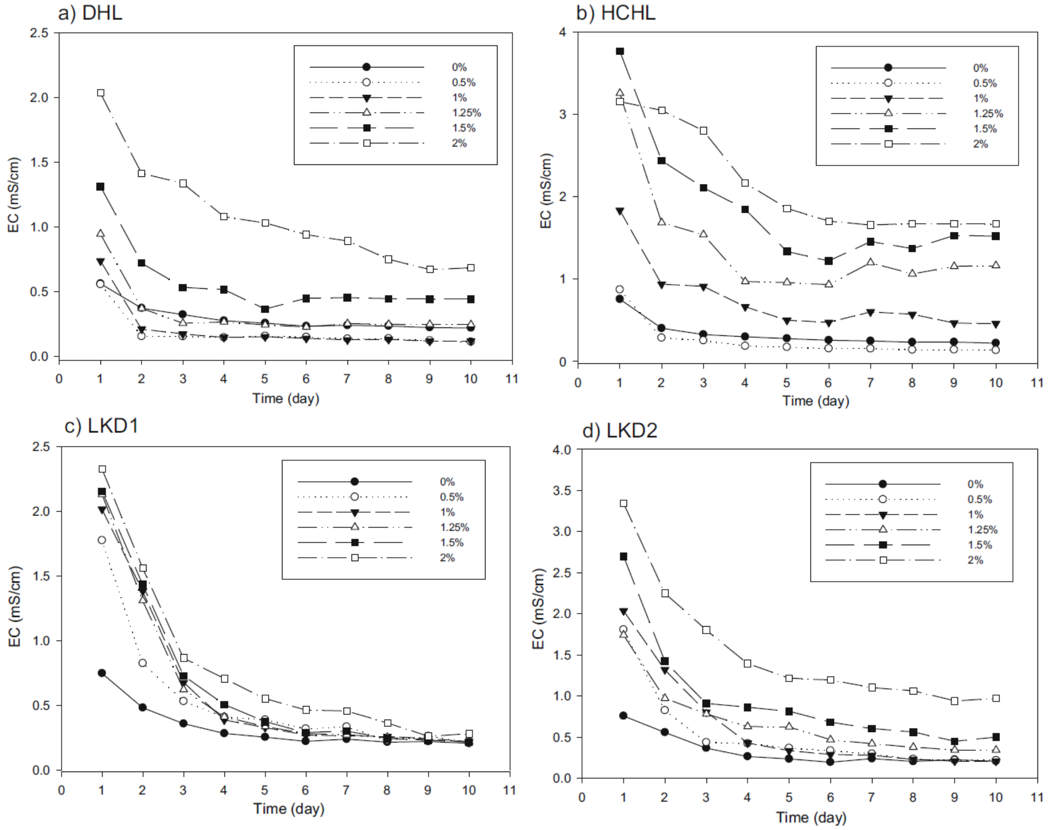

Figure 3-4: The variations in EC of the leachate samples in 10 days for different application dosages of a) Dolomite Hydrated Lime (DHL); b) High Calcium Hydrated Lime (HCHL); c) High Calcium Lime Kiln Dust #1 (LKD1); d) High Calcium Lime Kiln Dust # 2 (LKD2)

Soil analysis results for Ca showed that the Ca content in the soil significantly increased by increasing the application dosage of the lime products since Ca is the primary element in their composition. Therefore, it is expected to enhance the Ca content of the soil. Regarding Mg in the soil, this significant increase can only be observed for DHL due to the considerable Mg content available in the composition of DHL. Furthermore, since the Mg content in the leachate was lower than that of the control, this could mean that most of the Mg released from DHL have precipitated.

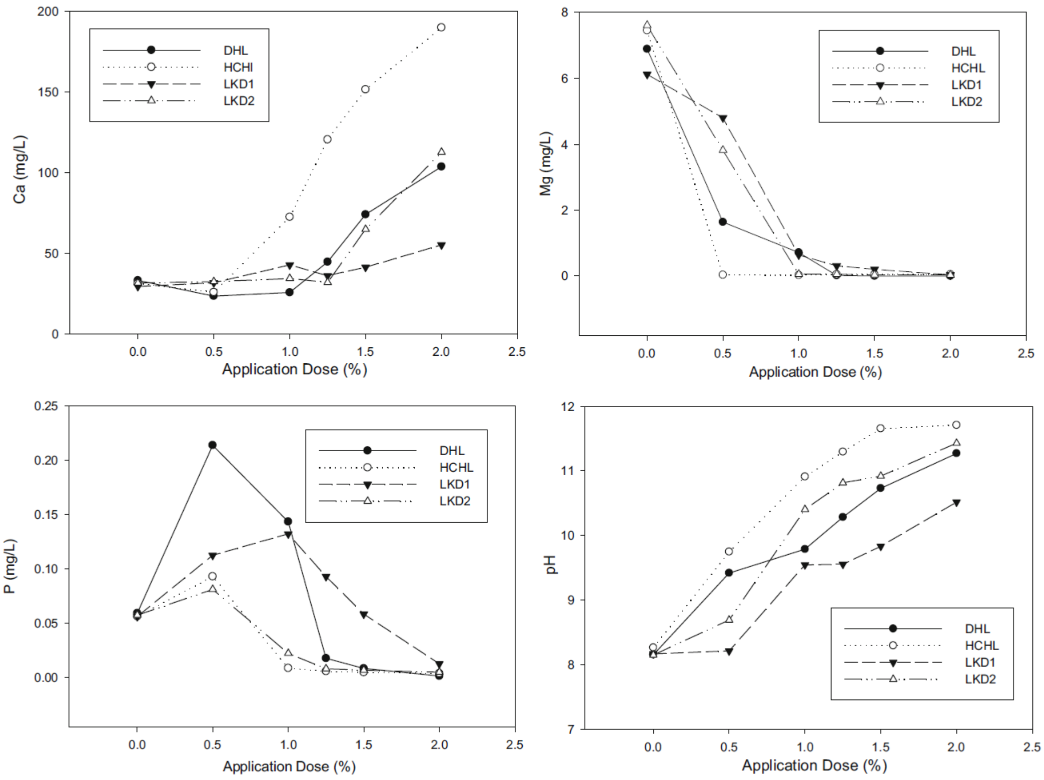

Figure 3-5 The effect of application dose on Ca, Mg, P concentrations and pH in leachate samples for the four lime products (Dolomite Hydrated Lime (DHL); High Calcium Hydrated Lime (HCHL); High Calcium Lime Kiln Dust #1 (LKD1High Calcium Lime Kiln Dust # 2 (LKD2))

3-4-3 Comparison and statistical analysis

Table 3-2 summarizes the chemical properties of the soil and leachate samples at the recommended application dose. At this dosage, Mehlich-3 extractable P in the soil showed a 19, 8.5, 5, and 18% increase compared to that of control for DHL, HCHL, LKD1, and LKD2, respectively. The results indicate that the addition of these four lime products at the recommended dosage is not only able to reduce P loss in leaching but has also led to an increased Mehlich-3 extractable P in soil. Based on the results, HCHL and LKD2 were able to reach the water quality guidelines at a lower dosage of 1% compared to 1.25 and 2% for DHL and LKD1, respectively.

Lime materials react with soil moisture and release Ca or Mg (in the case of dolomitic lime) cations. The finer the lime material, the quicker it will dissolve to release Ca (Wells, 2008). The reaction rate also depends on the chemistry of lime materials. Oxide or hydrated limes act very fast because they are more soluble (Wells, 2008). All four lime products used in this study had a fine white powder texture, and fast reactions were observed. In the case of HCHL, LKD1, and DHL, which have finer textures compared to that of LKD1 (Table 3-1), lower effective application dosages are achieved, and the equilibrium in P concentration was reached sooner (within five days). The contact area is another contributing factor in the effectiveness of these lime products in reducing P loss. The contact area is important when applying chemicals. Since clay particles are fine, they provide larger contact surfaces (Wells, 2008). The clay loam texture of the soil used in this study was beneficial along with the fine texture of the lime products.

The results from the univariate general linear model analysis showed that the treatment effects, as well as the interaction effect, were significant ($R^2=0.962$, $p<0.05$) with a total error of $8.918E^{-5}$. The post hoc tests in ANOVA showed that there is no significant difference between types of HCHL and LKD2 or DHL and LKD2 regarding P concentration ($p<0.05$), which means that they have shown similar performances. This correlates well with the amount of initial calcium added at 1% dose based on their total calcium content (0.367 and 0.338 g Ca as HCHL and LKD1 vs. 0.235 and 0.281 g Ca as DHL and LKD2). This emphasizes our previous conclusion that both HCHL and LKD2 have similar promising performances (at the recommended dose of 1%), and they can be used as alternatives. Given that LKD2 is a by-product and considerably cheaper (more than ten times), it is recommended over HCHL. It can be interpreted that total calcium content plays an important role in their performance with regards to P loss reduction.

3-4-4 Runoff study with a rainfall simulator

The recommended application dosages of 1.25, 1, 2, and 1% DHL, HCHL, LKD1, and LKD2 based on the leaching study were added to the soil, respectively, as a starting point. Table 3-3 summarizes the average values for both runoff and soil samples.

Table 3-3: Average values in runoff and soil samples with the application of the four lime products at the recommended dosage acquired from the leaching experiment

		Control	Dolomite Hydrated Lime (DHL)	High Calcium Hydrated Lime (HCHL)	High Calcium Lime Kiln Dust #1 (LKD1)	High Calcium Lime Kiln Dust #2 (LKD2)
Application dosage (%)		0	1.25	1.0	2.0	1.0
pH		7.59	9.20	9.45	8.95	8.85
In runoff (mg L^{-1})	Ortho-P	0.022	0.036	0.031	0.025	0.028
	TDP	0.045	0.052	0.034	0.042	0.037
	PP	0.013	0.043	0.039	0.100	0.085
	TP	0.057	0.095	0.073	0.142	0.122
	Ca	13.25	16.58	19.44	17.41	29.06
	Mg	1.46	1.46	1.48	1.54	1.04
In soil [£] (mg kg^{-1})	P	70.0	88.7	63.2	80.8	72.0
	Ca	5583	5674	11463	7286	15678
	Mg	254.0	2958.2	283.2	247.2	231.1
	K	155.2	142.6	153.6	149.5	165.3
	Al	690.6	689.0	766.5	808.2	894.4

[£] Mehlich-3 Extractable P, Ca, Mg, K and Al in soil

The results indicate that TDP was significantly reduced to 0.034 and 0.037 mg L^{-1} with the application of HCHL and LKD2, respectively, while DHL and LKD1 showed no significant difference in comparison with the control (TDP = 0.045 mg L^{-1}). However, TP was significantly increased with the application of all four lime products at the studied application dosages. This could be due to an increased PP, which is a result of P being attached to soil surfaces in the presence of lime products. Calcium cations in lime can result in an increased positive surface charge on the soil where more phosphate anions can be adsorbed. PP is a less available form of P for growth and, therefore, a less risk of eutrophication.

In terms of Mehlich-3 extractable P in soil, there were no significant differences between the control, LKD1, and LKD2. However, there was a significant difference between DHL, HCHL, and the control. A significant increase in Ca was seen in HCHL and LKD2 applications compared to control, while DHL and LKD1 did not show any significance in terms of Ca. Furthermore, there was only a significant increase in Mg for the DHL application as expected (Table 3-3). These results obtained in the runoff study cannot be fully compared to that of the leaching study since the runoff water is less in contact with soil and therefore, less exchange opportunity with the soil is present. Longer term experiments are required.

3-5 Conclusion

All four lime products were promising in reducing total dissolved phosphorus (TDP) loss in the leachate to less than 0.03 mg L^{-1}. The four lime products, namely dolomite hydrated lime (DHL), high calcium hydrated lime (HCHL), lime kiln dust #1 (LKD1) and lime kiln dust #2 (LKD2) were able to reduce total dissolved phosphorus from 0.056 to below 0.03 mg L^{-1} at the lowest application dose of 1.25, 1, 2, and 1% of DHL, HCHL, LKD1 and LKD2, respectively. It can be concluded that HCHL and LKD2 performed better in lower dosages. Given its lower cost, LKD2 is preferred and more practical. In the runoff study, HCHL and LKD2 were able to reduce TDP significantly. However, PP was significantly increased with the application of the four lime products. Further experiments are required to understand the mechanism of P reduction in the presence of lime in the long term and to optimize this process on a larger scale. The effect of increased pH as a result of lime application on crop growth needs to be studied. The results obtained from this project offer a promising management practice to improve the water quality of Quebec lakes and rivers at the source and help meet the existing guidelines to overcome the eutrophication issue.

3-6 Acknowledgements

This study was conducted at the Macdonald Campus of McGill University in collaboration with Graymont Inc. to whom we would like to express our sincere thanks. This research was funded by NSERC (Natural Sciences and Engineering Research Council of Canada). We would also like to especially thank Ms. Hélène Lalande for her valuable help in the analysis of the samples in Environmental Soil Laboratory, Department of Natural Resources, McGill University. Also, we would like to thank Sowsen Khatib and Azam Khowaja for their help in the runoff experiment setup and sample collection.

Connecting Text to Chapter 4:

After finding the minimum effective application dose for each product, high calcium hydrated lime and lime kiln dust were chosen for further studies. In the next chapter, we describe our study of the efficiency of lime in reducing phosphorus loss from three common soil textures. Given the importance of soil preferential pathways in the transport of phosphorus, intact soil columns were used and compared to that of laboratory repacked columns.

The following manuscript, titled “Lime application to reduce phosphorus release in different textured intact and small repacked soil columns,” is under review in the Journal of Soil and Sediments. The co-authors of this paper include Dr. Zhiming Qi, my supervisor, Michael J. Tate, marketing manager at Graymont, and Nikolas Romaniuk, a new products specialist at Graymont.

CHAPTER 4: LIME APPLICATION TO REDUCE PHOSPHORUS RELEASE IN DIFFERENT TEXTURED INTACT AND SMALL REPACKED SOIL COLUMNS

4-1 Abstract

Phosphorus (P) losses from agricultural fields through leaching are the main contributors to eutrophication of lakes and rivers in North America. The adoption of P-retaining strategies is essential to improve the environmental quality of water bodies. The main objective of this study is to evaluate lime as a soil amendment in reducing phosphorus concentration in the leachate from three common soil textures with neutral to alkaline pH. Phosphorus leaching from undisturbed soil columns (10 cm in diameter and 20 cm deep) as well as small repacked columns were investigated and compared in this study. Lime (high calcium hydrated lime) at the rate of 1% by air-dried soil mass was applied to the topsoil of the columns. Both sets of experiments followed a full factorial design with two factors of soil texture at three levels (sandy loam, loam, and clay loam) and treatment at two levels (control and limed) with three replicates. Scanning electron microscopy coupled with energy dispersive spectroscopy was performed on the control and limed soil samples to confirm the formation of calcium phosphate compounds. For both intact and repacked columns, dissolved reactive phosphorus (DRP) concentrations in the leachates from limed sandy loam and limed loam soil columns was significantly reduced, while DRP in the limed clay loam column leachates was not changed. Elemental mapping demonstrated that in limed sandy loam and loam soils, the calcium loadings on the soil surface were always linked with phosphorus. The formation of calcium phosphate compounds, as well as increased phosphate adsorption on the soil surface through Ca bridging, could be the two main phosphorus-lime retention mechanisms. Total dissolved phosphorus (TDP) in the leachates of limed loam and lime clay loam intact and repacked column was reduced, while there was no change in that of the sandy loam soil. In fine-textured soils, lime can increase TDP retention through the immobilization of organic phosphates. The impact of lime application on DRP and TDP varied with the soil texture. The lime-induced reduction in the DRP and TDP was variable between the intact and repacked columns demonstrating the importance of soil structure on phosphorus and lime interactions in the soil. Overall, lime application at the studied rate can be considered a promising soil amendment in mitigating phosphorus loss from non- calcareous alkaline soils.

Keywords: Dissolved reactive phosphorus; Hydrated lime; Soil texture; Alkaline soils; Leaching; Soil amendment; Scanning electron microscopy

4-2 Introduction

Phosphorus (P) loss from agricultural fields through leaching, in addition to runoff, is one of the main contributors to eutrophication of lakes and rivers in Quebec as well as North America (Jarvie et al. 2013; King et al. 2015). Historically, phosphorus, as the second essential nutrient for plant growth, was expected to be immobile as the soil was considered to have sufficient P absorbability (Gburek et al., 2005; Tan and Zhang, 2011). Therefore, fertilizer and manure applications were based on nitrogen (N) requirements. The N/P ratio in manure is lower than the crop uptake. As a result, nitrogen-based manure application resulted in P surplus and accumulation in the soil and consequently increased the risk of P leaching into water bodies (Gburek et al., 2000; Li et al. ,2013). Application of P in excess of plant requirements will leach beyond the topsoil mainly in the form of readily available inorganic P (Tian et al., 2017) and may cause negative impacts on the environmental water quality. Over the past two decades, several studies have reported significant amounts of P loss (in various forms) through leaching in tile drained fields (Eastman et al., 2010; Jamieson et al., 2003; Raid et al., 2012). With the installation of tile drainage, while the volume of runoff and particulate P loss decreases (up to 50-70%) (Ball Coelho et al., 2012), the amount of dissolved P loss through tile drains considerably increases (Jamieson et al., 2003; Tan and Zhang, 2011; Raid et al. 2012; King et al., 2014). The increased P loadings into the surface water bodies has led to excessive algal growth, and cyanobacteria bloom in the Great lakes area, especially in Lake Erie, which is the shallowest (Environment Canada, 2017). In 2014, P concentration in the Saint Lawrence River was reported twice as high as the Quebec water quality guideline (Environment Canada, 2016). The annual average P levels in Missisquoi Bay located in southern Quebec were reported as 0.06 mg L^{-1} in 2015, which is also twice as high as Quebec water quality standard for P at 0.03 mg L^{-1} (Lake Champlain Basin Program, 2016).

The soil P saturation index (PSI) is widely used to assess the risk of P desorption from the soil. The correlation between P saturation and P solubility is less predictable in neutral and alkaline soils with higher clay content (Beauchemin and Simard, 1999). Soil PSI should be used in addition to soil P tests (e.g., Mehlich-3) when considering a large range of soil types and pHs (Beauchemin and Simard, 1999). In Quebec, a critical PSI of 20 % is recommended above which dissolved P concentration will be higher than crop requirements, and the risk of P leaching will increase (Conseil des Productions Végétales du Québec 1996). Heckrath et al. (1995) suggested that in calcareous clay loams, soil Olsen P concentration higher than 60 mg kg^{-1} will result in weaker retention of P in the soil matrix. The relationship between extractable soil P and the total dissolved P (TDP) concentration in leaching is related to soil P sorption indices such as PSI, and it will vary with soil texture and depth (Sharpley 1995; Pizeghello et al. 2016). Phosphorus in the soil solution can be adsorbed onto clay or soil organic matter (SOM) surfaces in addition to forming compounds with Ca, Al, or Fe. Geochemical processes such as the dissolution of calcium phosphates and desorption of phosphate from clay minerals or Fe/Al oxides can be considered the main processes for P loss (Djemel et al., 2019; Gérard, 2016). Therefore, in addition to the accumulated P in soil, P leaching is affected by soil texture, soil structure, soil hydrology, pH, SOM as well as calcium (Ca), iron (Fe) and aluminum (Al) contents (Brock et al., 2007; Pote et al., 1996). Soil texture can affect phosphorus availability through its influence on soil physicochemical properties, adsorption-desorption mechanisms, and soil microbial activity (Suner and Galatini, 2015). Soil texture is largely connected with soil structure by infuencing the presence and formation of preferential pathways and soil macropores (King et al., 2014). Preferential flows will facilitate P loss over matrix flow through reduced interaction of leachate with the soil matrix (Chikhaoui et al., 2008; Cullum, 2009).

In agriculture, lime is primarily used to raise soil pH (Zimdahl, 2015). Lime is a calcium-containing inorganic material in which carbonate, oxide, and hydroxides are predominant. Lime can exist in three basic forms in a simple cycle: limestone ($CaCO_3$), Quicklime (CaO), and hydrated or slaked lime ($Ca(OH)_2$) (Oates, 1998). Hydrated lime or calcium hydroxide is produced by reacting quicklime with an adequate amount of water to convert calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) (Lewis, 2005; Zimdahl, 2015).

Liming can reduce phosphorus solubility in the soil through three processes: 1) precipitation which is the formation of calcium phosphate compounds, 2) enhanced adsorption by adhering onto clay minerals or Al/Fe oxides through cation bridging and 3) immobilization of soil organic phosphorus through the enhancement of microbial activity influenced by the lime and soil organic matter interactions (Haynes 1982). Liming can have different effects on various forms of P depending on its application rate, soil type, pH, and P saturation levels in the soil. Lime application to acidic soils will increase P availability while reducing Al toxicity up to a pH of 6-6.5 (Haynes 1982). However, in neutral to alkaline soils, the effect of lime on P solubility is more complex. Therefore, varying responses have been reported on the effect of liming on phosphorus availability (Haynes, 1982; Tunesi et al., 1999; Curtin and Syers, 2001; Kavak and Baykal, 2012; Ulén and Etana, 2014; Andersson et al., 2016; Blomquist et al., 2017; Eslamian et al., 2018; Simonsson et al., 2018). It is suggested that structure liming can reduce P loss from clayey soils in Sweden through the improvement of soil structure (Ulen and Etana 2014; Blomquist et al. 2017). The lime adsorbed onto clay surfaces will contribute to clay flocculation and consequently improve soil structure through increased soil aggregate stability and porosity (Anderson et al., 2016). A laboratory repacked column experiment with a clay loam soil showed that four different lime products applied at their optimum dosage were able to reduce phosphate concentrations in the leachates to below 0.03 mg L^{-1} (Eslamian et al., 2018). Laboratory desorption experiments showed that liming increased the solubility of the fertilizer added P in different soil textures ranging from silt loam to silty clay with an initial pH of 5.0-6.0 (Simonsson et al., 2018). Lime application to three acid soils in Brazil showed no effect on P adsorption. However, solution P was reduced for two soils with high exchangeable aluminum content (Anjos and Rowell, 1987).

The potential of lime as a soil amendment to decrease P release from neutral to alkaline soils has not been fully studied. In limed soil, the simultaneous effect of increased quantities of exchangeable Ca ions, together with an increased soil pH, will result in an unpredictable and soil-dependent equilibrium (Curtin and Syers, 2001). The increased Ca leads to more positive charges, while the pH increase will result in more negative surface charges. Little knowledge and few experiments exist on the interactions among lime application, P desorption, and soil type. Soil heterogeneity makes the prediction of soil response through theoretical models complicated.

Therefore, the main objective of this study is to evaluate the influence of lime as a soil amendment on P mobility across three different neutral to alkaline soil textures. Soil structure is also a key factor in the transport of P through the soil profile. Thus, P leaching, as influenced by the lime amendment, was investigated and compared through two experimental setups: 1) Field-scale intact soil columns 2) laboratory-scale repacked soil columns. The hypothesis is that lime application may decrease P release from the soil through lime induced P retention, mainly due to an increase in the number of active Ca ions in the soil solution. This response will be, however dependent on the soil type. It is expected that in coarse-textured soils liming will have similar results on P mobility in both intact and repacked soil columns while in the fine-textured soil, contrasting results may be observed due to the dominance of preferential pathways in this soil type.

4-3 Material & Methods

4-3-1 Soil sampling sites

Three common soils in Quebec with different physicochemical properties were used for this study: sandy loam, loam, and clay loam. The sandy loam and loam soils were collected from experimental agricultural fields located on the Macdonald Farm of McGill University in St. Anne de Bellevue, Quebec, Canada (45°24'41.3"N 73°56'23.6"W). The sandy loam field had grass coverage, while the loam soil was a soybean field with a soybean-corn-grass rotation. The loam soil lays on a calcareous till derived mainly from Beekmantown limestone, and it is classified as Brown Forest (or Entisols) well-drained St. Bernard Loam (AAFC, 1956; USDA-NRCS, 1999). The sandy loam soil was developed from sandy material over till, and it is classified as a moderately well to imperfectly drained Chicot fine sandy loam and belongs to the Brown Podzolic soil classification (or Entisols) (AAFC, 1956; USDA-NRCS, 1999). The clay loam soil was collected from a cornfield situated near Pike River, Quebec, Canada (45°07′44″ N; 73°03′04″ W). This soil has been reported to have a subangular blocky structure with a loam to clay loam till derived from the underlying calcareous rocks, and it is classified as immature soils (Entisols) (AAFC, 1948; USDA-NRCS, 1999). This calcareous clay loam soil was selected for this study since it was a common high phosphorus-containing soil in the area, which has been continuously causing water quality issues for the Piker River. Also, it would be interesting to investigate the effect of lime on this soil, as a worst-case scenario, being already high in Ca content. Soil samples for repacked columns, as well as the intact soil columns were collected from the same three fields in October 2017. The physical and chemical properties of the soils are summarized in Table 4-1.

Table 4-1: The physical and chemical properties of the soils

	Sandy Loam	**Loam**	**Clay Loam**
Soil texture[£] (%)			
• Sand	59	50	21
• Silt	32	38	39
• Clay	9	12	40
pH	7.35	7.55	8.10
Bulk density (g cm^{-3})	1.4	1.2	1.5
SOM[€] (%)	4.2	5.3	2.5
PSI[µ]	0.064	0.107	0.197
Total P (mg kg^{-1})	800	910	985
Total N (mg kg^{-1})	1598	1918	1064
Mehlich3-P (mg kg^{-1})	50	87	109
Mehlich3-Ca (mg kg^{-1})	2845	2225	5380
Mehlich3-Al (mg kg^{-1})	822	767	580
Mehlich3-Fe (mg kg^{-1})	208	300	340

£ Hydrometer method
€ Soil organic matter measured by loss on ignition
µ Phosphorus Saturation Index

Soils with slightly alkaline pH were selected for this study to evaluate the worst-case scenario where lime is not required to raise soil pH and merely added to soil as an amendment to reduce P release. Also, P is more available for plant uptake and leaching at soil pHs above 6.5 (Zimdahl, 2015).

Soil samples were collected from the topsoil (0-20 cm) at six random locations, and a composite sample was made. Before soil analysis, soil samples were air-dried and passed through a 2 mm opening sieve. Soil texture was measured by the particle size distribution test using the hydrometer method (Gee and Bauder, 1986). Plant available soil P, Ca, Mg, K, and Al were measured on the soil Mehlich-3 extracts (Mehlich, 1984). Total soil P and N were measured following the perchloric acid digestion procedure (Olsen and Sommers, 1982). The P and N content on the digested soils were measured by colorimetry using the Lachat instrument (QuikChem FIA+-8000 series), while the cations were measured by atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential). Soil organic matter percentage was measured by loss on ignition, and soil pH was measured in water at the soil to water ratio of 1:2. Bulk density was measured using the core method (volumetric cylinder method) (Grossman and Reinsch, 2002). Phosphorus saturation index (PSI) was calculated with Equation 4-3 where M3P, M3Al, and M3Fe represent the Mehlich-3 extractable P, Al, and Fe in soil (mg kg^{-1}), respectively (Jiao et al. 2004).

$$PSI = {}^{M3P}\!/_{(M3Al + M3Fe)} \qquad \text{Eq. (4-3)}$$

4-3-2 Lime

The high calcium hydrated lime used in this study is a fine dry white powder, which has an available lime index as calcium hydroxide of 92.8 percent, total Ca content as calcium oxide of 73.4 percent, average bulk density of 0.467 g cm^{-3} and Brunauer-Emmett-Teller (BET) surface area of 14 m^2 g^{-1} (Eslamian et al., 2018). The approximate magnesium oxide, silica, ferric oxide, alumina, total sulfur, calcium carbonate, and moisture content of this product are 0.8, 1.2, 0.2, 0.4, 0.17, 2.3, and 0.7% total mass, respectively. The neutralizing value of this lime product

($CaCO_3$=100) is 129 percent. The product has 97 percent passing from the 0.075 mm opening sieve (# 200).

4-3-3 Intact soil columns

To simulate P leaching and to preserve natural soil structure, intact soil columns were used in this experimental setup. For this purpose, cylinder PVC pipes of 10 cm in diameter and 20 cm in height with beveled bottom edges were prepared. The column was placed on the soil, and force was applied with a hammer, through a wooden board as an intermediate, to push the column into the soil without disturbing the soil inside the column. When the desired depth was achieved (20 cm), the surrounding soil was excavated to release the soil core. An end cap was placed at the bottom of the columns for transport purposes. This experiment followed a full factorial design with two factors of soil texture type in 3 levels (sandy loam, loam, and clay loam) and lime treatment in 2 levels (no lime and limed). Three replicates were assigned for each of the six treatments. Therefore, at each soil type location, six intact soil columns were excavated (3 control and three limed) within a 2 m by 2 m area leading to a total of 18 columns. To prepare the limed soil columns, one percent by soil weight of high calcium hydrated lime was mixed in with the top 5 cm of the soil (Eslamian et al. 2018) one week before the commencement of the first leaching event. This lime application dose is approximately equivalent to the 7t ha^{-1} application rate at the field scale. A nylon monofilament screening fabric with a 31-micron opening was placed at the bottom of the columns to prevent coarse soil loss while partially filtering the leachate (Glaesner et al., 2011; Kjaergaard, 2004). A connecting screw joint and silicon glue were used to seal the perimetrical bottom edge of the soil cores. Phosphorus leaching from these intact soil columns was conducted in two phases. During phase one (indoor), the intact soil columns were placed in a cold room at 11˚C temperature, which is the average fall temperature for this region. Artificial rainwater (0.012 mM $CaCl_2.2H_2O$; 0.015 mM $MgCl_2$.6H2O; 0.12 M NaCl; pH = 7.8; EC = 0.024 dS m^{-1}) was passed through the columns at 1.5 mm h^{-1} intensity for 8 hrs daily at zero tension (by gravity) for 5 consecutive days (Glaesner et al., 2011). Leachate samples were collected from the bottom container daily. Later, the intact columns were incubated in the cold room at 5˚C until spring 2018 (for six months). The intention was to examine if the lime application in the previous fall will still be effective on P leaching in the following spring and summer. During phase two (outdoor), the columns were placed outside in the open-air field (Macdonald Campus Farm) to receive natural rainfall. Leachate samples were collected after significant rain events from late May to October (5 sampling dates). A Hobo rain gauge with a data logger (Onset RG3) was installed in the field to measure the hourly rainfall and collect temperature data.

All leachate samples were analyzed for pH, dissolved reactive phosphorus (DRP), total dissolved phosphorus (TDP), dissolved Ca, Mg, and K. A 25 mm nylon syringe filter with 0.45-micron opening was used to filter the samples for DRP and TDP analysis immediately after sample collection. The samples were later stored in the fridge (5ºC) until analysis (within 72 hours). The DRP was measured on the filtered leachate samples directly with the molybdate blue colorimetry method (Lachat Instruments, 2007) using Lachat Instruments with the detection limit of 0.01 mg L^{-1} while for the analysis of TDP, the filtered samples where digested with persulfate and autoclaved for 30 min prior to analysis by colorimetry (detection limit of 0.02 mg L^{-1}) (O'Halloran and Cade-Menun, 2007; Murphy and Riley, 1962).

4-3-4 Repacked laboratory columns

The repacked laboratory leaching study was carried out with the column miscible displacement method (Eslamian et al., 2018; MacDonald et al., 2004). This experimental setup was designed to be compared to the indoor intact soil columns. Given the small diameter of the syringes and repacking the soil, this experiment negates the effect of soil macropores and soil structure. This experiment followed a full factorial design as well, with two factors of soil texture at three levels and lime treatment at two levels. Respectively, 82.41, 86.01, and 72.18 g of sandy loam, clay loam, and loam soil were packed into 60 ml syringes (3 cm diameter) equivalent to each soil's bulk density and resulting in 10 cm of soil. Lime was mixed in with the top 2.5 cm of soil at 1% by air-dried soil weight. This is equivalent to 0.105, 0.094, and 0.115 g of Ca in sandy loam, loam, and clay loam soils, respectively. High-density polyethylene frits with 0.45-micron opening were placed on both ends of the soil to prevent soil loss, filter the leachate, and create similar conditions on both ends (MacDonald et al., 2004). Each day, 25 mL of artificial rainwater at the intensity of 1.1 mL h^{-1} was passed through the syringe using a programmable vacuum extractor (SampleTek, model 24VE) for five consecutive days. The artificial rain intensity in this experiment is equal to 1.5 mm h^{-1} rainfall similar to the indoor intact soil columns experiment.

All leachate samples were analyzed for pH, DRP, TDP, dissolved Ca, Mg, and K. A 25 mm nylon syringe filter with a 0.45-micron opening was used for the dissolved portion of the samples. Soil samples were extracted from the syringes at the end of the experiment, air-dried, and analyzed for nutrients using methods previously described in soil section 4-3-1.

Scanning electron microscopy (SEM) coupled with energy dispersive X-Ray spectroscopy (EDS) (Hitachi, SU3500 model) was used to compare the chemical elemental distribution of control soils with the limed ones. For this purpose, 10-15 random sites on the surface of different soil samples (with and without lime) for the three soil types were observed using SEM. Elemental mapping, coupled with EDS, was performed to show the connection between Ca and P loadings in the lime-treated soils.

4-3-5 Statistical analysis

The multivariate general linear model and analysis of variance (ANOVA) in SPSS (IBM, version 24) were used to study the effect of the two factors (soil texture and lime treatment) on the P concentration of the leachate as well as the difference between indoor intact and repacked columns. Post-hoc tests (Tukey and Duncan) were used to evaluate the significant difference among the levels of a factor.

4-4 Results & Discussions

4-4-1 Intact soil columns (phase I: Indoor)

There was a significant difference in the effect of the lime amendment on P concentration in the leachates from the different soil textures ($p<0.05$). In the sandy loam and loam soil columns, the DRP concentration in leachates of the limed soil columns was significantly ($p<0.05$) lower than that of the control columns in all five days of leaching (Figure 4-1). There was a 40 and 70% decrease in the mean (5-day) DRP of the limed sandy loam and loam soil leachates, respectively, in comparison with control soil leachates (Table 4-2). There was no significant difference in DRP of limed and control clay loam leachates (Table 4-2).

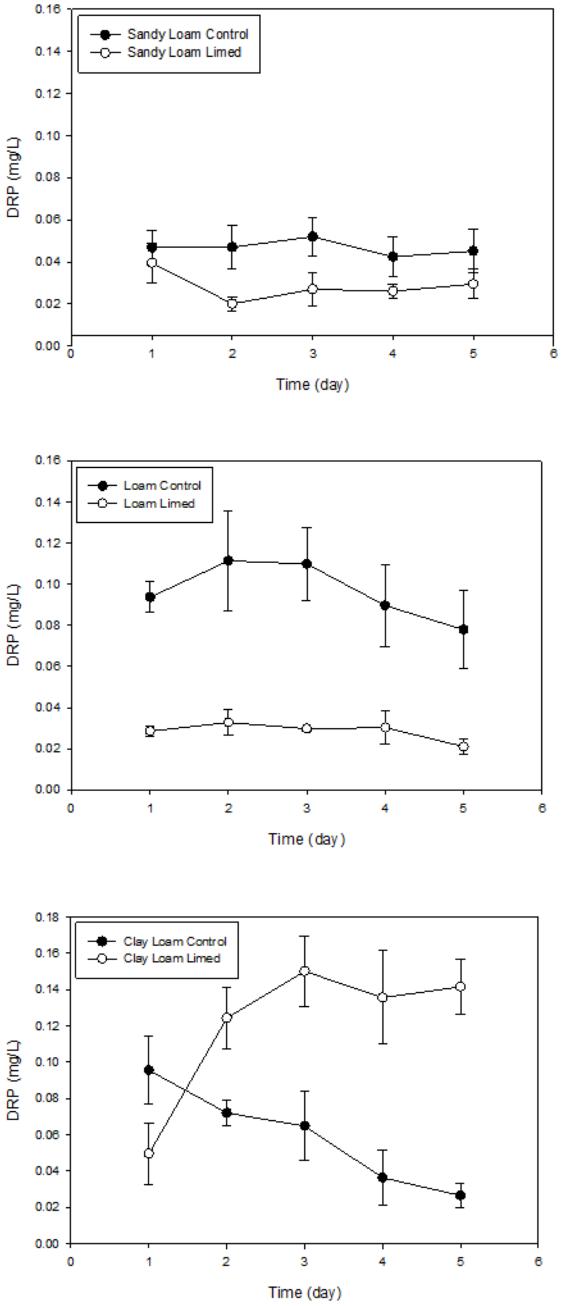

Figure 4-1: Dissolved reactive phosphorus (DRP) concentration in the leachates from indoor intact soil columns (11˚C) (Error bars represents standard error values)

Table 4-2: Average five-day leachate properties for intact soil columns in the cold room (11˚C)

	Sandy Loam		Loam		Clay Loam	
	Control	Limed	Control	Limed	Control	Limed
pH	$7.21^{*}\pm0.2$	$7.51^{*}\pm0.3$	7.75 ± 0.2	7.73 ± 0.2	7.74 ± 0.1	7.88 ± 0.2
DRP$^{£}$ (mg/L)	$0.047^{*}\pm0.02$	$0.028^{*}\pm0.01$	$0.096^{*}\pm0.04$	$0.028^{*}\pm0.01$	$0.059^{*}\pm0.03$	$0.120^{*}\pm0.05$
TDP$^{€}$ (mg/L)	0.126 ± 0.05	0.147 ± 0.05	$0.399^{*}\pm0.10$	$0.238^{*}\pm0.09$	$0.365^{*}\pm0.2$	$0.249^{*}\pm0.05$
Ca (mg/L)	$22.3^{*}\pm4.2$	$40.1^{*}\pm2.6$	$28.4^{*}\pm6.4$	$42.8^{*}\pm5.7$	$14.6^{*}\pm1.9$	$50.6^{*}\pm3.3$
Mg (mg/L)	$4.9^{*}\pm1.2$	$9.7^{*}\pm0.3$	$6.3^{*}\pm1.1$	$9.7^{*}\pm1.8$	$1.5^{*}\pm0.6$	$6.7^{*}\pm0.9$
K (mg/L)	$2.0^{*}\pm1.5$	$1.3^{*}\pm0.8$	$4.1^{*}\pm2.0$	$1.6^{*}\pm0.3$	$1.1^{*}\pm0.2$	$2.2^{*}\pm0.1$
Fe (mg/L)	$2.3^{*}\pm0.7$	$1.9^{*}\pm0.7$	$2.3^{*}\pm0.8$	$0.6^{*}\pm0.2$	$1.0^{*}\pm0.3$	$0.3^{*}\pm0.2$

* Significant difference between control and limed ($p<0.05$) in each row

values are the average of 3 replicates in the 5 days of leaching ± standard deviation

£ Dissolved reactive phosphorus

€ Total dissolved phosphorus

The DRP in the leachate of the limed clay loam columns was lower than the control for the first leaching event but continued to increase, whereas the DRP in the control clay loam leachates dropped to 0.026 mg L^{-1} by the end of day five (Figure 4-1). Long vertical cracks were observed in the control soil columns as a result of wetting and drying, causing the rainwater to pass through the column instantly without adequate interaction time with the soil matrix. The applied artificial rainwater on the limed soil column took approximately ten times longer time to pass through the column. The formation of preferential pathways such as cracks in clayey soils can lead to the rapid movement of surface applied liquids (Djodjic et al., 1999; Van Es et al., 2004; Glaesner et al., 2011b). Therefore, it is suspected that the P concentration in the control clay loam leachates is affected by preferential pathways at this phase.

There was a significant difference in the concentrations of dissolved Ca, Mg, K, and Fe between the limed and control for all soil types ($p<0.05$) (Table 4-2). The Ca concentration in the leachate from the limed sandy loam, loam, and clay loam columns were respectively about 2, 1.5, and 3 times higher than that of the control leachates (Table 4-2). Dissolved Ca concentration in the leachate of control sandy loam and control loam soil was proportionate to the Mehlich-3 extractable Ca in the soils (Table 4-1). For this reason, a higher concentration of Ca in the leachate of the control clay loam column was also expected owing to its considerably higher initial Ca content and being a calcareous soil. Nonetheless, lower-than-expected Ca concentration in the leachate of the control clay loam columns was detected. This could again be attributed to the presence of preferential pathways in the control clay loam columns.

Phosphate (DRP) adsorption on clay and metal oxide surfaces is enhanced through the increased Ca ions in the soil solution as result of liming (Haynes, 1982). The increase in the Ca ions near negatively charged surfaces results in less negative adsorption surfaces, which will lead to increased adsorption and decreased desorption of phosphate ions (Barrow and Shaw, 1979; Barrow et al., 1980). Calcium ions can act as cation bridges for binding more phosphate on the soil surface (He et al., 1992). While the formation of calcium phosphates through precipitation could be another potential retention process, at low P concentration levels such as soil solution, adsorption is suggested to be the dominant retention mechanism (Haynes, 1982).

Total dissolved P (TDP) in leachate of limed loam and lime clay loam columns was significantly reduced by 40 and 32%, respectively. However, there was no significant difference between the control and limed sandy loam leachates. While the DRP in limed clay loam leachate was significantly higher, the TDP in the limed clay loam leachates was significantly lower than control (Table 4-2). This could mean that more dissolved organic phosphate (TDP – DRP) is lost in the control clay loam column through preferential pathways such as the observed cracks. In the limed clay loam and limed loam soils, lime has affected the dissolved organic P portion in the leachate. The finer fraction of soil is associated with organic P pools (Suner & Galantini, 2015). Depending on the pools of C and P in soils, liming can stimulate mineralization or immobilization of soil organic P. In soils with a higher C/P ratio, net immobilization could be more favorable (Enwezor, 1976). Higher contents of SOM in the loam soil and higher clay content in the clay loam soil as compared to the sandy loam soil (Table 4-1), may have contributed to immobilizing more dissolved organic P in the soil as a result of liming.

Apart from sandy loam, no significant difference was observed between the pH in limed and control leachates (Table 4-2). The pH in the sandy loam soil was increased only by approximately 5 percent. The little to no change in the pH at this lime application dose could be attributed to the alkaline nature of the soils and their buffering capacity. Furthermore, the no pH change could also imply that the changes in the P mobility are mostly due to retention processes induced by an increased Ca content as opposed to changes in P solubility induced by pH.

4-4-2 Intact soil columns (Phase II: outdoor)

The total daily rainfall and average daily temperature for the duration of outdoor intact soil column experiment (31 May to 11 October 2018) are plotted in Figure 4-2. For this period, the total average temperature and rainfall were calculated as 21.5˚C and 2.6 mm per day, respectively. The minimum and maximum temperatures were measured as 7.4 and 31.7˚C, respectively, while the maximum rainfall was logged as 34.6 mm on 4 June 2018.

There was a significant difference between the P concentration in the leachates collected from different soil columns ($p<0.05$) (Table 4-3 and Figure 4-3). Dissolved reactive P in the leachates of the limed sandy loam and limed loam columns were significantly lower than that of their controls by 34 and 63%, respectively (Table 4-3 and Figure 4-3), which is similar to the indoor experiment (40 and 70%, respectively). However, there was no significant difference in the DRP concentration in leachates of limed and control clay loam columns. During this phase, due to the natural moist conditions and frequent rain showers, there were no longer visible cracks present in the control clay loams columns.

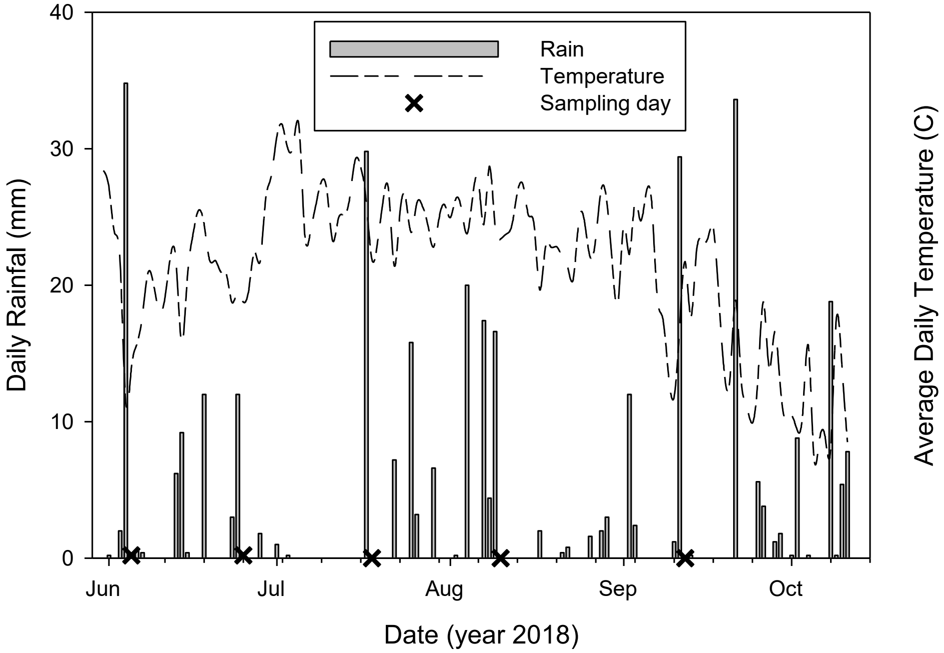

Figure 4-2: Daily rainfall and average temperature for the duration of intact soil column outdoor leachate sampling (June to Oct. 2018)

While the dissolved Ca content in leachate increased significantly in the sandy loam and loam soil types, no significant difference was observed between the Ca content of the control and limed clay loam leachates (Table 4-3). The clay loam soil is a calcareous soil with high initial calcium content (5380 mg Ca per kg soil-Mehlich-3) (Table 4-1). Higher buffering capacity and the higher clay content (more than 30%) could be the other reasons for the non-significant effect of lime application on the studied clay loam soil. Comparing the DRP in the control clay loam leachate in the outdoor phase (0.270 mg L^{-1}) with that of the indoor phase (0.059 mg L^{-1}) provides evidence that the lower DRP in the latter was due to preferential flows.

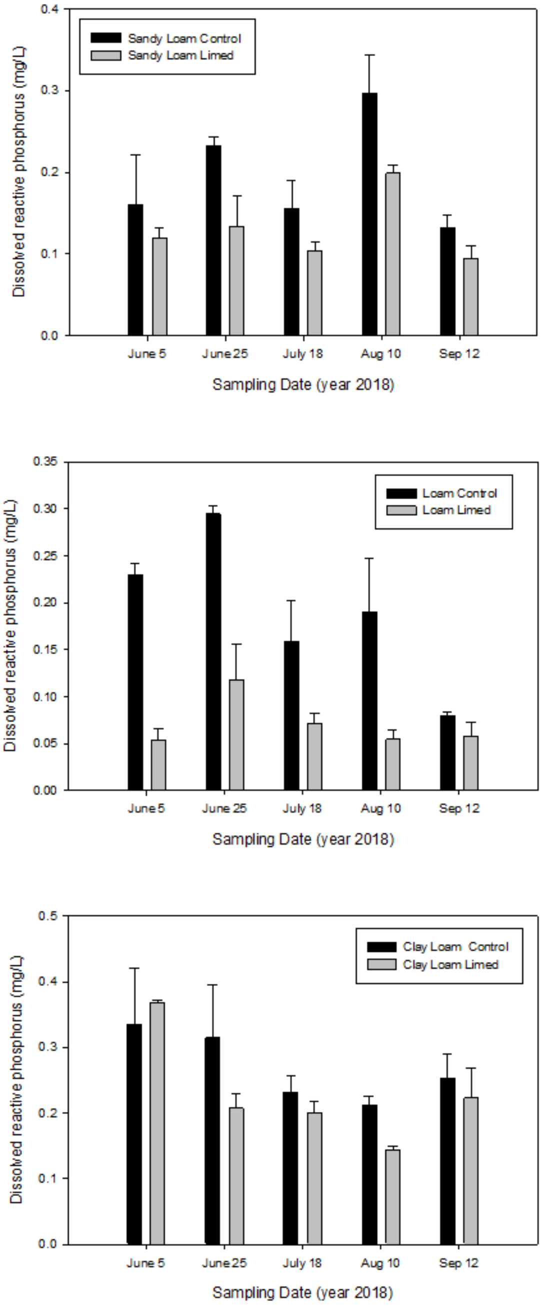

Figure 4-3: Dissolved reactive phosphorus concentrations in leachates from outdoor intact soil columns for the five sampling dates (Error bars represents standard error values)

Table 4-3: Average five sampling dates leachate properties for the outdoor intact soil columns from Jun-Oct

	Sandy Loam		Loam		Clay Loam	
	Control	Limed	Control	Limed	Control	Limed
pH	7.31±0.1	7.48±0.1	7.78±0.1	7.75±0.1	8.10±0.1	8.15±0.1
DRP$^{£}$ (mg/L)	0.196^{*}±0.07	0.130^{*}±0.04	0.191^{*}±0.08	0.071^{*}±0.03	0.270±0.05	0.229±0.08
TDP$^{€}$ (mg/L)	0.249±0.09	0.162±0.05	0.231±0.1	0.106±0.03	0.291±0.03	0.276±0.06
Ca (mg/L)	24.4^{*}±9.4	121.5^{*}±59.1	101.4^{*}±47.1	181.8^{*}±62.2	222.7±61.1	250.5±99.8
Mg (mg/L)	3.6^{*}±1.7	18.5^{*}±8.9	15.7^{*}±5.7	33.7^{*}±6.8	26.6^{*}±10.9	20.9^{*}±8.3
K (mg/L)	2.0^{*}±1.6	2.6^{*}±1.7	1.5±0.8	2.4±1.7	6.1^{*}±2.4	8.6^{*}±2.6

* Significant difference in each row between control and limed ($p<0.05$)

values are average of 3 replicates in 5 days of leaching ± standard deviation

£ Dissolved reactive phosphorus

€ Total dissolved phosphorus

Liming did not significantly affect TDP in either of the three soil types during this phase. The lack of significant difference could be due to large variability (standard deviation) between the replicates influenced by factors such as high temperature, increase in soil microbial activity as well as the presence of bugs and insects counteracting the lime-induced effect.

In general, the DRP and TDP concentrations in the leachate samples collected during the outdoor experiment were significantly higher than that of the indoor phase ($p<0.05$) (Tables 4-2 and 4-3). This increase could be attributed to the seasonal variations related to P concentrations. In late spring and summer, increased concentrations of labile P forms, as well as organic P forms, are reported to be linked to warmer temperatures (Fabre et al. 1996). Also, lower levels of water flowing through the soil profile could be another reason for higher concentrations of P, Ca, Mg, and K in soil leachates during the outdoor experiment.

Since the indoor and outdoor experiments showed similar performances in reducing DRP in limed sandy loam and lime loam soil columns, it could imply that lime application in previous fall could still be effective in retaining P in the following growing season.

4-4-3 Small repacked laboratory columns

In this laboratory experiment, DRP in the limed sandy loam and limed loam soil column leachates were significantly reduced by 67 and 38%, respectively (Table 4-4). While lime did reduce DRP in the laboratory repacked limed sandy loam and limed loam column similar to that of the intact columns, however, different percentages of reduction were observed (compare with approximately 40 and 70% for indoor intact sandy loam and loam columns). This difference could demonstrate the influence of soil structure on the lime-induced P retention and transport in the soil matrix. Higher phosphate retention was reported for the laboratory repacked limed sandy loam while higher phosphate retention was reported for the intact indoor limed loam soil.

Table 4-4: Average five consecutive day leachate properties for small repacked soil columns

	Sandy Loam		Loam		Clay Loam	
	Control	Limed	Control	Limed	Control	Limed
pH	7.95±0.1	7.79±0.1	7.45±0.1	7.50±0.1	8.06±0.1	7.89±0.1
DRP£ (mg/L)	0.086*±0.03	0.028*±0.01	0.098*±0.01	0.061*±0.03	0.247±0.005	0.236±0.03
TDP€ (mg/L)	0.143±0.01	0.152±0.01	0.180*±0.01	0.145*±0.01	0.293*±0.004	0.241*±0.01
Ca (mg/L)	50.1*±2.7	63.9*±2.2	17.4*±0.5	30.6*±1.6	42.1*±1.8	32.3*±5.0
Mg (mg/L)	8.7±0.6	7.1±0.2	2.3*±0.1	4.1*±0.3	5.1*±0.2	2.8*±0.6
K (mg/L)	1.8±0.03	1.7±0.03	2.4±0.1	2.3±0.3	0.66±0.08	0.79±0.3

* Significant difference between control and limed in each row ($p<0.05$)

values are average of 3 replicates in 5 days of leaching ± standard deviation

£ Dissolved reactive phosphorus

€ Total dissolved phosphorus

Dissolved reactive P leaching from the sandy loam soil illustrated a decreasing trend in the five consecutive days (Figure 4-4). This behavior could be attributed to the lower initial soil P content and PSI in this soil (Table 4-1). Available P can become more limiting in sandy soil as compared to clay soils given the same amount of initial P concentration and P plant uptake (Olsen & Watanabe, 1963).

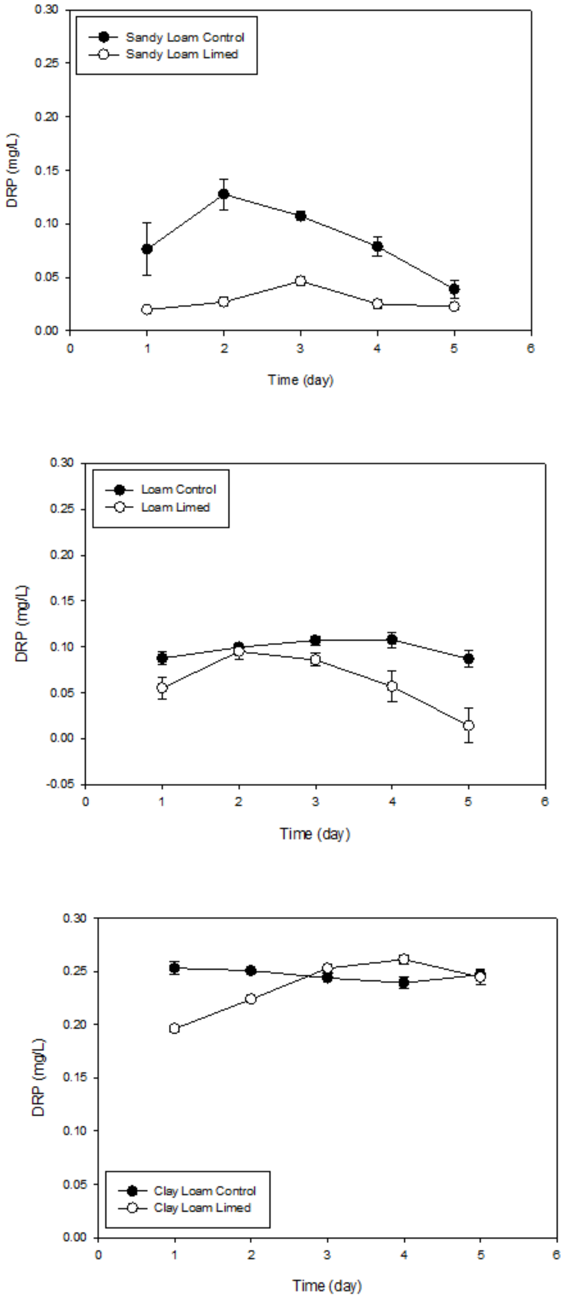

Figure 4-4: Dissolved reactive phosphorus (DRP) concentrations in leachates from small repacked columns for five consecutive days (Error bars represents standard error values)

The cumulative DRP loss in the five days of leaching correlated with the PSI of the three different studied soils (R^2= 0.911 for control; R^2=0.735 for limed) with sandy loam having the least P loss and lowest PSI and clay loam having the biggest P loss and the highest PSI (Table 4-5). This agrees with previous findings stating the correlation between DRP loss and initial soil P and PSI (Beauchemin and Simard, 1999; Sharpley, 1995). The total DRP loss was reduced from 9.74 to 2.96 mg in sandy loam and from 12.21 to 7.66 mg in the loam soil. The total DRP loss from the clay loam soil was not significantly reduced. Comparing repacked column results with that of indoor intact columns provides further evidence that DRP reduction in the indoor control clay loam leachate was due to preferential flows.

Table 4-5: Mehlich-3 extractable soil properties for repacked columns after 5-day leaching*

	Phosphorus	Calcium	Aluminium	Iron	PSI$^{\alpha}$	P/Ca
	mg kg^{-1}					
Sandy Loam						
Control (no lime)	50.4^{a}±0.8	2845.5^{a}±53.7	786.9^{a}±8.6	212.9^{a}±3.5	0.050^{a}	0.018^{a}
Limed (top 2.5 cm)	66.2^{b}±0.9	4794.5^{b}±157.6	717.7^{b}±28.8	229.6^{b}±1.7	0.070^{b}	0.014^{b}
Limed (bottom 7.5 cm)	53.5^{c}±0.4	2876.8^{a}±61.4	782.3^{a}±16.6	231.1^{b}±5.1	0.053^{a}	0.019^{a}
Loam						
Control (no lime)	81.6^{a}±1.3	2225.7^{a}±33.6	765.7^{a}±16.7	279.8^{a}±13.5	0.078^{a}	0.037^{a}
Limed (top 2.5 cm)	94.8^{b}±1.2	4391.0^{b}±294.7	623.2^{b}±30.2	262.6^{a}±5.0	0.107^{b}	0.022^{b}
Limed (bottom 7.5 cm)	83.8^{a}±1.6	2444.7^{a}±78.7	748.2^{a}±12.1	271.8^{a}±5.6	0.082^{c}	0.034^{c}
Clay Loam						
Control (no lime)	113.8^{a}±3.2	5384.0^{a}±178.9	579.0^{a}±10.6	375.4^{a}±8.1	0.119^{a}	0.021^{a}
Limed (top 2.5 cm)	126.0^{b}±0.8	6605.5^{b}±298.9	613.9^{b}±2.8	384.9^{a}±3.3	0.126^{b}	0.019^{a}
Limed (bottom 7.5 cm)	117.9^{a}±1.4	5681.3^{a}±394.2	568.3^{a}±10.3	377.4^{a}±4.4	0.125^{b}	0.021^{a}

* The same letters in each column for each soil indicate no significant difference ($p<0.05$)

α Phosphorus saturation index

values are average of 3 replicates in 5 days of leaching ± standard deviation

Similar to the indoor intact columns, TDP in the leachate of limed loam and limed clay loam soil columns was significantly reduced by 19 and 18%, respectively. These percentages are considerably lower than the 40 and 32% reduction in the TDP of limed loam and limed clay loam indoor intact columns. This demonstrates that soil structure and preferential flows play an important part in the lime-induced TDP retention in the soil.

There was a significant difference between DRP and TDP of control clay loam columns, while there was no significant difference between the two in the limed clay loam columns. This could imply that lime may have encouraged the conversion of dissolved organic P compounds to DRP compound such as orthophosphate.

In the clay loam soil, despite a higher clay content, lime failed to enhance a DRP reduction in the leachates. The calcareous nature and initial high Ca and P content of this soil along with preferential pathways could all be accounted as the contributing factors.

Despite mixing similar amounts of lime as Ca, the three soil types responded differently (Table 4-5). While the Mehlich-3 extractable Ca (M3-Ca) in the topsoil limed sandy loam and limed loam columns was increased approximately by 100%, the M3-Ca for the limed clay loam soil was increased by only 20 percent (Table 4-5). Again, this is due to higher initial Ca content and buffer capacity of this soil. The Mehlich-3 extractable phosphorus (M3-P) in the topsoil of all three limed soil columns was significantly increased by 12 - 32%.

4-4-4 Soil image analysis

The elemental distribution of the studied soils (control and limed) was identified by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectrometer (EDS). Mapping the Ca and P distributions on the different soil samples confirmed that calcium-phosphates were the dominant P forms in the limed soil. In limed sandy loam and loam soils, the P loading overlapped with the Ca loading (Figures 4-5 and 2-6 parts d, e & f), indicating a Ca-P bond. Whereas in the control sandy loam and control loam soils, P loadings were not always associated with Ca loadings (Figures 4-5 and 4-6 parts a, b & c). In the control sandy loam soil samples, P was, in some cases, associated with iron. The average Ca content in the control sandy loam was increased from 1.86 to 3.86 % in the limed sandy loam soil, and the average P content was also increased from 0.066 to 0.12%, respectively. For the loam soil, Ca was increased from 2.61% in the control to 6.49% in the lime soil, and P was similarly increased from 0.081 to 0.265%, respectively. In both cases, the percentages of Ca and P in limed soils were almost twice as much as the Ca and P in the control soils. In the case of clay loam soils, all phosphorus loadings were associated with Ca loadings regardless of lime since this is a calcareous soil. No significant difference was spotted between the elemental distribution of the control and limed samples (Figure 4-7). This further demonstrates the non-significant effect of the added lime on P retention in the calcareous clay loam soil.

The EDS elemental mapping results agreed with our leaching experiment results. In all cases, there was a correlation between Ca and P content in the soil. In alkaline or calcareous soils, phosphates are present as calcium or magnesium phosphates. Calcium phosphates are often concentrated in the coarser fractions of the soil (Mackenzie and Amer, 1964). This could further explain the effectiveness of lime in DRP reduction in the leachate of sandy loam and loam soils with considerably higher coarser fraction as opposed to the clay loam soil.

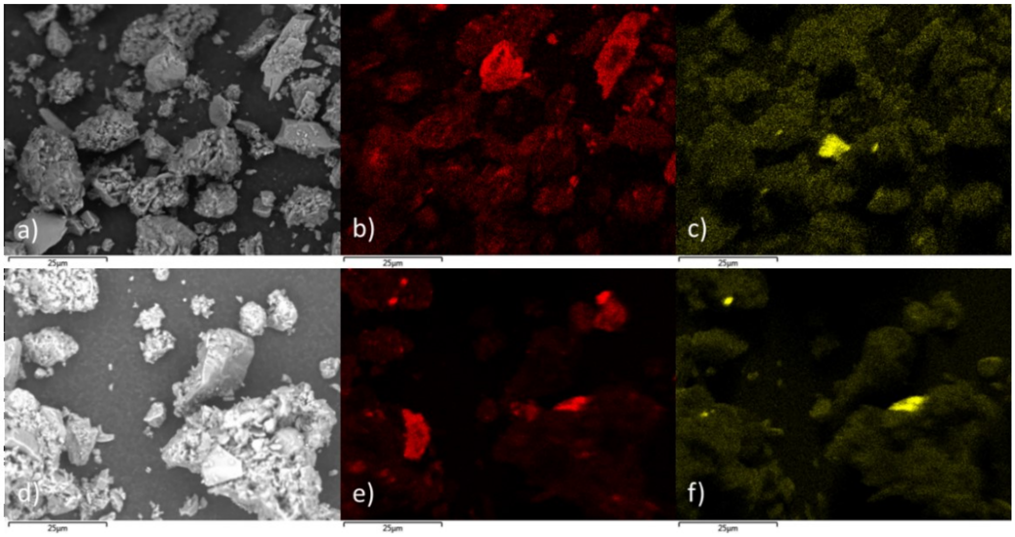

Figure 4-5: Sandy loam SEM-EDS mapping (25µm scale): a) Electron image of sandy loam control; b) Calcium mapping of sandy loam control; c) Phosphorus mapping of sandy loam control; d) Electron image of sandy loam limed; e) Calcium mapping of sandy loam limed; f) Phosphorus mapping of sandy loam limed (this site was selected as the representative of 10 random sites).

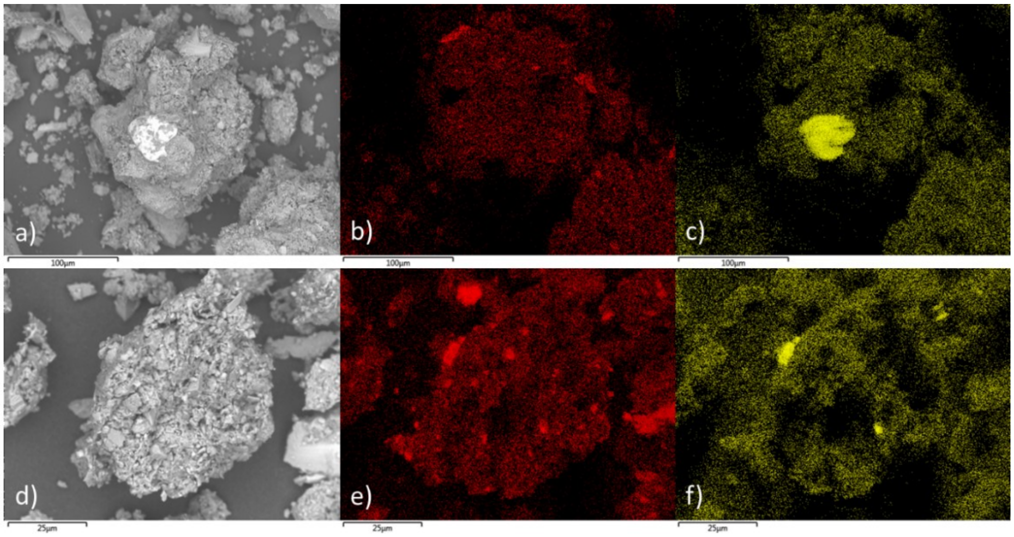

Figure 4-6: Loam SEM-EDS mapping (25µm scale): a) Electron image of loam control; b) Calcium mapping of loam control; c) Phosphorus mapping of loam control; d) Electron image of loam limed; e) Calcium mapping of loam limed; f) Phosphorus mapping of loam limed (this site was selected as the representative of 10 random sites).

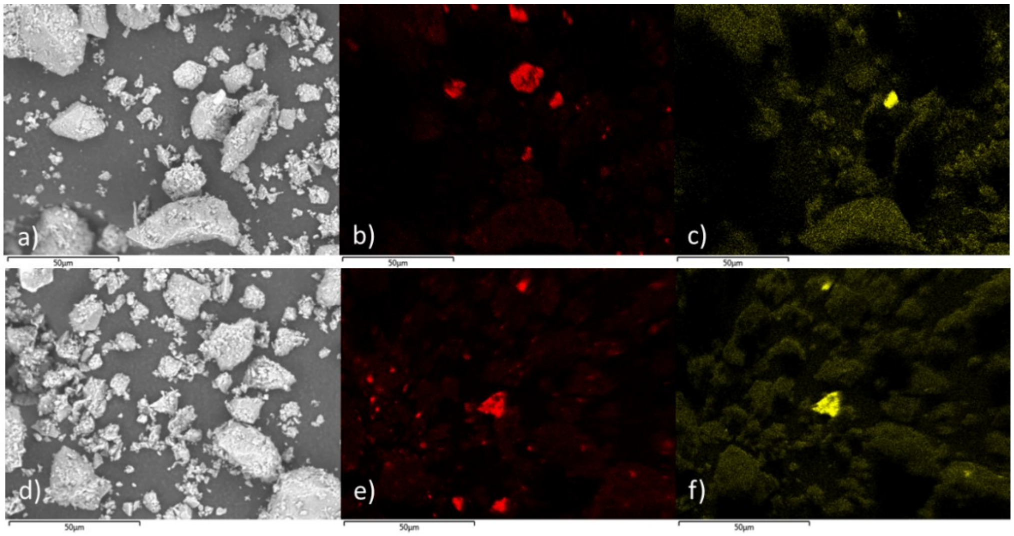

Figure 4-7: Clay loam SEM-EDS mapping (50µm scale): a) Electron image of clay loam control; b) Calcium mapping of clay loam control; c) Phosphorus mapping of clay loam control; d) Electron image of clay loam limed; e) Calcium mapping of clay loam limed; f) Phosphorus mapping of clay loam limed (this site was selected as the representative of 10 random sites).

4-4-5 Overall Implications

All three experimental setups demonstrated the potential of lime as soil amendment to reduce DRP in the alkaline sandy loam and loam leachate. The indoor experiments (intact and repacked) reported reduced TDP in the loam and clay loam leachates emphasizing the role of temperature and natural conditions on the limed-induced dissolved organic P immoblization. The difference in the extent of DRP and TDP reduction across the three experiments provides evidence of the influence of preferential flows and climatic conditions on lime and P solubility interactions in the soil.

The results also showed that lime can reduce DRP in the leachate of sandy loam and loam soils, while enhancing the Mehlich-3 extractable P in the soil, which is available for plant uptake (Table

4-5). Therefore, lime not only reduces DRP release from the soil, it can also enhance plant available P in the soil. The addition of the lime at this rate, increases the Ca content in the soil which is beneficial to the plant and provides more adsorption sites for P retention. Since lime-induced P retention mostly targets orthophosphates through adsorption, this mechanism is easily reversable whenever needed for plant uptake.

The PSI significantly increased from 0.050 to 0.070 in the limed sandy loam, from 0.078 to 0.107 in the limed loam soil and from 0.119 to 0.126 in the clay loam soil (Table 4-5). This is despite a lime-induced decrease in the DRP loss from the sandy loam and loam soils. Meanwhile, the P/Ca ratio in sandy loam, and loam soils significantly decreased from 0.18 to 0.14 and 0.37 to 0.22, respectively (Table 4-5). There was no significant difference between the P/Ca ratio in control and limed clay loam soils. As confirmed by SEM-EDS images, in calcareous or limed soils, phosphate-calcium compound are the main P compounds. Therefore, the P/Ca ratio is suggested as an additional P loss risk assessment factor for water quality management.

4-5 Conclusion

The study of intact and laboratory repacked soil columns revealed that the effect of lime on P mobility is varies by soil texture and is influenced by soil structure. Lime as a soil amendment can reduce dissolved reactive phosphorus (DRP) release from the studied alkaline sandy loam and loam soils in both intact and repacked columns. However, lime was not effective in reducing DRP release from the alkaline calcareous clay loam soil. Lime also reduced total dissolved phosphorus (TDP) concentration in the leachate from the finer-textured soils (loam and clay loam) in both indoor intact and repacked columns. The extent of lime-induced DRP and TDP reduction was different across intact and repacked columns implying the influence of soil structure and preferential flows on the P and lime interaction in the soil. The risk of P loss is associated with soil type. Given the importance of soil texture on the lime-induced P sorption and release, further field-scale research is recommended on different soil types especially on alkaline calcareous soils. Lime could be a promising P immobilizing soil amendment for neutral and non-calcareous alkaline soils to reduce DRP release from agricultural soils in hopes of ameliorating the eutrophication of surface water bodies.

4-6 Acknowledgements

This study was conducted at the Macdonald Campus of McGill University in collaboration with Graymont to whom we would like to express our sincere thanks. This research was funded by NSERC (Natural Sciences and Engineering Research Council of Canada) and Graymont. We would also like to express our special gratitude to Ms. Hélène Lalande for her valuable help in the analysis of the samples in Environmental Soil Laboratory, McGill University. Finally, we would like to thank Jessica Lui, Nianchao Luo, Amandeep Singh Sandhi, and Birkhoff Li for their contribution to the sampling collection, preparation, and analysis.

Connecting Text to Chapter 5:

The effect of lime application on phosphorus leaching was found to be dependent on soil texture, and the importance of soil structure was observed. Therefore, for the next step, the performance of lime on reducing phosphorus in leaching was evaluated on yet another soil type (sandy) in lysimeters at a medium field-scale experiment and under natural conditions. Also, we wanted to know whether the application of lime at the studied rate to a neutral soil would negatively affect crop growth.

Chapter 5, titled "The effect of lime on phosphorus leaching and soybean growth in sandy lysimeters," is ready to be submitted to the Journal of Plant and Soil. The co-authors of this manuscript include Dr. Zhiming Qi, my supervisor, Dr. Shiv O. Prasher, a professor in the same department, Mike Tate, marketing manager at Graymont, and Nikolas Romaniuk, new product specialist at Graymont.

CHAPTER 5: THE EFFECT OF LIME ON PHOSPHORUS LEACHING AND SOYBEAN GROWTH IN SANDY LYSIMETERS

5-1 Abstract

Lime as a high calcium-containing material can be an effective soil amendment to bind phosphorus in the soil, which potentially reduces the chances of eutrophication in downstream water bodies. However, there is limited study on the effect of lime on phosphorus leaching, especially in alkaline soils since this application is often associated with concerns for crop growth as a result of an undesirable pH increase. The main objective of this study was to evaluate the potential of lime in reducing dissolved phosphorus release from the soil without having adverse effects on soybean growth. Also, fall versus spring lime application was compared in terms of dissolved phosphorus concentration in the soil water. For this purpose, sandy lysimeters 100 cm high and 45 cm in diameter installed on the ground were employed. Lime at an application dose of 1% by soil (air-dried mass) was applied to the top 5 cm of the lysimeters. Soil water samples were collected from two sampling depths (7 and 30 cm) and at five sampling dates during the growing season (from May to October). The results indicated that lime application was able to reduce soluble reactive phosphorus concentration in the leachates by 50% (from 0.080 to 0.03 mg L^{-1}, $p<0.05$), while it did not significantly affect the total dissolved phosphorus concentrations in the soil water. The presence of plants did not affect the phosphorus concentration in the soil water. Soybean yield was significantly ($p<0.05$) increased to 2345 kg ha^{-1} in the limed lysimeters compared to 2165 kg ha^{-1} in the unlimed ones. The pH, P, Ca, Al, and Fe in the limed soil were significantly altered, but this change had no effect on the nutrient content either in the grains or the leaves. In addition to soluble reactive phosphorus, fall lime application was able to significantly reduce total dissolved phosphorus as well and resulted in a less soluble Ca release in the soil water. It was concluded that lime could be promising in reducing soluble reactive phosphorus release from the sandy soil without interfering with the soybean growth at the studied application rate.

Keywords: Soluble reactive phosphorus; Soybean yield; Sandy Lysimeters; Fall lime application; Lime.

5-2 Introduction

Eutrophication as a result of nutrient enrichment is one of the main water quality issues around the world leading to hypoxia, fish mortality and negative impacts on the ecosystem (Rabalais et al., 2001; Chen et al., 2007; Environment Canada, 2016; Lake Champlain Basin Program, 2016; Schindler et al., 2012; Bol et al., 2018). Traditionally nitrogen (N) in the form of nitrate was considered the main contributor to the eutrophication of lakes and river. However, recent research has proven phosphorus (P) to be the limiting nutrient for aquatic life and freshwater quality (Smith and Schindler, 2009; Jarvie et al., 2013). While P was deemed less mobile than nitrate owing to soil's sufficient P adsorbing capacity, the over-application of fertilizer and manure in excess of plant P requirement has led to the accumulation of P in agricultural soils (Jarvie et al., 2013). The total dissolved P concentration of only 0.2 mg L^{-1} in the soil solution could be enough to support plant growth (Majumdar et al., 2005). The surplus P will leach or runoff in either dissolved or particulate P form into surface water bodies.

Non-point sources such as agricultural activities account for considerable amounts of P loads into Canadian waters (Sharpley et al. 2013; Jarvie et al. 2013, 2017; Kleinman et al., 2015; King et al., 2015). Approximately 150 lakes have been affected by the cyanobacteria bloom in Quebec alone

(MSSS, 2007). The annual average P concentration in the Missisquoi Bay of the Lake Champlain, located in southern Quebec, was reported as 0.06 mg L^{-1} in 2016 being two times more than the Quebec water quality standard for P at 0.03 mg L^{-1} (Lake Champlain Basin Program, 2016). High P levels associated with eutrophication have been reported for the St. Lawrence River in Quebec, Lake Erie (one of the Great Lakes), as well as in Lake Winnipeg for the past decades (Michalak et al., 2013; Environment Canada, 2016; Environment Canada, 2018). A critical water quality guideline of 0.03 mg L^{-1} was set by the provinces of Quebec and Ontario in Canada to avoid further eutrophication of surface water (Environment Canada, 2004). Watershed management tools and practices have been employed during the past decades to mitigate the P-induced eutrophication (Jarvie et al., 2013). However, these practices have been unsuccessful in mitigating P losses, especially in dissolved forms (Kleinman et al., 2015). Soluble reactive P (SRP) is the most readily bioavailable fraction of P for plant uptake and as well as transport through subsurface drainage or runoff. Rapid algal growth associated with eutrophication is directly connected to this form of P. Therefore, strategies minimizing the release of SRP are urgently needed.

There is still much uncertainty involving nutrient management and eutrophication prevention. Surface application of soil amendments to reduce P desorption could be an effective measure alongside preventive agricultural practice. However, limited studies are available in this area of knowledge to allow for full-scale application (King et al., 2015).

Lime as high calcium oxide and carbonate calcium-containing material could be a promising soil amendment to immobilize P in soil and increase soil P sorption capacity. Agricultural lime is commonly used to adjust soil pH and remove soil acidity. However, the application of lime to neutral or alkaline soils solely as a P immobilizing soil amendment has not been studied at the field scale. Little knowledge exists on the interaction of lime and P transport in neutral soils. There is often the concern of an undesirable increase in the soil pH resulting in a negative impact on plant health and yield due to limited nutrient availability (such as Fe and Mn) associated with higher pHs.

The soil response to liming regarding P is largely dependent on lime application rate, soil type, pH, soil P levels, and texture. While lime application to acidic soils could increase P availability by reducing Al toxicity up to a pH of 6-6.5 (Haynes, 1982), in neutral to alkaline soils, higher soil pH and the increase in the Ca ions can lead to precipitation of calcium phosphate compounds and/or reduced phosphorus availability by increasing soil P adsorption (Haynes, 1982). On the contrary, liming can also increase phosphorus availability by contributing to the mineralization of soil organic phosphorus (Haynes, 1982). Varying responses have been reported on the effect of liming on phosphorus availability in different soils (Haynes, 1982; Tunesi et al., 1999; Curtin and Syers, 2001; Kavak and Baykal, 2012; Ulén and Etana, 2014; Andersson et al., 2016; Blomquist et al., 2017; Eslamian et al., 2018; Simonsson et al., 2018). Previous research by the authors in laboratory repacked columns and intact alkaline soil columns showed that lime application to the topsoil at the optimum application rate of 1% by soil dry mass can significantly reduce soluble reactive P concentrations in the leachate (Eslamian et al., 2018). This response was, however, dependent on soil texture and its characteristics such as initial phosphorus concentration and soil structure. While fine-textured soils have, in theory, high P-retaining capacity and lower P leaching risks, the presence of preferential pathways, for instance through cracks, increases the risk of P loss from this soil type (Reid et al., 2012). Coarse textured soils such as sandy soil may be associated with high P desorption unless they have a low initial P level (King et al., 2015). Furthermore, each soil's unique combination of physical and chemical properties makes the prediction of the effect of lime on P desorption more challenging.

High initial soil P levels and low soil P sorption capacity are two factors influencing considerable subsurface transport of P through soils (Beauchemin and Simard, 1999; King et al., 2015). Sandy soils, as well as soils with high organic matter content, often have a lower P adsorption capacity (King et al., 2015) and, hence, a higher risk of P loss. High soil organic matter content in soil often lowers the P binding capacity of the soil, which, in turn, will lead to more P desorption (Yang et al., 2019). Therefore, for this study, sandy soil with a rather high organic matter content was selected as worst-case scenario soil with potentially low P sorption capacity.

Application of lime to soils with Al toxicity due to lower pHs can increase soybean yield. A 10% yield increase was reported by applying dolomite lime to the top 20 cm of soybean soil on a tidal land in Thailand at 10% Al saturation level (Wijanarko and Taufiq, 2016). Based on a study conducted on a Red Oxisol (pH = 5) in Brazil, lime application with the rate of 100% of the amount required to raise the soil base saturation to 70% (about 3 t ha^{-1}), did not cause micronutrient deficiency under consecutive no-tillage practices (Moreira et al., 2017). A study on the quality and yield of soybean in Brazil as influenced by liming showed that either surface or incorporated lime application did not affect grain yield (Caires et al., 2006). Varying responses have been reported for soybean and lime interactions for the soils in Iowa, having a pH range of 5.3 – 5.8 (Mallarino et al., 2011). A target pH of 6.5 is recommended for most crop plants including soybean (Mallarino et al., 2011; Goulding, 2016).

The time of lime application is often dependent on factors such as soil properties, crop type, and lime particle size. Fall or spring application of lime to the field are the common practices. Depending on the particle size of the lime, a longer period (from months to a year) may be required for lime to break down and react with the soil. For pH adjustment purposes, the fall lime application will give the soil about five months to take effect and reach the ideal soil pH by spring before seeding. However, the effect of spring versus fall application of lime on P availability in the soil has not been studied.

The authors previously found that lime applied as a soil amendment to reduce soluble reactive phosphorus is effective at the laboratory-scale and in small intact soil columns having sandy loam, loam, or clay loam textures. In this study, we investigated this hypothesis in a medium-scale field study in sandy soil lysimeters under natural conditions in the presence of soybean during a full growing season under two lime application times. Therefore, the main objective of this study was to investigate if the lime applied as a soil amendment, at the studied rate, can reduce dissolved P release from sandy soil lysimeters without disturbing soybean growth in a neutral-pH soil. This study included the following sub-objectives: 1) effect of lime on dissolved P concentration in soil water solution; 2) effect of lime application on soybean yield and 3) comparison between the spring versus fall lime application regarding dissolved P concertation.

5-3 Materials and Methods

5-3-1 Site

The field study was carried out using fifteen PVC lysimeters installed on the Macdonald Campus Farm of McGill University, St. Anne-de-Bellevue, Canada (45°24'41.3"N 73°56'23.6"W). The cylindrical lysimeters were 100 cm high with a 45 cm diameter. At the bottom of each lysimeter, a PVC sheet and a 5-cm-opening drainage pipe were installed to drain excess water and to prevent anaerobic conditions in the soil column. The lysimeters were first built and packed with sandy soil at a bulk density of 1.35 g cm^{-3} about 20 years ago. This sandy soil has 91% sand content and is a

Ste-Amable complex, Ferro-Humic podzol soil (Elsayed and Prasher, 2014; Alizadeh et al., 2016). The physical and chemical properties of the sandy soil are summarized in Table 5-1.

Table 5-1: High calcium hydrated lime and sandy soil properties (Eslamian et al., 2018)

Properties	**High Calcium Hydrated Lime**	**Properties**	**Sandy Soil**
Available lime index as CaO, %	70.3	Soil texture (%):	
Total calcium, %	52.4	sand	91
Total magnesium, %	0.5	silt	5
Silica, %	1.2	clay	4
Alumina, %	0.4	pH	6.65
Ferric oxide, %	0.2	Bulk density (g cm^{-3})	1.35
Total sulfur, %	0.2	Soil organic matter (%)	2.95
Calcium carbonate, %	2.3	Total P (mg kg^{-1})	749.0
Neutralizing value ($CaCO_3$ = 100), %	129	Total N (mg kg^{-1})	1178.9
Bulk density, g cm^{-3}	0.462	Total Ca (mg kg^{-1})	4187.7
pH (Saturated solution at 25˚C)	12.45	Total Mg (mg kg^{-1})	1025.4
Solubility in water (10˚C), g L^{-1}	1.85	Total K (mg kg^{-1})	1718.4

The lysimeters received natural rainfall. A Hobo data logging rain gauge (Onset RG3) was installed in the field to collect rainfall and temperature data in one-minute intervals (Figure 5-1a). The rain gauge was installed at the same level as the lysimeter topsoil. The rain data was recorded for the duration of the experiment, which lasted from late May to October 31, 2018.

Figure 5-1: Image of the field lysimeters setup and sampling tools: a) Rain gauge; b) Ceramic cup slim water sampler; c) Vacuum hand pump; d) water sampler at two sampling depths

5-3-2 Experimental design

The effect of lime on the P concentration of the soil water samples and soybean growth was studied using 12 lysimeters. Soybean was selected as it is one of the most common field crops in Quebec. Considering the plants were cultivated in lysimeters 100 cm above the ground, soybean has a shorter full-grown height compared to corn, making it a better choice. Soybean has medium sensitivity to soil pH changes (Mallarino et al., 2011). Also, in Quebec, no fertilizer is added for soybean as it has N fixing capability. The treatment included two factors of lime (no lime; with lime) and plant (no plant; with plant) in 3 replicates. The soil water samples were collected from two sampling depths (7 cm, 30 cm) and at five sampling dates during the growing season. The lysimeters were randomly assigned. Lime was applied to 6 lysimeters one week before sowing.

For comparing the effect of fall versus spring lime application, nine lysimeters were assigned. This experiment included one factor of lime application time (fall, spring) in 3 replicates, and three lysimeters with no lime application were used as controls. Similarly, soil water samples were collected from two sampling depths on five sampling dates. The fall lime was applied in November 2017 at the end of the previous growing season, while the spring lime was applied in May 2018 one week before soybean planting. The fall lime lysimeters were covered until May 2018. Therefore, they did not receive any precipitation from November 2017 to May 2018.

5-3-3 Lime

High calcium hydrated lime is fine white powder produced by reacting quicklime with a sufficient amount of water to convert calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) (Lewis, 2005;

Zimdahl, 2015). High calcium hydrated lime (referred to hereafter as lime) provided by Graymont was mixed with the top 5 cm of several soil columns at the application rate of 1% by air-died soil mass. This is the optimum application dose to reduce P concentration in leachate based on the previous laboratory repacked column studies (Eslamian et al., 2018). This application rate is approximately equal to 7 t ha^{-1}. It is suggested that adjusting soil acidity by liming in soybean fields under no-tillage practice is most effective in the top 5 cm layer (Caires et al., 2006). The properties of the high calcium hydrated lime are presented in Table 5-1.

5-3-4 Soybean

Five soybean (*Glycine max*) seeds were sown in each of the six lysimeters on May 24, 2018. No fertilizer was added. The soybean growth was monitored weekly through height measurement and Soil plant analysis meter development meter (SPAD 502 meter) readings of the leaves' greenness. Leave samples were collected at R1 (begin of blooming), R5 (beginning seed), and R7 (beginning maturity). Leaves were sampled at the earlier stage (R1) as Mn deficiencies in soybeans, especially in soils treated with lime, are common (Moreira et al., 2006; Moreira et al., 2017). Depending on the leaf size, 3-5 random samples were collected from each lysimeter at each sampling date. Leave samples were washed with double deionized water and dried at 60°C for 24 hours and analyzed for nutrient content using the sulfuric acid wet digestion method (Parkinson and Allen, 1975) and atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential).

At R8 (full maturity), the pods were harvested, dried, weighed and counted for yield calculation. The grains as well the husks were washed and dried at 60°C for 24 hours, ground and later digested with sulfuric acid (Parkinson and Allen, 1975) to analyze for nutrient content using atomic adsorption spectroscopy. The yield was measured as the average total grain weight per surface area of the lysimeter for each treatment.

5-3-5 Soil sampling

Soil samples were collected every month from the top 5 cm of the soil during the growing season (5 sampling dates) to evaluate the effect of lime and the plants on the soil. At each sampling date, three soil samples were collected from each lysimeter, air-dried, sieved through a 2 mm mesh and later digested using the Mehlich-3 extraction method (Mehlich, 1984) for extractable P, Ca, Mg, K, Al, Fe and Mn content analyzed by atomic adsorption spectroscopy. Soil organic matter percentage was measured by loss on ignition, and soil pH was measured in water at soil to water ratio of 1:2.

Volumetric soil moisture content (θ_v) (cm^3 cm^{-3}) was calculated using Equation 5-1 (Scott, 2000):

$$\theta_v = \frac{wet-dry}{dry} \times BD \qquad \text{(Equation 5-1)}$$

Where *wet* is the mass of the wet soil, *dry* is the mass of the dried soil in gram, and *BD* is the bulk density of the soil in g cm^{-3}.

5-3-6 Soil water sampling

Two holes at depths of 7 cm and 30 cm from the soil surface were drilled into the sides of the lysimeters (Figure 5-1d). Since the lime was applied to the top 5 cm, the 7 cm water sampling depth was selected to sample the soil water directly below the lime application, while the 30 cm depth represented the topsoil just below the root zone.

Slim ceramic cup water samplers (Soil Moisture Equipment Corp, model 1905L6) (Figure 5-1b) were inserted vertically into the side holes (at 7 cm and 30 cm depths) for soil water collection (Figure 5-1d). The water sampler unit is 24 cm long and consists of a 2.2 cm outside diameter tube, a porous ceramic cup with a 2 bar (200 kPa) air-entry value, a Santoprene stopper, neoprene tubing and clamping ring. Neoprene tubing is used as an access port for sample extraction and evacuation. An extraction kit consisting of sampling bottles and appropriate tubing connections, as well as a vacuum hand pump, was required to evacuate the water sample (Figure 5-1c).

During the growing season, soil water samples were collected every 2-3 weeks and/or after each significant rainfall event (5 sampling dates). Soon after a significant rainfall, a vacuum in the order of 50-60 centibar was applied to all ceramic cup water samplers. Clamping rings were slipped over the folded neoprene tubing to seal the sampler and to hold the vacuum allowing the created vacuum to gradually attract the soil water through the porous ceramic cup and into the water sampler. It is important that the ceramic cup be wet and in contact with soil all the time. After a maximum of 24 hours, using a hand pump and the extraction kit, the water collected in the water sampler was extracted into sampling bottles. The water samples were kept in a cold room (5°C) until analysis.

The soil water samples were analyzed for soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), soluble Ca, Mg, and K. The ceramic cup has a porosity of less than 0.45 micron, therefore, the water samples were not required to be filtered for soluble contents. For the same reason, we were not able to measure particulate P in the water samples. Soluble reactive P was measured directly on the collected water samples using Lachat Instruments (QuikChem FIA+-8000 series). Lachat uses the colorimetry method for P analysis. For TDP analysis, samples were digested with persulfate (1:1) and autoclaved for 30 min prior to analysis by Lachat (Murphy and

Riley, 1962; O’Halloran and Cade-Menun, 2007). The soluble Ca, Mg, and K were analyzed on the 1:20 diluted samples using atomic adsorption spectroscopy.

5-3-7 Statistical analysis

To determine the significance of the studied factors on the dependent variables, the one-way Analysis of Variance (ANOVA) as well as a multivariate generalized linear model in Statistical Package for Social Sciences (SPSS) (IBM, version 24) were used. For factors with more than two levels, post hoc tests such as Least significant difference (LSD) and Tukey were employed to determine the significant difference between the groups, while for factors with two levels, a T-test was performed. For all statistical analyses, the significance was set to 0.05.

5-4 Results and Discussions

5-4-1 Weather data

The rainfall and temperature data recorded during the 2018 growing season on the sandy lysimeter site is graphed in Figure 5-2. The five sampling dates marked on the graph include June 7, June 20, July 18, September 25, and October 10. The sampling dates were collected after significant rainfall events a minimum of 3 weeks apart. We were not able to collect complete sets of samples in August and early September due to plant water needs. Sampling dates where more than half of the samples were missing were not included in the statistical analysis. During the recorded growing season (May 31 to Oct 12), the total average temperature and rainfall were calculated as 21.5˚C and 2.6 mm per day, respectively. The minimum temperature was measured as 7.4 on October 2, while the maximum temperature was recorded on July 7 at 31.7˚C. The maximum rainfall was logged as 34.6 mm on 4 June 2018, while the cumulative rainfall for this recorded period was 347.8 mm.

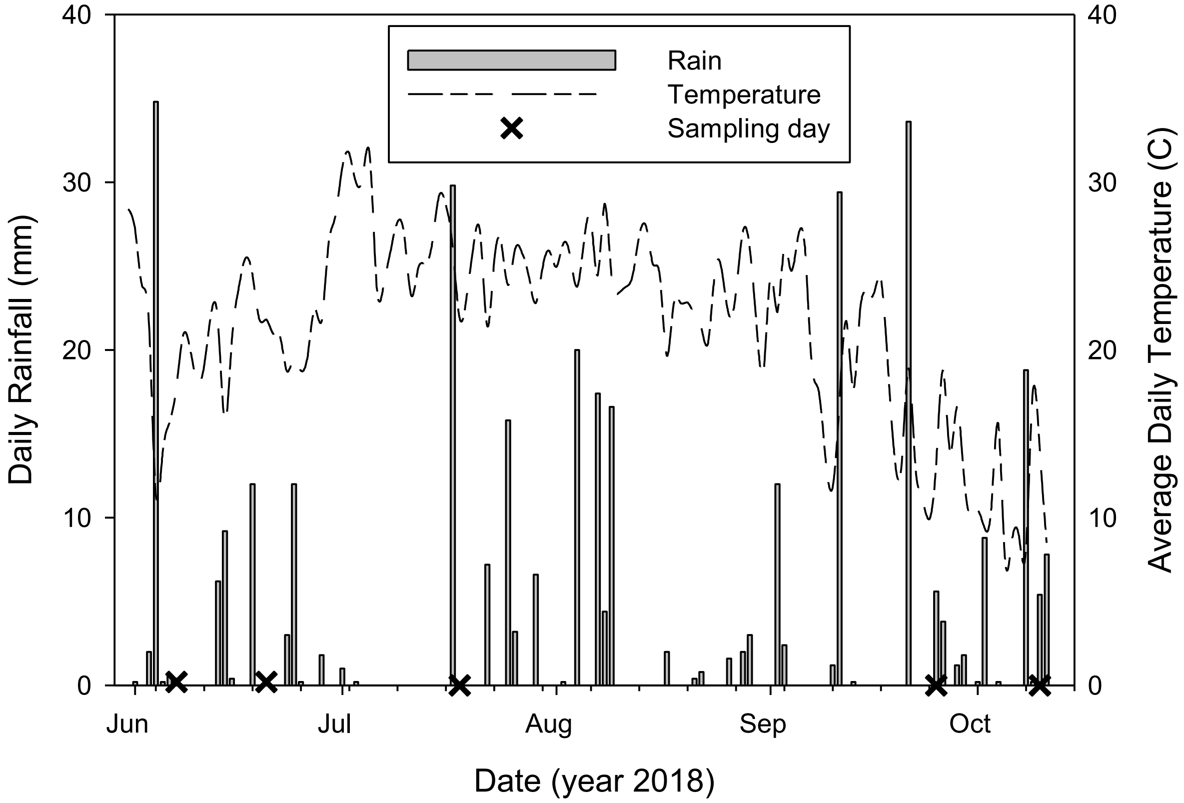

Figure 5-2: Total daily rainfall and average daily temperature data of the sandy lysimeter site for the growing season (May 31 to Oct 12, 2018)

5-4-2 Soil water solution

The results of the effect of the lime amendment in the sandy lysimeters (with or without soybean) on the dissolved P concentration in soil water solution are summarized in Table 5-2. The values presented in Table 5-2 are the average of the five sampling dates, two sampling depths, and thee replicates. Soluble reactive P (SRP) was significantly reduced by 50% in the solutions collected from the limed lysimeters regardless of having a plant or not. The soybean did not affect the SRP concentration in the soil water collected from the lysimeters. There was no significant difference observed between the total dissolved P (TDP) as influenced by lime application or soybean planting. However, there was a significant difference between SRP and TDP in each treatment. The difference between SRP and TDP represents some dissolved organic phosphate complexes. Soil organic matter content and factors that affect microbial activity, such as temperature, greatly influence the dissolved organic phosphorus portion. The results show that lime mainly targets the SRP (orthophosphate) form of P. SRP is the most readily available form of P that will leach into surface water bodies causing increased algal growth. Therefore, SRP is the form of P that is often targeted the most to prevent eutrophication (Darch et al., 2014; Wang & Jiang, 2016).

For both SRP and TDP, there was a significant difference between the two sampling dates in June in comparison with the other three sampling dates. While the average SRP and TDP concentration in the soil water samples on June 7 and June 20 was measured at 0.090 and 0.228 mg L^{-1}, respectively, the average was measured at 0.025 and 0.093 mg L^{-1} for July 18, Sept. 25 and Oct. 10, respectively. The TDP had a decreasing trend from June to Oct. This could demonstrate the seasonal variation in the P concentrations (Fabre et al., 1996). Higher temperatures are often associated with greater P release, especially in the organic P form due to increased microbial activity. Also, more P is released during the first rainfall events. Later in the season, the P release is diminished due to plant uptake. Furthermore, soil TDP release is affected by the soil P content and saturation levels (Sharpley 1977; Pizzeghello et al., 2016). As more P is lost through leaching and plant uptake, the available P content is reduced, leading to smaller P releases consequently. This effect could be more pronounced in sandy soils, compared to clayey soil, having lower P retention capacity. Yang et al. (2007) also concluded that the highest concentration of reactive P release happened during the first and second leaching events from the studied laboratory sandy soil columns amended with lime.

Table 5-2: The properties of the soil water collected from the sandy lysimeters

mg L^{-1}	Soluble Reactive P	Total Dissolved P	Soluble Ca	Soluble Mg	Soluble K
No lime No Plant	$0.080^{a} \pm 0.012$	$0.177^{a} \pm 0.019$	$50.52^{a} \pm 7.03$	$8.54^{a} \pm 1.55$	$6.78^{a} \pm 0.49$
No Lime with Plant	$0.074^{a} \pm 0.012$	$0.170^{a} \pm 0.019$	$36.01^{a} \pm 6.89$	$3.15^{c} \pm 0.86$	$1.79^{b} \pm 0.61$
With Lime No Plant	$0.031^{b} \pm 0.014$	$0.144^{a} \pm 0.021$	$54.03^{a} \pm 8.02$	$6.57^{b} \pm 1.14$	$1.77^{b} \pm 0.97$
With Lime with Plant	$0.042^{b} \pm 0.012$	$0.133^{a} \pm 0.018$	$40.39^{a} \pm 1.08$	$3.99^{c} \pm 0.55$	$1.59^{b} \pm 0.39$

Values are average of 5 sampling dates (and 3 replicates) during the soybean growing season ± Standard error

Different letters represent significant difference among the groups in each column (Tukey & LSD; $p<0.05$)

There was a significant difference between the SRP concentration in the samples collected from the two different sampling depths with the lower depth (30cm) having a lower SRP content of on average 0.037 ± 0.009 mg L^{-1} compared to 0.063 ± 0.007 mg L^{-1} for the higher depth (7cm). This could be due to plant uptake as the water travels through the soybean root zone.

While the soluble Ca in the four different treatments was analyzed statistically similar, the soluble Mg, on the other hand, was significantly reduced in the treatments with plants by 50% and in the treatments with lime but no plant by 25% in comparison with the treatment with no lime and no plant (Table 5-2). The soluble K was considerably reduced by 70% in all three treatments in comparison with the control treatment. This could mean that both lime application and the presence of plants contributes to a reduced K in the solution. While the reduced Mg as a result of plant uptake is compensated with the Mg release from lime. This results in a higher Mg in the solution from the limed but no plant lysimeters compared to the planted lysimeters (with and without lime).

Overall, the results indicated that lime mainly affects the SRP portion of the leachate P through the potential formation of calcium phosphates, which is consistent with the findings of Yang et al. (2007). Increased soil P sorption capacity induced by lime could be another reason for a reduced SRP as a result of liming (Eslamian et al., unpublished). The Ca released from lime could act as a bridge between the negatively charged soil surface sites and phosphate anions, therefore, increasing the potential for phosphate bonding in the soil (He et al., 1992). While the soluble Ca concentrations in the leachate did not change significantly, this could further verify the formation of calcium phosphates or Ca bridging on the soil surface. Otherwise, an increased Ca concentration in the leachates collected from the limed lysimeters would have been expected due to the significant amount of Ca release from the lime into the soil solution.

5-4-3 Soil

To investigate the effect of lime amendment and plants on soil properties, the average soil properties for five sampling dates are summarized in a Table 5-3. Either lime or plants did not significantly affect soil moisture content. The average soil moisture content at the sampling dates was 0.25 ± 0.05 cm^3 cm^{-3} at the top 5 cm sampling depth.

Table 5-3: Soil properties of the lysimeter topsoil during the growing season

	Soil Moisture (cm^3 cm^{-3})	pH first sampling	pH last sampling	P$^{£}$ mg kg^{-1}	Ca$^{£}$ mg kg^{-1}	Al$^{£}$ mg kg^{-1}	Fe$^{£}$ mg kg^{-1}
No lime no plant	$0.24^{a} \pm 0.07$	$6.65^{a} \pm 0.08$	$6.73^{a} \pm 0.08$	117.3^{a}	1056.7^{a}	1193.2^{a}	145.4^{a}
No lime with plant	$0.25^{a} \pm 0.04$	$6.76^{a} \pm 0.08$	$7.12^{b} \pm 0.19$	111.8^{b}	1272.3^{a}	1175.9^{a}	144.2^{a}
With lime no plant	$0.25^{a} \pm 0.02$	$8.42^{b} \pm 0.04$	$8.2^{c} \pm 0.04$	106.1^{c}	5841.3^{b}	918.4^{b}	117.2^{b}
With lime with plant	$0.28^{a} \pm 0.05$	$8.40^{b} \pm 0.01$	$8.15^{c} \pm 0.03$	111.1^{b}	5599.0^{b}	918.9^{b}	121.9^{b}

Values are average of all soil sampling dates and 3 replicates during the growing season ± standard deviation.

Different letters represent a significant difference between the groups in each column (Tukey & LSD; $p<0.05$).

£ Mehlich-3 extractable

The Mehlich-3 extractable P in the soil was significantly reduced as influenced by both lime and plant compared to the treatment with no lime and no plant (117.3 mg kg^{-1}). While the limed alone (no plant) treatment showed the lowest extractable P content (106.1 mg kg^{-1}), this decrease was alleviated with the presence of plant (111.1 mg kg^{-1}). Mehlich-3 extractable P of higher than 31 mg kg^{-1} is suggested to be very high and beyond soybean requirement (Mallarino et al., 2013). Therefore, this change is considered small and not of importance at the soil contents scale.

The lime application significantly increased the Mehlich-3 extractable Ca in the soil about four times regardless of plant presence, while Mehlich-3 Al and Fe were significantly reduced by 25 and 15%, respectively. The presence of soybean plants did not affect the extractable Ca, Al, or Fe in the soil. The pH of the limed soil was increased from 6.73 to 8.4 on the first sampling date. However, on the last sampling date, the pH of the limed soil was reduced to 8.15, while the pH of the planted soil (no lime) was increased to 7.12 from 6.73. The decrease in Mehlich-3 extractable Al and Fe correlates well with soil pH. The Fe^{3+} and Fe^{2+} solubility (mol L^{-1}) in the soil reduces by 1000 and 100 times, respectively, for every unit pH increase (Lindsay, 1974; Fageria et al., 2002). The Mehlich-3 extractable Mg, K, and Mn in soil were not significantly affected by the lime application and soybean cultivation. Despite having lower Mehlich-3 extractable soil P, Al, and Fe in the limed soils, no visible deficiency was noticed in the soybeans.

5-4-4 Soybean growth

The effect of the lime amendment on the soybean growth and performance is discussed in this session. Four out of the fived planted soybean seeds yielded in all lysimeters. The soybean yield in the unlimed lysimeters was calculated as 2165 kg ha$^{-1,}$ while for limed soil, the yield was 2345 kg ha^{-1} (Table 5-4). There was no significant difference between the plant height, greenness, soybean grain, and pod count per lysimeter in the limed and unlimed soil. However, the grain weight per lysimeter was significantly higher for the limed soils resulting in a higher yield (Table 5-4). Therefore, it could be concluded that lime application at the studied dose slightly (10%) increased grain yield rather than negatively affecting soybean growth.

Table 5-4. Soybean yield and physical properties in limed/non-lime sandy lysimeters

	Plant Max height (cm)	SPAD reading	No. pods per lysimeter	Bean mass per lysimeter (g)	Bean Count in each lysimeter	Yield (kg ha^{-1})
Plant-no Lime	52.3 ± 3.6	42.5 ± 0.2	44.0 ± 1.0	34.4* ± 1.1	132 ± 3	2165* ± 66
Plant-lime	50.1 ± 3.8	43.3 ± 1.6	43.0 ± 2.5	37.3* ± 0.8	128 ± 7	2345* ± 47

Values average of 3 replicates ± Standard deviation;

* T-test significant difference (p=0.022)

The Canadian soybean average yield in 2018 was reported as 2861 kg ha^{-1} (Soy Canada statistics, 2018). The total number of seeds planted per square meter of soil in our study was less than the common agricultural practice due to the wall confinement of the lysimeters and the placing of seeds to ensure a minimum of 10 cm spacing. While 480,000 seeds per hectare for row widths of 19 cm is recommended (OMAFRA, 2009), our five seeds per lysimeters were equivalent to approximately 315,000 seeds per hectare. This explains the lower than average yield in our study compared to the Canadian average soybean yield.

It should also be noted that on July 17, 2018, the soybeans were attacked by Japanese beetles (*Popillia japonica*). To prevent damage due to their big population, all lysimeters were covered with nets. This may have slightly affected light penetration or rainfall reception in the soybean lysimeters and thereby the overall yield. Since this was applicable for all lysimeters, therefore, this effect is neglected for comparison purposes between the limed and unlimed soils.

It was observed that in the limed soil lysimeters, germination occurred a couple of days later than the unlimed treatments, and consequently, all growing stages took place at a slight delay and more slowly in comparison to the soybeans in unlimed soil. While the unlimed soybean progressed more rapidly through the full seed (R6) and maturity stages (R7 and R8), these stages were longer for the soybeans in limed lysimeters. This could explain the higher yield associated with higher bean weight in the limed soybean. The soybean in the limed lysimeter spent a more time in the R6 stage before quickly entering maturity stages allowing for grain filling.

The nutrient content in soybean pod shell, bean, and leaves as influenced by lime soil amendment is summarized in Table 5-5. The T-test statistical analysis at a 5% significance level indicated that there was no significant difference in the nutrient availability in the soybean components grown in the limed versus the unlimed soil at the studied rate except for Ca content in beans and Mg content in the leaves. This indicates that the change in pH and nutrient availability in the soil as induced by the lime amendment did not negatively impact the nutrient availability in the soybeans.

Table 5-5: Nutrient content in different soybean components affected by lime soil amendment

mg g^{-1}	Treatment	P	N	Ca	Mg	K	Mn	Fe
Bean shells	No lime	0.54	7.49	10.32	5.86	7.98	0.01	0.05
	Lime	0.58	5.29	11.28	5.21	9.48	0.00	0.03
Beans	No lime	5.85	60.05	2.10^{*}	1.86	19.02	0.01	0.11
	Lime	6.00	52.36	1.93^{*}	2.08	18.28	0.01	0.08
Leaves	No lime	1.86	32.42	18.29	4.57^{*}	6.43	0.03	0.12
	Lime	1.74	32.21	17.81	3.74^{*}	7.48	0.02	0.13

* Significant difference (<0.05)- T-test

5-4-5 Fall versus spring lime application

The effect of fall vs. spring application of lime on the P in soil water and soil properties was investigated, and the results are summarized in Tables 5-6 and 5-7, respectively. For reference on the performance of lime, the results are compared to the unlimed treatment.

Table 5-6: Leachate properties for the Fall vs. Spring lime application study

mg L^{-1}	Soluble Reactive P	Total Dissolved P	Soluble Ca	Soluble Mg	Soluble K
No lime	$0.080^{a} \pm 0.012$	$0.177^{a} \pm 0.019$	$50.52^{a} \pm 7.03$	$8.54^{a} \pm 1.55$	$6.78^{a} \pm 0.49$
Spring Lime	$0.031^{b} \pm 0.014$	$0.144^{a} \pm 0.021$	$54.03^{a} \pm 8.02$	$6.57^{b} \pm 1.14$	$1.77^{b} \pm 0.97$
Fall Lime	$0.033^{b} \pm 0.012$	$0.132^{b} \pm 0.019$	$35.1^{b} \pm 3.61$	$5.02^{b} \pm 0.86$	$1.84^{b} \pm 0.67$

Values are average of 3 replicates for 5 sampling date during growing season± standard error

different letters represent a significant difference between the groups in each column (Tukey & LSD; $p<0.05$)

Table 5-7: Soil properties for the Fall vs. Spring lime application study

	Soil Moisture ($cm^{3}\ cm^{-3}$)	pH first sampling	pH last sampling	P mg kg^{-1}	Ca mg kg^{-1}	Al mg kg^{-1}	Fe mg kg^{-1}
No Lime	$0.24^{a} \pm 0.07$	$6.65^{a} \pm 0.08$	$6.73^{a} \pm 0.08$	117.3^{a}	1056.7^{a}	1193.2^{a}	145.4^{a}
Spring Lime	$0.25^{a} \pm 0.02$	$8.42^{b} \pm 0.04$	$8.2^{b} \pm 0.04$	106.1^{b}	5841.3^{b}	918.4^{b}	117.2^{b}
Fall Lime	$0.23^{a} \pm 0.10$	$8.11^{b} \pm 0.11$	$8.22^{b} \pm 0.04$	107.2^{b}	8010.3^{c}	770.0^{c}	95.8^{c}

values are average of 3 replicates and all soil sampling dates ± standard deviation

different letters represent a significant difference between the groups in each column (Tukey & LSD; $p<0.05$)

While the SRP in soil water was reduced for both spring and fall lime applications, there was no significant difference between the spring and fall lime applications. Total dissolved P, on the other hand, was only significantly reduced in fall lime application. Therefore, there was a significant difference between the TDP collected from fall and spring limed soil waters. The TDP correlated well with the soluble Ca in the soil water samples. Similarly, the soluble Ca only in the fall-applied limed soil was significantly different from unlimed, and spring limed soils. However, the soluble

Mg and K in soil waters correlated with the SRP concentration in the soil waters, and no significant difference was observed between that of the spring and fall applications.

There was no statistically significant difference between the soil moisture content, pH, or the Mehlich-3 extractable P content of the fall and spring lime applications. However, the soil Mehlich-3 extractable Ca was significantly higher in the fall lime application in comparison to the spring application. The Mehlich-3 extractable Al and Fe contents were significantly lower in the fall application compared to that of the spring lime and unlimed treatments. The lower soil Al and Fe contents in fall lime treatment is associated with higher Ca contents in this treatment.

Despite the higher available Ca content in the fall-applied lime treatments, a smaller concentration of soluble Ca was released in the soil water. Also, although the same amount of lime was added to both spring and fall lime treatments, the extractable Ca in the fall treatment is about 40% higher than that of the spring application. This could mean that the fall lime is more stable in the soil. Cumulative total Ca loss in leachate from spring lime lysimeters was higher than that of the fall lime (11.50 vs. 7.11 mg) during the five sampling events. While the Ca from fall-applied lime had enough time to bind with soil, for the spring lime treatment, significant amount of Ca may have been lost through the first spring rainfall right after application. Furthermore, the effect of lime on P adsorption in the soil is connected to wetting and drying cycles after and at the time of lime application. If the wetting and drying cycles happen before the lime has had time to react with the phosphate, it could lead to a decreased P adsorption (Haynes, 1982).

Given the ability to reduce TDP in addition to SRP, less Ca loss and higher stability, fall lime application is suggested to be preferred to spring lime application on the studied sandy soil.

5-5 Conclusion

The study of the lime amendment on P concentration in soil water and soybean yield in sandy lysimeters was conducted. Also, the fall versus spring application of the lime was compared regarding P concentration. It can be concluded that the application of lime at the studied rate of 1% by soil weight to the topsoil of the sandy lysimeters can reduce soluble reactive P (SRP) by 50% in the soil water samples. However, total dissolved P (TDP) was not significantly affected. The presence of plants in the lysimeters showed no effect on the SRP or TDP release in the soil water. While soil properties such as pH, Ca, Al, and Fe were changed through the lime application, no negative impact was observed on the soybean growth. Soybean yield was slightly increased in the limed soil. Furthermore, fall lime application was able to reduce TDP in addition to SRP significantly, therefore it may be preferable over spring lime application. Overall, it can be concluded that lime application as a soil amendment to reduce SRP release from the studied sandy soil could be a promising measure to reduce P losses into surface water bodies without disturbing soybean growth and yield. However, long-term field-scale studies on other soil textures and crops are recommended to study the potential of this soil amendment fully.

5-6 Acknowledgements

This study was conducted at the Macdonald Campus of McGill University in collaboration with Graymont, to whom we would like to express our sincere thanks. This research was equally funded by NSERC (Natural Sciences and Engineering Research Council of Canada) and Graymont. We would also like to express our special gratitude to Ms. Hélène Lalande for her valuable help in the analysis of the samples in Environmental Soil Laboratory, McGill University. Finally, we would like to thank Birkhoff Li, Azam Khowaja, and Cheng Qian for their assistance in the field sample collection, preparation, and laboratory analysis.

Connecting Text to Chapter 6:

After finding the effectiveness of lime in reducing soluble reactive phosphorus in the leachate from different soils without interfering with soybean growth, in the next chapter, we explored the mechanism involved in the lime-induced phosphorus retention in the soil. We wanted to know if adsorption is the dominant mechanism, how much does the hydrated lime increase the soil phosphorus adsorption capacity in the four previously studied soils. The results were compared to that of lime kiln dust.

Chapter 6 which is titled “Lime amendments to enhance phosphorus adsorption capacity in alkaline soils” was co-written by the following authors: Dr. Zhiming Qi, my supervisor, Cheng Qian, Master’s student in Environmental Engineering at McGill, Mike Tate, marketing manager at Graymont and Nikolas Romaniuk, new products specialist at Graymont. This paper is under review in the Journal of Environmental Science and Pollution Research.

CHAPTER 6: LIME AMENDMENTS TO ENHANCE PHOSPHORUS ADSORPTION CAPACITY IN ALKALINE SOILS

6-1 Abstract

Reduction in the dissolved P desorption from agricultural soils could be an effective measure to prevent eutrophication. Lime is a high calcium-containing mineral that can have promising but varying responses on P desorption depending on soil type. The main objective of this research was to evaluate and compare the potential of hydrated lime and lime kiln dust, its cheaper alternative, as soil amendments to increase soil P adsorption capacity and to reduce dissolved P desorption from four different neutral to alkaline soil textures (sandy, sandy loam, loam, and clay loam). A batch adsorption study with varying P concentrations of 0, 0.2, 0.4, 0.6. 0.8, and 1.0 mM P, adsorbent dose of 1% lime by air-dried soil mass at a fixed pH of 6.5 was carried out. The adsorption data fit well on both Freundlich and Langmuir adsorption isotherms. Both hydrated lime and lime kiln dust significantly increased the Freundlich adsorption coefficient by 3.2, 2.4, 2.0, and 1.6 times in loam, sandy, sandy loam, and clay loam soils, respectively. Although the hydrated lime showed higher potential to increase the Langmuir maximum adsorption capacity in comparison to lime kiln dust, they both exhibited similar performance in increasing the adsorption affinity in soils. At low phosphorus concentration ranges such as soil solution, adsorption affinity could serve as a better index. The cumulative phosphorus desorption in the ten consecutive days agreed with the adsorption results. Therefore, lime kiln dust as a by-product could be a promising soil amendment to increase soil phosphorus adsorption capacity leading to less phosphorus desorption to water bodies.

Keywords: Phosphorus; Lime; Adsorption; Desorption; Soil Adsorption Capacity; Langmuir Isotherm; Freundlich Isotherm.

6-2 Introduction

Phosphorus (P) loss from non-point sources such as agricultural fields is one of the main contributors to the eutrophication of lakes and rivers (; Jarvie et al., 2013; Sharpley et al., 2013; Dari et al., 2017). Phosphorus has been considered as the limiting nutrient in watershed management tools to mitigate eutrophication of surface water bodies (Jarvie et al., 2013). Traditional agricultural practices are inadequate in controlling P losses, especially in the dissolved forms (Kleinman et al., 2015). In Lake Erie, which is the shallowest of the Great Lakes, total and particulate P loadings were considerably reduced through nutrient management practices such as regulation of P-based fertilizer application. However, dissolved P forms have been significantly increasing throughout the years (Kleinman et al., 2015). Conservative agricultural practices aimed at reducing particulate P loss led to an increased soluble reactive P transport into Lake Erie (Javie et al., 2017). Dissolved P increase in lakes and rivers leads to a direct increase in algal growth since it is the readily available form of P for plant uptake. Phosphorus concentration in the Saint Lawrence River located in southern Quebec, Canada, was reported twice as high as the water quality guideline (Environment Canada, 2016). Reduced dissolved P desorption from agricultural soils could be a promising measure in reducing the dissolved P loadings to the surface water bodies through subsurface leaching and surface runoff. The application of soil amendments to increase soil P adsorption capacity could lead to a decreased P desorption from the soil.

Phosphorus is mainly found as orthophosphate (HPO_4^{2-}, $H_2PO_4^{1-}$) in the soil solution. Phosphorus removal from soil solution can occur through two major mechanisms of adsorption and/or precipitation. For calcareous soils, two pathways are suggested: partitioning on soil surfaces and precipitation induced by calcium ions in solution (Tunesi et al., 1999). It has been reported that in low concentrations (less than 1 m*M* P), adsorption predominated while in higher concentrations precipitation was the controlling mechanism (Holford et al., 1974; Jiao et al., 2007). At high phosphate concentrations (more than 1m*M* P), calcium phosphates precipitate at pH values greater than 5.5 (Haynes, 1982). Phosphorus in soil solution can be adsorbed on clay, carbonate, or hydroxides (adsorption process), or it can be precipitated as calcium phosphate insoluble solids (precipitation process). The latter is dependent on the concentration of calcium (when exceeding solubility limits) and pH (Tunesi et al., 1999).

The reactions at the soil solution and soil surface interface influence adsorption and desorption of soil phosphorus (Haynes, 1982). The sorption of P in soil is found to be very complex, since some of the adsorbed phosphates might take the reversible path (desorption) while some are strongly fixed in the soil and not subject to exchange (Griffith et al., 1973). Phosphorus desorption is directly related to P available for the plant as well as P transport in leaching. The amount of 0.2 mg L^{-1} of dissolved P in soil solution is considered sufficient to support plant growth (Majumdar et al., 2005). Dissolved P content in excess of the plant requirement will leach beyond the top soil and cause water quality issues for the receiving water body. Increasing soil's P adsorption capacity could lead to less dissolved P loss from agricultural fields. Phosphate specific adsorption is formed as inner-sphere surface complexes and as a ligand exchange (Sposito, 1989). In adsorption, phosphate anions in solution and the soil metal complexes form covalent bonds while displacing hydroxyl groups on the surface of the soil particle (Goldberg and Sposito, 1984; 1985). In acidic soil conditions, P anions form covalent bonds with iron and aluminum complexes, whereas in alkaline or limed soils, they form calcium and magnesium compounds. Phosphate in soil solution can also be adsorbed onto clay surfaces that have hydroxyl surfaces.

Application of lime, as a major source of calcium, could enhance calcium phosphate precipitation, which is an insoluble form of P. This reaction is often slow and irreversible. In terms of adsorption, the effect of liming is more complex and unpredictable. On one hand, liming can also increase soil pH by increasing the negative charges in soil and decreasing the HPO_4^{2-} anions. This could lead to a decrease in phosphate adsorption. However, on the other hand, the positive calcium cations released from lime could affect the surface charge, making it less negative, and therefore, increasing P adsorption. Calcium can counteract the pH effect (Tunesi et al., 1999). Liming can also impact phosphate availability through a third mechanism of the mineralization or immobilization of soil organic P by affecting soil microbial activities (Haynes, 1982). Liming acid soil has been reported to promote P fixation in soil without interfering with P requirements for crop growth (Majumdar et al., 2005). However, the application of lime as a soil amendment to increase the soil adsorption capacity on neutral to alkaline soil has not been fully studied. Eslamian et al. (2018) suggested that lime application at a rate of one percent by soil air-dried mass to the topsoil can significantly reduce P desorption from agricultural soils at a laboratory scale. Lime application to three acid soils in Brazil showed no effect on P adsorption. However, solution P was reduced for two soils with high exchangeable aluminum content (Anjos and Rowell, 1987).

Soil P adsorption capacity is an important factor in determining the risk of P loss in site assessment and management tools (King et al., 2015; Dari et al., 2017). Adsorption isotherm parameters such as Langmuir P bonding strength and the Freundlich adsorption coefficient can help predict P losses (Dari et al., 2017). Langmuir adsorption parameters can positively correlate with exchangeable aluminum, iron oxides, and clay content (Majumdar et al., 2005).

Phosphorus adsorption is the fastest and more dominant P removal process for lower P concentration ranges, such as soil solution. Application of lime as a soil amendment to increase soil P adsorption capacity in neutral to alkaline soils as a measure to mitigate eutrophication has not been comprehensively studied. Varying responses have been reported on the interactions between different lime amended soils and dissolved P. The effectiveness of lime products and the mechanisms involved in retaining P in different soil types is unpredictable. The main objective of this study is 1) to evaluate and compare the performance of hydrated lime [$Ca(OH)_2$] and lime kiln dust, as its less expensive alternative, on P adsorption and desorption from soil solution 2) to compare the performance of lime as P adsorbent in different soil types and 3) to find the P adsorption isotherm parameters for different soil types to help predict P loss.

6-3 Materials and Methods

6-3-1 Lime

High calcium hydrated lime (HC) and high calcium lime kiln dust (LKD) were used as phosphate adsorbents and soil amendments in this study. The two products were mixed with four different soil types at the optimum rate of one percent by soil weight (Eslamian et al., 2018). HC is produced by reacting quicklime with an adequate amount of water to convert calcium oxide (CaO) to calcium hydroxide ($Ca(OH)_2$) (Lewis, 2005; Zimdahl, 2015). LKD is the co-product from the calcination of high purity limestone. It is composed mainly of calcium carbonate ($CaCO_3$) and calcium oxide (CaO). Being a by-product, LKD is 10$ per ton which is ten times cheaper than HC. HC is a fine white powder, while LKD has a gray-yellowish color. The LKD has considerable amounts of calcium carbonate, silica, alumina, and carbon as compared to HC (Table 6-1). The bulk density of HC is lower than that of LKD owing to its smaller particle size distribution (Table 6-1).

Table 6-1: Physical and chemical properties of the two lime products

Physical and Chemical Properties	**High Calcium Hydrated Lime**	**High Calcium Lime Kiln Dust**
Available lime index as calcium oxide, %	70.3	23.0
Total calcium, %	52.4	40.2
Total magnesium, %	0.5	0.5
Silica, %	1.2	12.0
Alumina, %	0.4	5.1
Ferric oxide, %	0.2	1.9
Total sulfur, %	0.2	2.3
Total carbon, %	-	6.3
Calcium carbonate, %	2.3	37.9
Neutralizing value ($CaCO_3$ = 100), %	129	92.5
Bulk density, g cm^{-3}	0.462	1.235
pH (Saturated solution at 25˚C)	12.45	12.45
Solubility in water (10˚C), g L^{-1}	1.85	1.31
Brunauer–Emmett–Teller (BET) surface area, m^2 g^{-1}	11.35	1.17
Percent passing 0.075 mm sieve (No. 200)	97	60

6-3-2 Soil

Four different soil types (sandy, sandy loam, loam, and clay loam) were used for the adsorption study (Table 6-2). The sandy soil was collected from outdoor lysimeters installed on the Macdonald Campus Farm of McGill University, St. Anne-de-Bellevue, Canada (45°24'41.3"N 73°56'23.6"W). This is a Ste-Amable complex, Ferro-Humic podzol soil (Elsayed and Prasher, 2014; Alizadeh et al., 2016). The sandy loam soil was collected from grassland on the Macdonald Farm and belonged to the moderately well to imperfectly drained Chicot fine sandy loam classification (AAFC, 1956). The loam soil is classified as Brown Forest well-drained St. Bernard Loam derived mainly from Beekmantown limestone (AAFC, 1956). The loam soil was collected from an experimental field with corn-soybean-grass rotation situated on the Macdonald farm as well. The clay loam soil belongs to the Brown Podzolic category, and it is derived from underlying calcareous soils (AAFC, 1948). The clay loam field with corn cover was situated near Pike River, Quebec, Canada (45°07′44″ N; 73°03′04″ W).

Table 6-2: The physical and chemical properties of the soils

	Sandy	**Sandy Loam**	**Loam**	**Clay Loam**
Soil Texture, %				
- Sand	91	59	50	21
- Silt	5	32	38	39
- Clay	4	9	12	40
pH	6.7	7.35	7.55	8.10
Bulk density[€], g cm^{-3}	1.1	1.4	1.2	1.5
Soil organic matter[£], %	3.1	4.2	5.3	2.5
Me3-Phosphorus[†], mg kg^{-1}	119	50	87	109
Me3-Calcium[†], mg kg^{-1}	1070	2845	2225	5380
Me3-Aluminium[†], mg kg^{-1}	1200	822	767	580
Total Phosphorus, mg kg^{-1}	690	800	910	985
Total Calcium, mg kg^{-1}	4043.9	20183.2	6019.7	26902.4

€ Bulk density was measured with the core method (volumetric core cylinder)
£ soil organic matter content measured on loss on ignition
† Mehlich3 extractable

All soil samples were obtained from the topsoil layer using the composite sampling. The soils were passed through a 2mm sieve prior to analysis. Soil texture was identified using the hydrometer method (Parkinson and Allen, 1975). The pH of the soils was measured by the 1:2 soil to water ratio method using pH meter (Fisher Scientific, model AR10). Bulk density was measured using the standard cylinder core method. Soil organic matter content was measured with the loss on ignition method (Nelson and Sommers, 1996). Total phosphorus and total calcium were measured on the hydrogen peroxide/sulfuric acid digested samples (Olsen and Sommers, 1982) using the Lachat instrument (QuikChem FIA+-8000 series) and atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential), respectively. The plant-available P, calcium, and aluminum were measured using the Mehlich-3 extraction method (Mehlich, 1984).

6-3-3 Phosphorus adsorption

A full factorial batch adsorption experiment was designed to evaluate and compare the phosphate adsorption of four different soil types amended with HC and LKD. Two factors of soil type at four levels (sandy, sandy loam, loam, and clay loam) and soil amendment at three levels (no amendment, amended with HC and amended with LKD) with three replicates were chosen for this study. Phosphate solutions having concentrations of 0, 0.2, 0.4, 0.6, 0.8, and 1 m*M* P were prepared using monopotassium phosphate (KH_2PO_3) and 0.01 *M* K from KCl (potassium chloride) (Jiao et al., 2007). It is assumed that at phosphorus concentrations of higher than 1 m*M*, adsorption is no longer the dominant mechanism, and precipitation will start to dominate P retention in the solution (Harold et al. 1974). Lime amendments (HC and LKD) were mixed with the soil at the optimum rate of one percent soil weight (Eslamian et al., 2018). This optimum rate was also validated through an initial optimum dose experiment using 0, 0.5, 1, and 1.5 % of HC for the loam soil type. Two grams of soil were added to 30 ml of the various phosphorus solutions (Jiao et al., 2007). pH is an important factor in P adsorption since it affects the soil surface charge and determines the chemical speciation of phosphate. In order to have a constant and comparable pH among the amended and non-amended soil sample solution and to ensure the application of adsorption isotherms, the pH of all solutions was adjusted to a pH of 6.5 and buffered with morpholino propane-sulfonic (MOPS) 1.0 M solution. MOPS is an acid buffer with a molecular formula of $C_7H_{15}NO_4S$ and it is considered a non-chelating agent (Mao et al., 2012; Kumar et al., 2019). Experimental results also showed the MOPS does not complex with or have any effect on the adsorption procedure and the phosphate concentration. The optimum pH range for most plants is 5.5–7.0, therefore, an average pH of 6.5 was selected for this adsorption study (Lauchli and Grattan, 2012). All samples were shaken for 48 hours at 200 rpm at room temperature and later centrifuged for 40 min at 4000 rpm. pH was measured on the supernatant of the soil phosphate solution samples. For phosphate analysis with Lachat instrument (QuikChem FIA+-8000 series), the solutions were filtered with a 0.45 µm nylon syringe filter. Lachat uses the colorimetry method for phosphate analysis (Murphy and Riley, 1962). Soluble calcium in the solutions was measured using an atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential) on diluted samples.

6-3-4 Adsorption isotherms

Adsorption isotherms are empirical descriptive models. They are plotted as adsorbed P (mg kg^{-1}) against P in solution (mg L^{-1}). The amount of adsorbed P is calculated as the difference between the initial P concentration in the solution (added P) and P concentration in the solution at equilibrium per adsorbent in the solution. Some adsorption models can present further information about the adsorption process through the model constants. The limitation of these models is that they are only valid under a certain condition for which they are described (e.g., specific pH). Two adsorption isotherms, namely Freundlich and Langmuir, were used in this paper to describe the P adsorption onto different soils treated with HC and LKD.

The Freundlich isotherm model (Freundlich, 1926) is described by Equation 6-1:

$$Q = K_F {C_e}^{1/n} \qquad \text{(Equation 6-1)}$$

Where Q is the amount of P adsorbed per unit weight of soil (mg kg^{-1}), C_e is the P concentration in the solution at equilibrium. K_F is the Freundlich sorption coefficient, which is linked to the adsorption capacity, and n indicates the intensity of sorption, which varies with the heterogeneity of the material. Adsorption data fitted on to the Freundlich model is considered to represent a multi-layer process where the amount of adsorbed solute per unit adsorbent mass progressively increases (Chung et al., 2015). The linear form of the Freundlich model (Equation 6-2) was used to fit the adsorption data and to find the constants:

$$\log Q = \log K_F + \frac{1}{n}\log C_e \qquad \text{(Equation 6-2)}$$

The Langmuir adsorption isotherm model (Langmuir, 1918) is described as Equation 6-3:

$$Q = Q_{max}\frac{K_L C_e}{1+K_L C_e} \qquad \text{(Equation 6-3)}$$

Where Q is the amount of P adsorbed per unit weight of soil, Q_{max} is the maximum adsorption capacity, K_L is the adsorption constant, which may be related to the binding strength of P on soil surfaces and C_e is the concentration of P in the solution at equilibrium. The Langmuir model assumes the adsorption process to take place on a mono-layer (Chung et al., 2015). At low phosphate concentrations, the term adsorption affinity can be defined from the Langmuir model (Beck & Schultz, 1972; Suresh-Kumar et al., 2017; Kelly Vargas and Qi, 2019). As C_e approaches zero, the Langmuir becomes as Equation 6-4:

$$Q = Q_{max}\, K_L\, C_e \qquad \text{(Equation 6-4)}$$

Where $Q_{max}.K_L$ (slope of the curve) is calculated as the adsorption affinity of the adsorbent at low concentrations (Suresh Kumar et al., 2017). This could be a useful term to compare the P adsorption affinity of the two lime-based amendments for these different soils as P concentration in soil solution is normally lower than 0.5 mg L^{-1} and P levels of lower than 0.025 mg L^{-1} are recommended to prevent the eutrophication of surface water bodies (Suresh-Kumar et al., 2017; Kelly Vargas and Qi, 2019). The adsorption data were fitted on the linear form of the Langmuir model (Equation 6-5) to obtain Langmuir adsorption parameters:

$$\frac{C_e}{Q} = \left(\frac{1}{Q_{max}}\right) C_e + \frac{1}{K_L Q_{max}} \qquad \text{(Equation 6-5)}$$

6-4-5 Phosphorus desorption

The phosphate desorption experiment followed a full factorial design using the flow method (; Macdonald et al., 2004; Jiao et al., 2007; Eslamian et al., 2018). This method attempts to simulate the P leaching from the topsoil. However, the effect of soil preferential pathways is neglected here. Fifty grams of each different type of soil (sandy loam, loam, clay loam) treated with one percent HC per soil weight were packed into 60 mL tubes at each soil's bulk density (Eslamian et al., 2018). Polyethylene frits (0.45 µm opening) were placed on both ends to prevent soil loss, filter the leachate, and to create similar conditions on both ends. Artificial rainwater (0.012 mM $CaCl_2.2H_2O$; 0.015 mM $MgCl_2.6H2O$; 0.12 M NaCl; pH = 7.8; EC = 0.024 dS m^{-1}) (Glaesner et al., 2011) was passed through the syringes using a programmable vacuum extractor (SampleTek, model 24VE) in a cold room at 6°C temperature to mimic average fall temperature and to prevent microbial activity. The intensity of the rainwater leaching was set at 1.1 mL h^{-1} based on average total precipitation in the region in fall (September to December). The desorption events lasted for ten consecutive days, and leachate samples were collected daily and analyzed for pH, electrical conductivity, and orthophosphate. Electrical conductivity was measured with a conductivity meter (Radiometer Copenhagen, CDM 83).

6-4-6 Data analysis

Analysis of variance (ANOVA) in SPSS (IBM, version 24) was used to study the effect of two independents factors of soil type and lime treatment on the P adsorption capacity of the soils as well as the calculated adsorption isotherm parameters. Post-hoc tests (Tukey and Duncan) were employed to evaluate the significant difference among levels of a factor ($p<0.05$). The adsorption data were regressed to fit the linear form of the adsorption isotherm models. Different initial soil properties were correlated against various fitted adsorption isotherm parameters to discuss the interactions. Significant correlations ($R^2 > 0.7$) are reported and discussed.

6-5 Results and Discussions

6-5-1 Adsorption

Based on initial batch adsorption studies, the best application dose to significantly increase the soil P adsorption capacity the most was found at 1% lime (HC or LKD) by air-dried soil for loam (e.g., 0.02 g HC in 2 g Soil) (Figure 6-1).

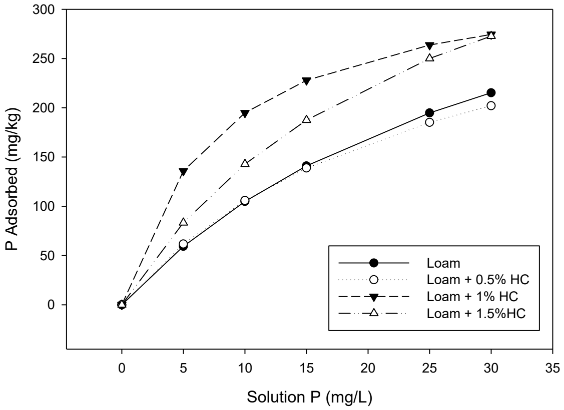

Figure 6-1: Fitted Langmuir Phosphorus adsorption isotherm for loam soil with different high calcium hydrated lime (HC) doses (0, 0.5, 1 and 1.5%)

Although the 1.5% application dosage showed higher adsorption capacity compared to the unlimed soil, its adsorption capacity was significantly lower than that of the 1% dose ($p<0.05$). The 0.5% application dose showed no significant difference in the soil adsorption capacity in comparison to the unlimed soil. These findings agree with the small leaching column study presented by Eslamian et al. (2018) where the 1% application dosage of HC and LKD were found as minimum effective dose for significantly reducing the P concentration of the column leachates from a clay loam soil to below 0.03 mg L^{-1} while the 0.5% application dose significantly increased the P concentration in the leachates. The optimum application dose of 1% (w/w) was applied to all other soils for further adsorption studies.

The batch adsorption studies on the effect of HC and LKD on P adsorption capacity of the four different textured soils showed that lime could significantly increase the P adsorption capacity of all four soils ($p<0.05$). Adsorption data were fitted onto Freundlich and Langmuir isotherm models (Figures 6-2 and 6-3). The calculated isotherm parameters for both adsorption models are summarized in Table 6-3.

Table 6-3: Parameters for the fitted Freundlich and Langmuir models using the adsorption data

	Freundlich			**Langmuir**				**Removal Efficiency 0.2 m*M* P**
	R^2	**n^{α}**	**K_F^{β}**	**R^2**	**Q_{max}^{γ}**	**K_L^{δ}**	**Adsorption Affinity**	
					mg kg^{-1}		**L kg^{-1}**	**%**
Sandy	0.912	1.60	22.71	0.644	250.0	0.07	16.53	49.3
Sandy + HC†	0.978	1.91	56.89	0.828	476.2	0.10	48.78	75.9
Sandy + LKD£	0.977	1.55	53.72	0.901	333.3	0.15	49.02	75.7
Sandy Loam	0.986	1.93	26.79	0.943	181.8	0.20	36.63	52.2
Sandy Loam + HC	0.998	1.93	46.75	0.977	285.7	0.13	38.17	70.8
Sandy Loam + LKD	0.942	3.37	58.76	0.988	185.2	0.11	19.49	67.7
Loam	0.945	1.74	17.77	0.831	169.5	0.07	11.98	44.1
Loam + HC	0.982	2.33	55.53	0.933	243.9	0.19	45.45	78.2
Loam + LKD	0.995	2.97	57.36	0.994	188.7	0.23	42.92	66.6
Clay Loam	0.998	1.88	30.38	0.979	222.2	0.10	21.79	57.5
Clay Loam + HC	0.996	1.62	43.77	0.961	384.6	0.10	37.17	69.8
Clay Loam + LKD	0.987	2.21	54.06	0.958	277.8	0.14	38.02	69.9

α Freundlich adsorption intensity constant; β Freundlich adsorption capacity coefficient; γ Langmuir maximum adsorption capacity; δ Langmuir adsorption coefficient; † High calcium hydrated lime; £ High calcium hydrated lime kiln dust

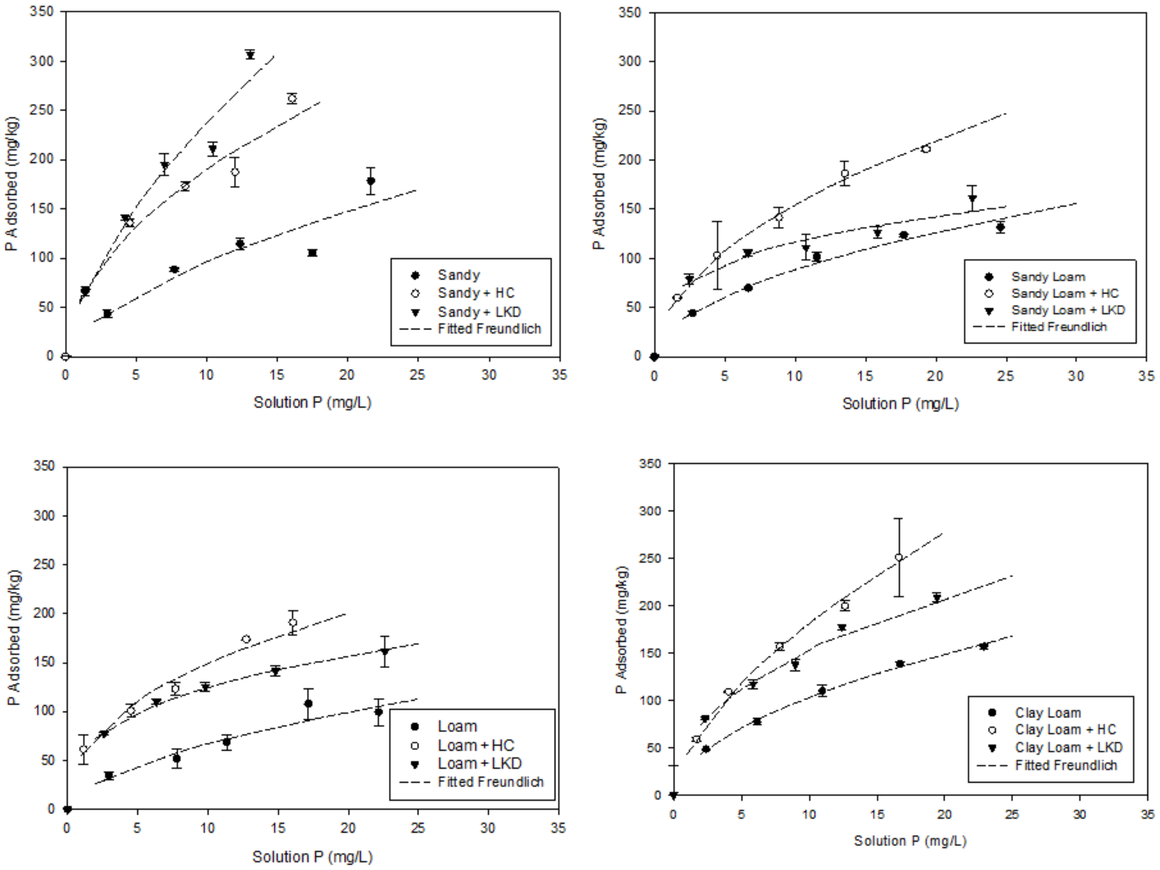

Figure 6-2: Phosphate adsorption in unamended soil, amended with 1% high calcium lime (HC), and amended with 1% lime kiln dust (LKD) for sandy, sandy loam, loam and clay loam soil types. The data points are average of three replicates, and the dashed lines are the fitted Freundlich model and error bars represent standard deviation.

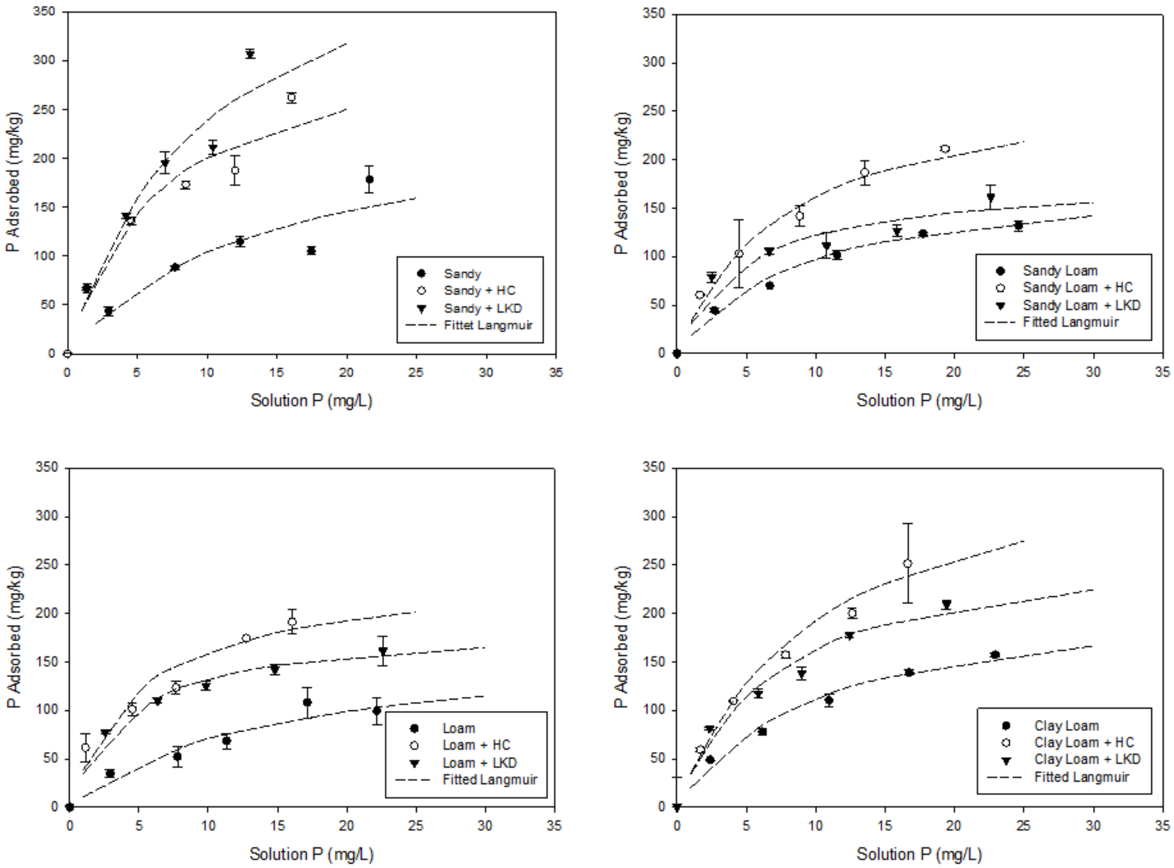

Figure 6-3: Phosphate adsorption in unamended soil, amended with 1% high calcium lime (HC), and amended with 1% lime kiln dust (LKD) for sandy, sandy loam, loam and clay loam soil types. The data points are average of three replicates, and the dashed lines are the fitted Langmuir model and error bars represent standard deviation.

The results showed that soil P adsorption could be best described by the Freundlich model, with an average R^2 of 0.974 compared to 0.911 for the Langmuir model. The Langmuir model assumes a monolayer for adsorption and hence, has a maximum adsorption capacity (Chung et al., 2015). Whereas, Freundlich isotherm is an empirical model where the amount of adsorbed P continuously increases with the increase in the solution P, unlike the Langmuir model where it reaches a plateau. P adsorption in soil solution could take place on two types of surfaces. One is high energy with high binding strength but a low maximum adsorption capacity, the other is a low energy surface with a lower binding strength and higher maximum adsorption capacity (Jiao et al., 2007). The unlimed sandy soil did not fit very well on the Langmuir model for an initial P concentration of 1 m*M* (R^2=0.644). This could be explained by higher aluminum content of this soil where, at this concentration, phosphate may be adsorbed on newly precipitated aluminum oxides (Anjos and Rowell, 1987), and adsorption is no longer the dominant mechanism.

Lime amended soils (HC and LKD) had a significantly higher Freundlich adsorption coefficient (K_F), Langmuir maximum adsorption capacity (Q_{max}), adsorption affinity and removal efficiency (at 0.2 mM P) compared to the non-amended soils ($P<0.05$) (Table 6-2) with the exception of Q_{max} induced by LKD for sandy loam as well as adsorption affinity in the same soil. There was a significant difference in the response of each soil type to lime application in terms of the adsorption parameters. There was no significant difference between the performance HC and LKD for the Freundlich adsorption coefficient, Langmuir adsorption affinity, and P removal efficiency at 0.2 mM P initial concentration. However, there was a significant difference between the Langmuir maximum adsorption capacity increase induced by HC and LKD with HC exhibiting a higher increase.

Lime, on average, increased the Freundlich adsorption coefficient (K_f) 3.2, 2.4, 2.0, and 1.6 times in loam, sandy, sandy loam, and clay loam soils, respectively. Therefore, the Freundlich adsorption coefficient, which describes the soil adsorption capacity in the limed soil, was increased, on average, twice as much as the unlimed ones with the loam soil having the highest increase from 17.77 to 57.36.

The P removal efficiency (%) in the 0.2 m*M* solution P is presented in Table 6-3. There was no significant difference between the performance of HC and LKD in P removal from the solution (P

<0.05). The removal efficiency of the limed soils was significantly increased by 53, 32, 64, and 21% for sandy, sandy loam, loam, and clay loam soils, respectively ($P<0.05$).

HC and LKD amended soils both showed the same performance for the adsorption affinity. On average, adsorption affinity was increased by lime amendment to 3.6, 3.0, 1.7, and 1.0 times in loam, sandy, clay loam, and sandy loam soils, respectively. The results show that while adsorption affinity could be increased by three times in loam and sandy soils, lime induced no change in the adsorption affinity of the sandy loam soil. This could be attributed to the low initial soil P and P saturation index (0.048) in this soil.

Lime amendment promoted an increase in the Langmuir maximum adsorption capacity of all four studied soil, but this increase varied by soil and lime amendment type. According to the Langmuir model (Table 4-3), soils amended with 1% HC had the highest maximum adsorption capacities with an average 40% increase in comparison with the unlimed soils. The increase in the Q_{max} induced by HC was 1.9, 1.7, 1.6 and 1.4 times for sandy, clay loam, sandy loam, and loam, respectively, while Q_{max} was increased 1.3, 1.3, 1.1 and 1.0 times by LKD for sandy, clay loam, loam and sandy loam, respectively. The results show that HC can promote a higher maximum adsorption capacity in the soil as compared to LKD. While HC enhanced a higher maximum adsorption capacity but in soil solution where we deal with lower P concentration (close to zero), adsorption affinity could be a better index (Beauchemin and Simard, 1999). Langmuir maximum adsorption capacity can be more meaningful for soil solution in the concentration range of 0–5 mg L^{-1} (Holford, 1982). While LKD has less calcium content and may promote less P adsorption sites on soil, but at low P concentration, LKD can perform similar or even better than the HC. The existence of considerable amounts of silica, alumina, and carbon could compensate for less calcium in LKD.

The average lime-induced (HC and LKD) increase in the Langmuir maximum adsorption capacity negatively correlated with the soil organic matter content in the soils (R^2=0.748). This means the lime was able to increase the maximum adsorption capacity more in sandy and clay loam soils (1.9 and 1.7 times, respectively) with lower soil organic matter contents of 3 and 2.5%, respectively. Soil organic matter is one of the important factors influencing P adsorption and desorption in soils. More organic matter can increase P availability by decreasing the maximum P adsorption capacity and P bonding strength (Majumdar et al., 2005; Yang et al., 2019). The greater increase in Q_{max} of the limed sandy and clay loam could also be attributed to the considerably higher aluminum content in the sandy soil and higher clay and calcium content in the clay loam soil (Table 4-2). Aluminum, calcium, and clay all provide adsorption sites for P (Haynes, 1982; Sposito, 1989). Lime in soils with more exchangeable aluminum could decrease dissolved P soil in solution (Anjos and Rowell, 1987).

Langmuir adsorption coefficient (K_L), which represents the bonding strength, was significantly ($p<0.05$) increased with the addition of lime for all soils except for sandy loam. The sandy loam soil has the lowest initial soil P and P saturation ratio, which leads to less desorbed P and having a higher tendency to retain P in the soil even without the addition of lime.

No correlation was found between the increase in the adsorption capacity, and the aluminum, iron, calcium, or clay content of the studied alkaline soils ($R^2<0.1$). This confirms that the increase in P adsorption is, in fact, influenced by the addition of lime, and other adsorption impacting factors are not responsible for this increase. However, Majumdar et al. (2005) found that Langmuir adsorption maximum was correlated with aluminum, iron oxides, and clay content of the studied acidic alfisols and entisol. Overall, there was a negative correlation between the initial soil adsorption capacity and the increase induced by the lime amendments. Soils with lower adsorption capacity, such as the loam soil, yielded the highest increase in the adsorption capacity with the addition of lime, while the clay loam soil with the highest initial P adsorption capacity resulted in the lowest increase.

Lime can increase the adsorption capacity of soils by acting as a direct adsorbent for P as well as modifying and enhancing the phosphate adsorption sites on the soil. P adsorption in the soil is regarded as an inner sphere specific adsorption process where there is ligand exchange with an anion such OH^- (Sposito, 1989). The phosphate anions in the solution can form covalent bonds with soil metal complexes and calcium by replacing the hydroxyl groups on the soil surface (Goldberg and Sposito, 1984). Anderson et al. (1995) also found that soil Ca content and pH is the two factors that have the most influence on the P retention in soils. Since in this adsorption study, soil pH was kept constant, the effect of pH on the availability of phosphate anions was negligible. Therefore, the lime application was the sole factor leading to an increase in phosphate adsorption. The positive calcium cations released from lime could affect the surface charge by promoting a less negative surface charge and hence, increasing P adsorption sites on the soil surface (Tunesi et al., 1999). The results confirmed that this increase is dependent on the soil type with varying soil physicochemical properties. While the calcareous clay loam and high aluminum sandy soils can promote the highest maximum adsorption capacities, at lower P adsorption ranges such as the soil solution range, all soils can perform similarly. The Freundlich isotherm results where a multi-layer adsorption surface is assumed also yielded similar performance for HC and LKD where loam soil exhibited the highest increase, and the clay loam the lowest.

6-5-2 Desorption

The column desorption experiment revealed that the lime amendment could significantly reduce P desorption from the studied soil types ($P<0.05$). The cumulative desorbed phosphate for the ten cumulative desorption days is shown in Figure 6-4. The slope of the regressed lines can be considered as the desorption rate. Application of lime reduced the dissolved P desorption rate from 0.174, 0.104, and 0.047 to 0.004, 0.01, and 0.004 for clay loam, loam, and sandy loam soils, respectively. The control clay loam soil has the highest desorption rate, while all limed soils have close to zero desorption rates. Phosphorus desorption from each soil was significantly different and correlated with their initial Mehlich-3 extractable and total P in soil with clay loam having the biggest amount of P desorption (1.535 mg kg^{-1}) and sandy loam having the smallest P loss (0.514 mg kg^{-1}).

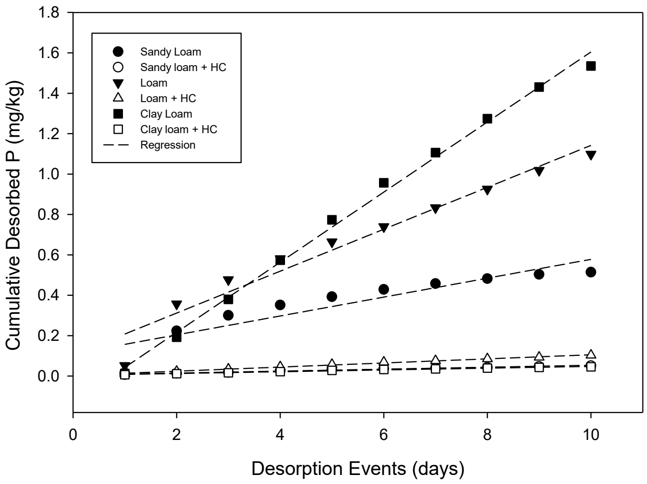

Figure 6-4: Cumulative phosphate desorption in sandy loam, loam, and clay loam soils amended with high calcium lime (HC).

Lime amendment at the rate of 1% HC was able to significantly reduce the cumulative P desorption after ten days to from 0.514 to 0.051 mg kg^{-1} in sandy loam, from 1.098 to 0.103 in loam and from 1.535 to 0.045 clay loam soils. The desorption results agree with the adsorption study where lime was successful in increasing the P adsorption capacity of soil, leading to less P desorption. The average desorbed P in the ten desorption events (mg kg^{-1}) negatively correlated with the Langmuir adsorption affinity parameter (R^2=0.929). This means the higher the soil P adsorption affinity, the lower the average P desorption from the soil.

6-5 Conclusion

Given the eutrophication phenomena of the lakes and rivers is mainly caused by the increased dissolved P leaching from agricultural lands, amending the soil at source could be a promising mitigation measure. The batch adsorption study on the high calcium hydrated lime and lime kiln dust showed that lime as a soil amendment, at the studied recommended dose, can increase the P sorption capacity of various soil types with neutral to alkaline soil pH. The increased soil P adsorption capacity could consequently lead to less P desorption from the soil profile. The results confirmed that the amount of lime-induced increase varies by soil type. There was no significant difference in the performance of the two lime products in the overall increase in the soil P adsorption capacity. While the high calcium hydrated lime was able to increase the Langmuir maximum adsorption capacity more, the P adsorption affinity induced by both lime products was similar at lower P concentrations. Therefore, at soil solution P concentration ranges, lime kiln dust could serve as a cost-effective soil amendment in increasing the soil P adsorption capacity through the enhancement of P adsorption surfaces.

6-6 Acknowledgement

This research was conducted at the Macdonald Campus of McGill University in collaboration with Graymont to whom we would like to express our sincere thanks. This study was equally funded by NSERC (Natural Sciences and Engineering Research Council of Canada) and Graymont. We would also like to express our special gratitude to Ms. Hélène Lalande for her valuable help in the analysis of the samples in Environmental Soil Laboratory, McGill University.

Connecting Text to Chapter 7:

Both hydrated lime and lime kiln dust reduced phosphorus release from agricultural soil by increasing soil phosphorus adsorption capacity. However, the lime kiln dust is preferred for being a low-cost by-product. However, the application of these lime products can be often accompanied by the undesirable rise in soil pH, preventing the universal application of these phosphorus-immobilizing products. In the next chapter, we explored the concept of modifying the lime kiln dust to improve its efficiency further to retain more phosphorus in the soil and to develop a neutral pH product.

Chapter 7 is titled "Novel iron-coated lime kiln dust to increase soil phosphorus adsorption capacity," and it is co-authored by Dr. Zhiming Qi, my supervisor, Kevin Kelly, a PhD candidate in Bioresource Engineering at McGill, Mike Tate, marketing manager at Graymont and Nikolas Romanuik, new products specialist at Graymont. The following manuscript is ready to be submitted to a peer-reviewed journal.

CHAPTER 7: NOVEL IRON-COATED LIME KILN DUST TO INCREASE SOIL PHOSPHORUS ADSORPTION CAPACITY

7-1 Abstract

Phosphate desorption from agricultural soils is a contributing factor to the eutrophication of surface water bodies. The application of phosphorus immobilizing material could be an effective measure to retain phosphorus in soils. Current adsorbents are often costly. Lime kiln dust could be a potential low-cost adsorbent to retain phosphorus in the soil, however, there is often concern about the rise in pH and lower efficiencies. Therefore, a novel iron coated lime kiln dust was developed through thermo-hydrolysis of hexahydride iron chloride in a lime kiln dust suspension solution to develop an efficient soil amendment in increasing soil phosphorus adsorption capacity. The modified lime kiln dust offers a soil amendment that is neutral in pH and cost-effective. The new product was characterized using scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy, Brunauer–Emmett–Teller surface area analyzer, and atomic adsorption spectroscopy after nitric acid digestion. The adsorbent behavior was evaluated by a full factorial batch adsorption experiment having initial phosphorus concentrations in the range of 0-1 mM in three replicates. The iron-coated lime kiln dust was mixed with the soil at the rate of 1% (w/w). The results showed that the iron-coated lime kiln dust has an increased surface area by 30 times compared to the original lime kiln dust. While scanning electron microscopy demonstrated the presence of the iron load on the surface, the chemical analysis also confirmed the results with the new product containing 16% iron by weight. The adsorption data fitted well on both Freundlich and Langmuir isotherm models. The clay loam amended with the iron-coated lime kiln dust had phosphorus adsorption of 450 mg kg^{-1} (at 1mM P), having a 30% increase compared to that of the non-amended clay loam. The Freundlich adsorption coefficient was found to be 200.6, which is 2.5 times more than that of the non-amended soil. The Langmuir adsorption coefficient, as well as the adsorption affinity, were both increased approximately five times for the soil amended with the modified lime kiln dust. The iron-coated lime kiln dust also demonstrated a higher efficiency for phosphorus adsorption in comparison with the non-modified lime kiln dust at a fixed pH of 6.5. Given the simple development procedure, high efficiency, and low-cost final product, the iron-coated lime kiln dust could be a promising soil amendment to increase soil phosphorus adsorption as well as being an adsorbent for phosphorus removal from solutions.

Keyword: Orthophosphate; Lime kiln dust; Iron coating, Thermo-hydrolysis; Clay loam; Adsorption; Soil adsorption capacity

7-2 Introduction

Dissolved phosphorus (P) mainly in the form of phosphate is often the limiting nutrient for aquatic life, and in excess, it can lead to rapid eutrophication of lakes and rivers (Dodds et al., 2009; Lalley et al., 2016). Phosphate found in surface water bodies can come from sources such as agriculture runoff or leaching, industrial effluent, and municipal sewage (Sims et al., 1998; Lalley et al., 2016). Agricultural fields are responsible for approximately 50% of the non-point source P loading into the water bodies worldwide (Ortiz-Reyes and Anex, 2018; Sachdeva et al., 2019). Phosphorus applied more than crop requirements will leach beyond the topsoil in the form of readily available P and will consequently contribute to eutrophication having negative impacts on the aquatic biodiversity and environmental water quality. While water treatment techniques can be effective, but they are often associated with the high cost of material and maintenance (Dodds et al., 2009).

Resolving the issue of excess P loss at the source could be the best sustainable measure. Although the adoption of new and effective agricultural management practices is essential to mitigate this problem in the long term, reports have shown that these agricultural practices are often insufficient in controlling P losses, especially in dissolved forms (Kleinman et al., 2015). Phosphorus-reducing management practices in Lake Erie, the shallowest of the Great Lakes, considerably reduced total and particulate P loadings, however, dissolved P forms have been still increasing (Kleinman et al., 2015). Phosphorus concentration in the Saint Lawrence River, as well as Missisquoi Bay located in southern Quebec, Canada, was reported twice as high as the water quality guideline at 0.03 mg L^{-1} (Environment Canada, 2016; Lake Champlain Basin Program, 2016).

Phosphorus availability in the soil solution is determined by processes such as dissolution, desorption, and mineralization (Eduah et al., 2019; Gerard, 2016). Soil properties such as pH, metal oxides content, clay type, and percentage, ionic strength, calcium, and the competing anion contents could influence the dominance of these processes (Eriksson et al., 2015; Gerard, 2016; Eduah et al., 2019). Adsorption and desorption are important processes in determining the fate and transport of dissolved P through the soil profile and into the water bodies (Eriksson et al., 2015). Precipitation and dissolution can be of importance in soils with high concentrations of soluble P in the soil solution. In acid soils, P can precipitate with Fe and Al oxides while in alkaline, calcareous, or limed soils, P can form Ca or Mg phosphate compounds or enhance P adsorption onto soil surfaces with hydroxyl groups (Eriksson et al., 2015; Haynes, 1982). Adsorption is the dominant and preferred mechanism in low P concentrations (Suresh Kumar et al., 2019). Phosphate specific adsorption in the soil is regarded as an inner-sphere surface complex and as a ligand exchange (Sposito, 1989). In adsorption, phosphate anions in the solution and the soil metal complexes form covalent bonds while displacing hydroxyl groups on the surface of the soil particle

(Goldberg and Sposito, 1984). Application of P-sorbing soil amendments could be a promising measure in retaining the excess dissolved P in soil and preventing the acceleration of eutrophication due to P leaching. The application of P-adsorbing products as soil amendments as opposed to direct application to receiving waters could mitigate issues concerning water toxicity, pH changes, and re-application and maintenance cost. These materials could immobilize nutrients in the soil and release them when needed by plants as adsorption is an easily reversible process.

Eduah et al. (2019) studied the effect of corn cob and rice husk biochar as soil amendments on P sorption in two acid and one neutral soil. The biochar was applied at a rate of 1% by soil weight. The results showed that both types of biochar were able to increase soil P retention capacity in the neutral soil while it led to a decrease in P retention in acid soils. Phosphorus speciation is dependent on soil initial P levels and soil properties (Eriksson et al., 2015). The primary P-sorbing chemicals are Ca, Fe, and Al-based materials. Lime, as a high calcium-containing material, has a P-sorbing potential. The application of agricultural lime is a common method to raise soil pH to reverse the negative impact of soil acidity. Lime in wastewater treatment facilities is often used as a P adsorbent. Application of these metal oxide-based products to reduce P in lakes and sediments for eutrophication control has been studied (Berg et al., 2004; Anderson, 2004; Wang and Jiang, 2016). However, there is limited study on the application of lime as a P adsorbing soil amendment to neutral and alkaline agricultural soils. The effect of Ca-based products on P adsorption is dependent on product dose and Ca content as well as the properties of the receiving soil or water. A column laboratory-based experiment demonstrated that lime applied at 1% by air-dired soil mass could significantly reduce soluble reactive P contents in the leachate from a clay loam soil (Eslamian et al., 2018). Intact column leaching studies have shown that high calcium hydrated lime can reduce soluble reactive P desorption from two neutral pH sandy loam and loam soils

(Eslamian et al., unpublished). A comparative batch adsorption research conducted by the authors showed that lime kiln dust could increase the P adsorption capacity of 4 different soils type with alkaline pH by approximately 40% having similar performance to that of the high-quality hydrated lime especially in low soil solution P concentration ranges (Eslamian et al., unpublished).

Despite the potential of lime in retaining P is soil, a possible unwanted increase in the pH of lime amended soils is often a concern for crop growth. This greatly limits the adoption of lime as a universal P adsorbent, especially in neutral and alkaline soils at its full potential. Thus, a soil amendment with a neutral pH is required to only target P retention without changing the soil pH. Furthermore, there is a high cost associated with the application of high-quality lime. Therefore, modification of lime kiln dust, as a cheaper alternative to high-quality lime, with the intention to increase its efficiency and to achieve a neutral pH product could yield a promising cost-effective universal P fixing product.

Iron oxide is a commercial adsorbent for phosphate removal from solutions. Iron oxide as an adsorbent could contribute to new adsorption sites for phosphate through complexing with phosphate anions in addition to adjusting soil pH. The capacity of iron oxide adsorbents in P adsorption from lake water and solutions has been extensively studied (Chitrakar et al., 2006; Kanematsu et al., 2010; Sperlich et al., 2010 Lalley et al., 2015; Lalley et al., 2016;) Lalley et al. (2016) compared the performance of one commercial iron oxide with three modified ones (coated with Ag or/and Mg) on the removal of phosphate from lake water. The results showed that the sliver coated iron oxide offered higher Langmuir monolayer adsorption capacity for P removal from lake water (Lalley et al. 2016). The surface of adsorbents can be modified to enhance their sorption sites for potentially more phosphate adsorption. An additional advantage of these coated adsorbents is their extended lifetime and regeneration potential (Lalley et al. 2016).

Therefore, the main objective of this study is to develop a modified lime-based soil amendment with a neutral pH and an increased P adsorption capacity in soil. This study aims to 1) develop and characterize a novel iron-coated lime kiln dust; 2) evaluate the effect of the iron-coated lime kiln dust on soil P adsorption capacity; 3) compare the performance of novel iron-coated lime kiln dust with the original lime kiln dust in the soil at a fixed pH; 4) find the best-fitted adsorption isotherm and parameters to describe the adsorption of P in soil amended with lime kiln dust or the iron-coated lime kiln dust.

7-3 Material and Methods

7-3-1 Lime Kiln Dust (LKD)

Lime Kiln Dust (LKD) is the co-product from the calcination of high purity limestone. It is composed mainly of calcium oxide (CaO) and calcium carbonate ($CaCO_3$) at approximately 56.2 and 37.9%, respectively. This LKD has considerable amounts of silica, alumina, and carbon at 12, 5.1, and 6.3%, respectively. The ferric oxide content of the LKD is 1.9%. LKD has a gray-yellowish color with an average bulk density of 1.24 g cm^{-3} and 90% passing from the 0.600 mm sieve. Being a by-product, LKD is ten times cheaper than high-quality hydrated lime at approximately $10 per ton.

7-3-2 Iron coated lime kiln dust preparation

Two grams of LKD was added to 100 mL (2% w/v) of double deionized water in 4 replicates and let soak for 24 h (Villalba et al., 2010). The pH was read at 12.45. Later, 2.7 g of hexahydride ferric chloride ($FeCl_3.6H_2O$), which is equivalent to 0.1 M Fe, was added into the solution. As a result, the pH was reduced to 2.3. The solution was shaken for 4 hours at 200 rpm at room temperature and later, aged in an oven at 70º C for 48 h. This process includes the thermo-hydrolysis of Fe(III) ions (Villalba et al., 2010). The solution was shaken vigorously for 30 s every 4-6 h to ensure all LKD particles are in contact with the $FeCl_3$ solution. Later, the solution was centrifuged for 40 min at 4000 rpm, and the supernatant was removed. The iron-coated LKD was dried in the oven at 40°C overnight. The dried material was gently ground to form a uniform powder. The final product hereafter is referred to as the iron-coated lime kiln dust (LKDFe) and has an orange-tinted color.

7-3-3 Soil

An alkaline clay loam soil with high initial Ca, and P content was selected for this study as the worst-case scenario. The clay loam soil was collected from the plow layer (0-20 cm) of a cornfield situated near Pike River, Quebec, Canada (45°07′44″ N; 73°03′04″ W). This clay loam soil is derived from the underlying calcareous rocks, and it is classified as a Brown Podzolic soil (AAFC, 1948). The soil samples were air-dried and passed through a 2 mm opening sieve. This clay loam soil has 21, 39, and 40% sand, silt, and clay, respectively. The pH of this soil is 8.05. The total P in the soil is 985 mg $kg^{-1,}$ while the Ca is 26 902 mg kg^{-1} (Eslamian et al., unpublished). The Mehlich-3 extractable P and Ca for this soil which represents the amount available for plant uptake, are 109 and 5380 mg kg^{-1}, respectively.

7-3-4 Adsorption experiment

A batch adsorption experiment was designed to evaluate and compare the performance of the LKDFe on the phosphate adsorption of the clay loam soil. Phosphate solutions having concentrations of 0, 0.2, 0.4, 0.6, 0.8- and 1 mM P were prepared using monopotassium phosphate (KH_2PO_3) and 0.01 *M* K from KCl (potassium chloride) (Jiao et al., 2007). It is expected that at P concentrations less than 1 m*M*, adsorption is dominant while at higher concentrations precipitation may take over (Holford et al. 1974). The developed LKDFe product was mixed with the clay loam soil at the dose of 1% by soil weight (w/w). This dose was adopted from previous studies on the effect of different lime products on P adsorption and desorption in different soil textures (Eslamian et al., 2018; Eslamian et al., unpublished). Two grams of clay loam soil with and without the LKDFe amendment were added to 30 mL of the various phosphate solution in three replicates. The solutions were shaken for 48 hr at 200 rpm at room temperature and later centrifuged for 40 min at 4000 rpm. pH and phosphate were measured on the supernatant of the soil phosphate solution samples.

In order to compare the P adsorption capacity of the newly developed LKDFe with that of the original LKD, 2 g of soils amended either with LKDFe or LKD were added to 30 mL of varying phosphate concentration ranging from 0 - 1 mM P in three replicates. To ensure a fixed and comparable pH between the soil samples amended with LKDFe or LKD, the pH of all solutions was adjusted to 6.5 and buffered with a morpholino propane-sulfonic (MOPS) 1.0 M solution. MOPS an acid buffer with a molecular formula of $C_7H_{15}NO_4S$ and it is a non-chelating agent (Mao et al., 2012; Suresh Kumar et al., 2019). Experimental results have also confirmed that MOPS does not complex with or has any effect on the adsorption procedure and the phosphate concentration

(Eslamian et al., unpublished). A pH of 6.5 was selected as the optimum pH range for most plants is 5.5 – 7.0 (Lauchli and Grattan, 2012).

7-3-5 Analysis methods

pH was measured on the supernatant of the soil phosphate solution samples. The solutions were later filtered with a 0.45 µm nylon syringe filter prior to phosphate analysis with the Lachat instrument (QuikChem FIA+-8000 series). Lachat uses the colorimetry method for phosphate analysis (Murphy and Riley, 1962). Soluble calcium in the solutions was measured using an atomic adsorption spectroscopy (Varian SpectrAA 220 Fast Sequential) on the diluted samples.

Scanning electron microscopy (SEM) coupled with energy dispersive X-Ray spectroscopy (EDS) (Hitachi SU3500 model) was used to observe and quantify the iron loading on the surface of the lime kiln dust. Elemental mapping was performed on ten random sites of the LKDFe and LKD samples. Brunauer–Emmett–Teller (BET) surface area, pore diameter, and pore volume distribution were determined using Quantachrome autosorb automated gas sorption. Total Ca and total Fe in LKD, and LKDFe products were measured on nitric acid (HNO_3) digested samples using an atomic adsorption spectroscopy.

7-3-6 Adsorption isotherms

Adsorption isotherms can be employed to describe the specific relationship between the equilibrium P concentration in the solution, and the amount of P adsorbed on the surface of the adsorbent. Two common isotherms of Freundlich and Langmuir were used to analyze and compare the adsorption results. The Freundlich isotherm model assumes that the adsorption process takes place on a heterogeneous multi-layer surface (Chung et al., 2015; Lalley et al., 2016), where the amount of adsorbed solute per unit adsorbent continuously increases. The Freundlich model could be expressed as Equation 7-1 (Freundlich, 1926):

$$Q = K_F {C_e}^{1/n} \qquad \text{(Equation 7-1)}$$

Where, for our experiment, *Q* is the amount of *P* adsorbed per unit weight of soil (mg kg^{-1}), C_e is the P concentration in the solution at equilibrium. K_F is the Freundlich sorption coefficient, which is associated with adsorption capacity, and *n* indicates the intensity of sorption, which can vary with the heterogeneity of the material. The linear form of the Freundlich model (Equation 7-2) was used to fit the adsorption data and to find the constants:

$$\log Q = \log K_F + \frac{1}{n} \log C_e \qquad \text{(Equation 7-2)}$$

The Langmuir adsorption assumes the adsorption process to be limited to a mono-layer and all surface sites to be equivalent (Chung et al., 2015; Lalley et al., 2016). The Langmuir isotherm model (Langmuir, 1918) is described as Equation 7-3:

$$Q = Q_{max} \frac{K_L C_e}{1+K_L C_e} \qquad \text{(Equation 7-3)}$$

Where *Q* is the amount of P adsorbed per unit weight of soil, Q_{max} is the maximum adsorption capacity, C_e is the concentration of P in the solution at equilibrium, and K_L is the adsorption constant, which is related to the binding strength of P on soil surfaces. The adsorption data were fitted on the linear form of the Langmuir model (Equation 7-4) to obtain Langmuir adsorption parameters:

$$\frac{C_e}{Q} = \left(\frac{1}{Q_{max}}\right) C_e + \frac{1}{K_L Q_{max}} \qquad \text{(Equation 7-4)}$$

At low phosphate concentrations, as C_e approaches zero, the Langmuir isotherm can be rewritten as Equation (7-5) (Suresh-Kumar et al., 2017; Kelly Vargas and Qi, 2019):

$$Q = Q_{max} \, K_L \, C_e \qquad \text{(Equation 7-5)}$$

Where $Q_{max}.K_L$ being the slope of the curve, is defined as the adsorption affinity of the adsorbent at low concentrations (Suresh Kumar et al., 2017). This term is beneficial to compare the P adsorption affinity in soil solutions which are normally lower than 0.5 mg L^{-1} (Kelly Vargas and Qi, 2019) and P levels of smaller than 0.025 mg L^{-1} are recommended to prevent the eutrophication of surface water bodies.

The removal efficiency of the LKD and LKDFe in the presence of soil or alone in the P solution was calculated using Equation 7-6:

$$Removal\ Efficiency\ (\%) = \frac{(C_i - C_e)}{C_i} \times 100 \qquad \text{(Equation 7-6)}$$

Where C_i is the initial P concentration in the solution, and C_e is the final P concentration at equilibrium in mg L^{-1}.

7-3-7 Statistical analysis

For statistical analysis, analysis of variance (ANOVA) in SPSS (IBM, version 24) was used to evaluate the significance of the iron-coated lime kiln dust (LKDFe) on soil P adsorption capacity and to compare its performance to that of the original LKD in soil ($P<0.05$). The adsorption data were regressed to fit the linear forms of the adsorption isotherm models.

7-4 Results and Discussions

7-4-1 LKDFe properties

The properties of the LKDFe compared with the original LKD are summarized in Table 7-1. The pH of the LKD in a saturated solution at room temperature was measured at 12.45, whereas for LKDFe, it was 7.65. Therefore, through the iron-coating procedure, we were able to develop a modified LKD with a more neutral pH. This is due to the placement of considerable amounts of Fe ions on the surface of LKD and less Ca release in the solution per gram of material.

Table 7-1. Characteristics of the iron-coated lime kiln dust (LKDFe)

	pH	Ca %	Fe %	S_{BET}£ $m^2\ g^{-1}$	Pore Volume $cm^3\ g^{-1}$	Avg. Pore Dia. Å
Lime Kiln Dust (LKD)	12.45	43.1	0.53	1.168	0.0004	389.7
Iron coated lime kiln dust (LKDFe)	7.65	16.6	15.61	34.87	0.0144	177.1

£ Brunauer–Emmett–Teller (BET) surface area

The total Fe content of the LKDFe was increased from 0.53 to 15.61%. This is equivalent to 156.1 mg of Fe per gram of the product. While the LKD had 43.1% total Ca content; the LKDFe had a total Ca content of 16.6% by weight. The BET surface area of the modified LKD was measured as 34.87 $m^2\ g^{-1,}$ which is approximately 30 times more than that of the original LKD. A high calcium hydrated lime was measured to have a BET surface area of 11.35 $m^2\ g^{-1}$. Therefore, the LKDFe has a surface area of three times more than a high-quality lime. The BET surface area results correspond with the pore volume and pore size results. While the surface area of the modified LKD was increased, the pore volume increased about 30 times, and the average pore diameter was reduced to 177.1 Å. This means that the iron loading process increased the surface area of the lime kiln dust by increasing vacant sites and changing the pore size distribution (Wang et al., 2019). Figure 7-1 illustrates the pore volume distribution of LKD and LKDFe. A pore size of 20-500 Å is considered a mesopore, while a pore size of less than 20 Å is called micropore, and higher than 500 Å is a macropore (Zdravkov et al., 2007). While the majority of the pore volume in LKD had a pore size between 100 - 370 Å, in the LKDFe, the majority of the pore volume had a pore size of 10 – 100 Å. In Figure 7-1right, the pore volume distribution of both products is plotted on the same scale. This demonstrates that not only the pore size distribution of the LKDFe has changed, but also the pore volume has considerably increased by 30 times in the LKDFe product.

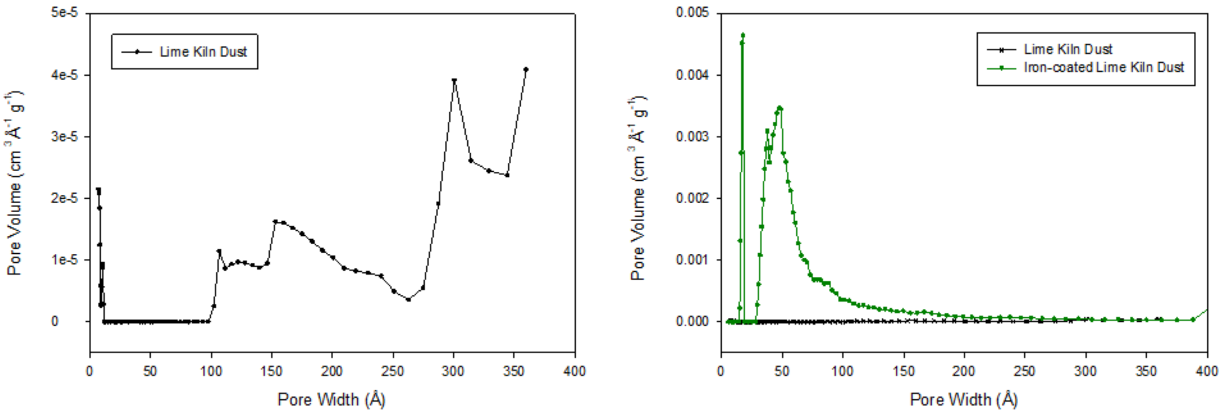

Figure 7-1: Pore size distribution of the original lime kiln dust (left) and comparison of pore sized distribution of lime kiln dust and iron-coated lime kiln dust at the same scale (right)

The placement of iron oxide crystals on the surface of the LKD has led to the creation of more micro and smaller size mesopores resulting in an overall larger pore volume in the LKDFe. A simultaneous increase in the surface area, pore volume as well as a decrease in the pore size of a product can result in increased adsorption capacity. Adsorbents with mesopores are ideal for phosphate adsorption in lower concentrations similar to that of soil solution and surface water bodies (Suresh Kumar et al., 2019; Suresh Kumar et al., 2017).

SEM surface morphology images of the LKDFe are illustrated in Figure 7-2. The EDS electron and elemental distribution of Ca and Fe for the same surface is mapped in Figure 7-3. For this selected surface area, the weight percentage of Ca and Fe using EDS was estimated as 12 and 18%, respectively. The average Ca and Fe content of 10 randomly selected LKDFe surfaces were measured at 16.2 ± 3.8% and 19.5 ± 1.7%, respectively, which is comparable with that of the chemically analyzed weight percentage of 16.6% and 15.6%, respectively. Based on the EDS elemental mapping, the surface morphology of points of interest (high Fe or Ca) are shown in smaller scales in Figure 7-2. The main image having a 50 μm scale is shown in the center (Figure 7-2d). While Figure 7-2c demonstrates a Ca-dominant area (38.8%), Figure 7-2a provides a smaller scale (5μm) view of part of Figure 7-2c being mostly covered by Fe. This resembles a cluster of rod-like particles of about 0.5 μm placed horizontally next to one another. Rod-like particles of 0.4-0.5 μm are reported to represent the formation of akageneite-like materials (Villalba et al., 2010). Akageneite is a form of iron oxides only formed in the presence of chloride or fluoride ions (Murad and Bishop, 2000). Figure 7-2f demonstrates an area of high Fe content shown at a smaller scale (5μm) in Figure 7-2g. This section presents larger crystals having other morphologies besides rod-like structure. The crystals in this section are around 2 μm, considerably bigger than the expected akageneite size (Villalba et al., 2010). This could be due to Ostwald Ripening phenomena where small crystals dissolve then re-crystallize over larger particles forming bigger crystals (Schwertmann and cornel 2000; Villalba et al., 2010). The initial non-homogenous surface of the LKD could have led to the deposition and formation of various crystals arrangements of the iron oxides on the LKDFe surface.

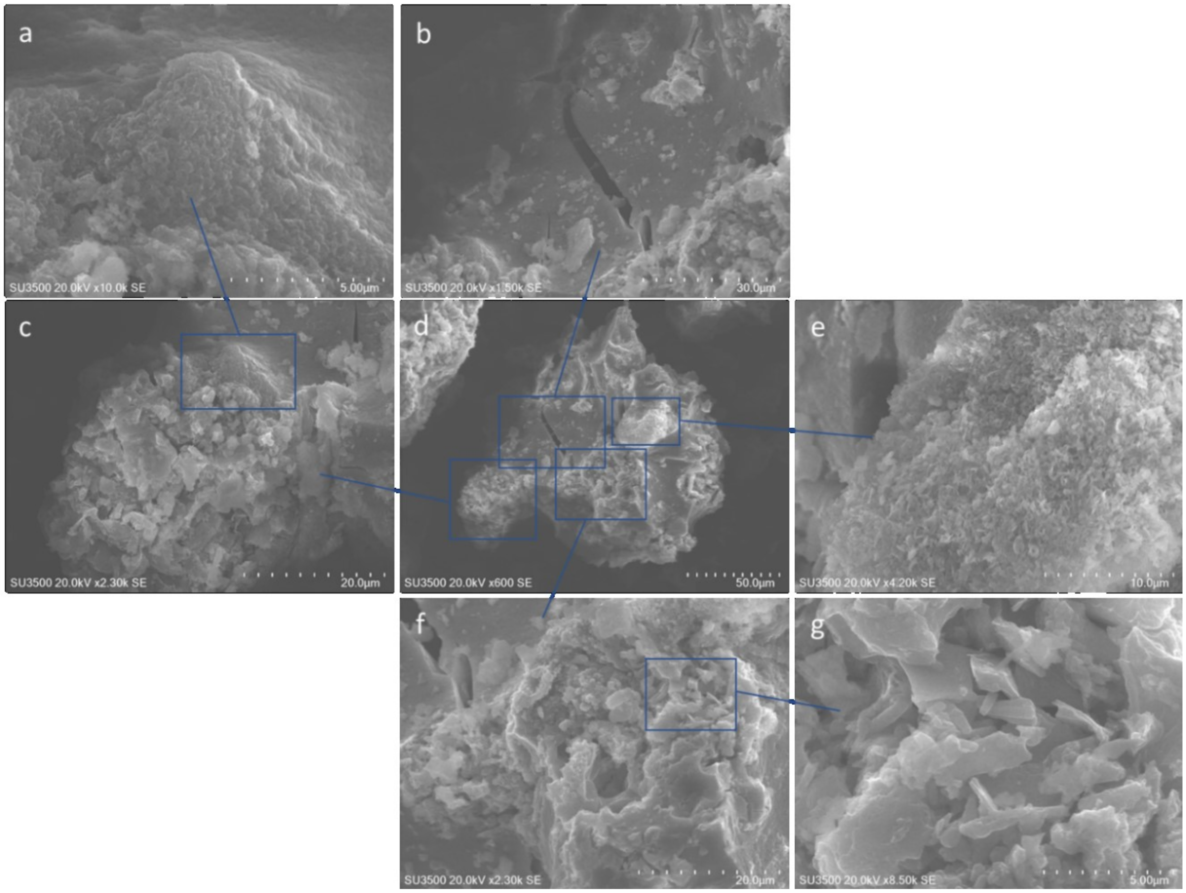

Figure 7-2: Surface morphology of the randomly selected surface area of the iron-coated lime kiln dust with different scales using scanning electron microscopy. The main image at 50µm scale is presented in the middle (d), while other images (a, b, c, e, f and g) represent points of interest (high Ca or Fe) on the main image at a smaller scale.

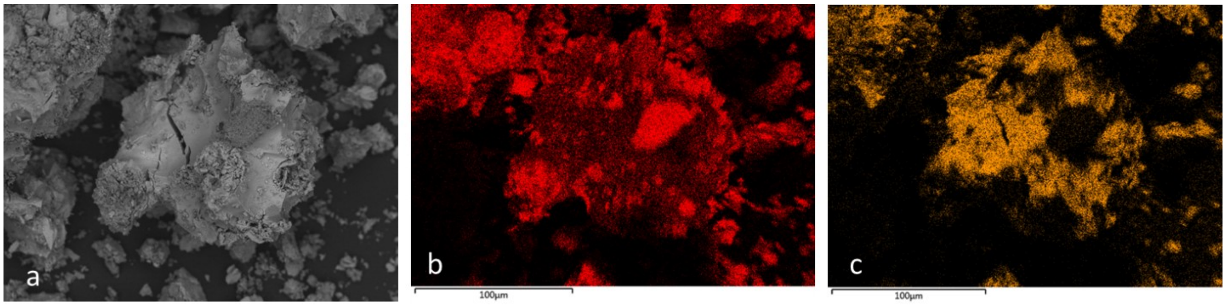

Figure 7-3: Scanning electron microscopy coupled with energy dispersive spectroscopy for a randomly selected surface area (same as Figure 7-2) of the iron-coated lime kiln dust product (100µm scale): a) electron image; b) elemental mapping of Ca; c) elemental mapping of Fe

The process of iron-coating the lime kiln dust yielded approximately 2 g of LKDFe for each replicate, which is an 80% product yield in terms of solids (2 g LKD+ 0.5 g Fe). While regarding Fe, a 59% yield was achieved. This means that out of the initial 0.56 g of Fe in the solution, 0.33g was coated on the LKD. It is reported that the thermo-hydrolysis process in the temperature range of 40-70°C results in the precipitation of around 30% of the total Fe in the solution (Schwertmann et al., 2000). Since the yield reached through the process of LKD iron-coating is higher, this could mean that the presence of LKD in suspension could have increased the Fe deposition yield (Villalba et al., 2010). Yields in the range of 57-87% were reported through iron-coating various clay minerals. The negative surface layers of the clays were suspected to help increase the hydrolysis of Fe (Villalba et al., 2010).

7-4-2 LKDFe adsorption

The batch adsorption results on the effect of the LKDFe on the P adsorption capacity of the studied clay loam soil demonstrated that amending the soil with 1% w/w LKDFe can increase the amount

P adsorbed up to 30%. Univariate general linear model statistics showed that the amount P adsorbed in the clay loam is significantly less than the amount P adsorbed on the clay loam amended with LKDFe ($p<0.0001$). The adsorption data fitted well on both Freundlich and Langmuir isotherm models with Freundlich having the best fit ($R^2=0.996$ vs. 0.964). The fitted Freundlich and Langmuir curves for both the clay loam and the clay loam amended with 1% LKDFe are illustrated in Figure 7-4. The adsorption isotherm parameters were calculated and are summarized in Table 7-2.

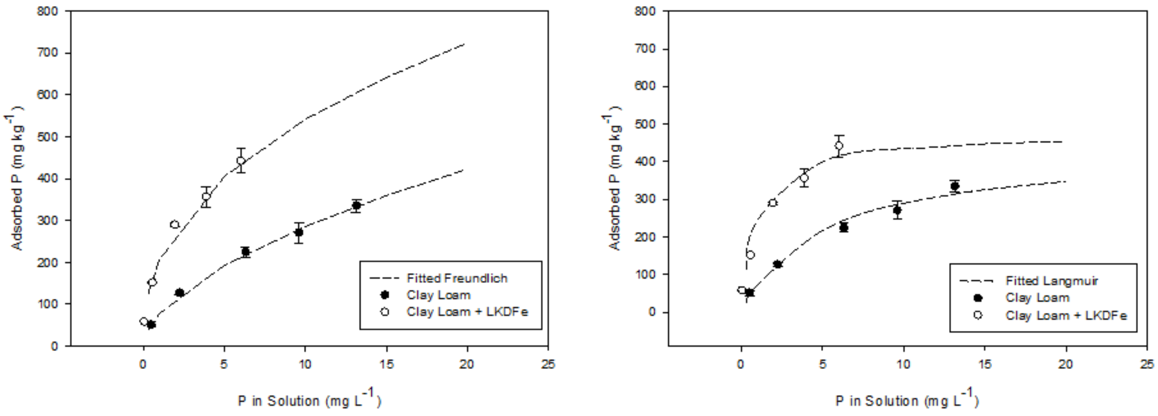

Figure 7-4: Phosphate adsorption data for control clay loam soil and clay loam amended with 1% Iron coated lime kiln dust (LKDFe) at pH of 7.65 fitted with Freundlich (left) and Langmuir (right) adsorption isotherm models. The data points are average of three replicates and error bars represent standard deviation

The Freundlich adsorption coefficient (K_F) was increased from 77.86 to 206.78, which is 2.65 times increase. The Freundlich sorption intensity (n) was increased from 1.77 to 2.36. The Langmuir adsorption coefficient (K_L), representing the sorption bonding strength, was considerably increased from 0.2 to 1.05. While the Langmuir maximum adsorption capacity (Q_{max}) was increased by only 10%, the adsorption affinity (AA) was increased from 88.5 to 500 L kg^{-1}.

Although the addition of LKDFe did not considerably increase the Q_{max} of the clay loam soil, the AA, on the other hand, was increased by 4.65 times. This would mean that based on the Langmuir adsorption isotherm where a monolayer sorption surface is assumed, the LKDFe performs best at lower P concentration ranges. In soil solutions where we deal with P concentrations in the range of 0-0.5 mg L^{-1}, AA could be a better P adsorption determining index for decision making. Furthermore, in lakes and rivers where the P water quality guideline is set at 0.025 mg L^{-1} to prevent eutrophication, AA could be a better indicator of the adsorbent's capability (Kelly Vargas and Qi, 2019).

Table 7-2: Freundlich and Langmuir adsorption isotherm parameters

	Freundlich			**Langmuir**			
	R^2	**n**	**K_F**	**R^2**	**k_L**	**Q_{max}** (mg kg^{-1})	**Adsorption Affinity** (L kg^{-1})
Clay Loam @ pH 7.65	0.999	1.77	77.86	0.960	0.20	434.78	88.5
Clay Loam + LKDFe @ pH 7.65	0.996	2.36	206.78	0.964	1.05	476.19	500.0
Clay Loam + LKD @ pH 6.5	0.954	1.88	100.56	0.991	0.33	416.67	137.0
Clay Loam + LKDFe @ pH 6.5	0.997	2.18	252.93	0.983	1.43	500.00	714.3

The addition of the LKDFe at the applied dose did not significantly change the pH of the clay loam soil. This is another benefit of the newly modified LKD. The LKDFe product can increase the P adsorption capacity of the soil without changing the soil pH. The soil can benefit from the advantages of Ca and Fe ions without the adverse changes of pH caused by Ca or Fe based products alone. The average Ca in the solution after adsorption was measured at 91.5 ± 4.6 mg L^{-1} for the clay loam alone and 113.9 ± 4.1 mg L^{-1} for the clay loam plus LKDFe solution. While the Ca release from the LKD and LKDFe alone was measured at 61.5 ± 8.4 and 36.1 ± 4.3 in the solution. The amount of soluble Fe in both solutions was measured as insignificant (<0.1 mg L^{-1}). Therefore, the LKDFe could be considered a stable product with insignificant Fe and less Ca release than the original LKD as well as having the neutral pH.

Phosphorus adsorption in soils includes a ligand exchange where phosphorus anions form covalent bonds with soil metal oxides by replacing the hydroxyl groups on the soil surface. The addition of the LKDFe will contribute to the presence of new metal oxides both in the form of Ca and Fe, therefore, offering an increased potential to form both iron and calcium phosphate complexes. The increased surface area and pore volume in the newly developed product can also lead to more vacant sites for phosphate adsorption on the adsorbent surface.

7-4-3 LKDFe and LKD comparison

To compare the performance of the modified LKD with that of the original in increasing the P adsorption capacity of the clay loam soil, a separate set of batch adsorption experiments at the fixed pH of 6.5 was conducted. A fixed pH was required to compare the adsorption results of the two products since the amendment of the soil at the studied dose with LKD would lead to an increase in soil solution pH up to 11.65 while the LKDFe results in no significant pH change ($p>0.05$). Univariate general linear model statistics showed that the amount P adsorbed in the clay loam amended with LKD is significantly different than the amount P adsorbed in the clay loam amended with LKDFe ($p<0.0001$). The results showed an average 20% increase in the amount P adsorbed by the LKDFe amended clay loam in comparison with the LKD amended soil at a pH of 6.5. The adsorption data fitted well on both Freundlich and Langmuir isotherm models (Table 7-2 and Figure 7-5). The Freundlich adsorption coefficient (K_L) for LKDFe was two times higher at 252.93 compared to 100.56 for LKD amended soil (Table 7-2). The LKDFe Langmuir adsorption coefficient was reported four times higher than that of the LKD, which could translate to a considerably higher P bonding strength in LKDFe amended the soil. Both maximum adsorption capacity and adsorption affinity were higher in the LKDFe amended soil at 500 mg kg^{-1} and 714.3 L kg^{-1}, respectively, while the Q_{max} was increased by 20%, AA was increased by 4.2 times.

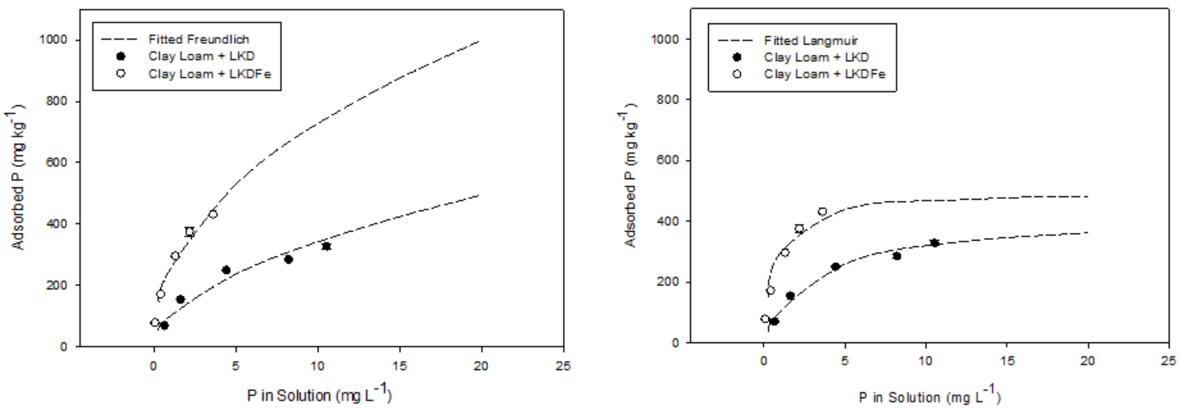

Figure 7-5: Phosphate adsorption data for clay loam amended with 1% unmodified lime kiln dust (LKD) and clay loam amended with 1% Iron coated lime kiln dust (LKDFe) at pH of 6.5 fitted with Freundlich (left) and Langmuir (right) adsorption isotherm models. The data points are the average of three replicates error bars represent standard deviation.

Comparing the adsorption results of the clay loam amended with LKDFe at its own pH (7.65) and the fixed pH (6.5) demonstrates that P adsorption capacity is higher at the pH of 6.5 with adsorption affinity having the highest increase (compare 500 L kg^{-1} at 7.65 pH to 714.3 L kg^{-1} at 6.5 pH). Adsorption is pH dependent by changing the availability of metals in soil. At lower soil pH concentrations, Fe is more available, potentially leading to a higher P adsorption.

7-4-4 Phosphorus removal efficiency

The removal efficiency of the soils amended with either LKD or LKDFe at the pH of 6.5 for each initial P concentration were compared and illustrated in Figure 7-6 (left image). The results indicated that, for all P concentrations, the soil amended with LKDFe showed a significantly higher removal efficiency on average by 20% ($p<0.0001$). Also, the removal efficiency of the LKD and LKDFe alone (without soil) in the P solution was measured and it is graphed in Figure 7-6 (right image). In this case, the adsorbent dose in the solution was 0.667 g $L^{-1,}$ and pH was fixed at 6.5. The LKDFe exhibited a considerably higher removal efficiency compared to that of LKD on average by 2.5 times. While the removal efficiency of the LKD was recorded in the range of 16 - 35%, for LKDFe, this range was 62 - 99%. Therefore, it can be concluded that this new product also has the potential to be used as an efficient and low-cost adsorbent for the removal of phosphate from water solutions.

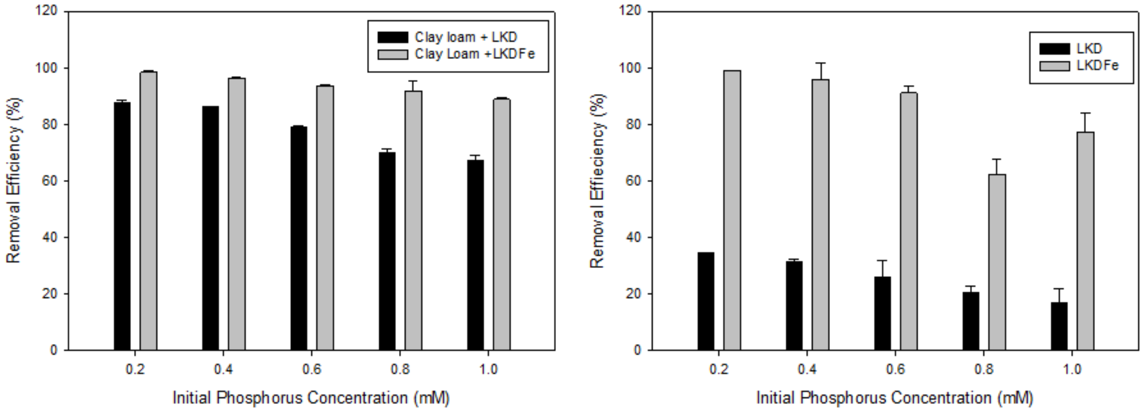

Figure 7-6: Removal efficiency of the iron-coated lime kiln dust (LKDFe) in comparison with the original lime kiln dust (LKD) mixed with soil (left image) and only in water solution (right image)

7-5 Conclusion

The lime kiln dust (LKD) was successfully iron-coated to develop a novel product, iron-coated lime kiln dust (LKDFe), with an increased adsorption capacity for P in the soil with an additional feature of neutral pH and low-cost. Comparing to LKD, LKDFe had an increased surface area, pore volume, and smaller pore size based on the surface area analysis. The image analysis, as well as chemical analysis of LKDFe, confirmed the presence of iron loads on the mineral. The batch adsorption results showed that the addition of the LKDFe as a soil amendment at the studied dose significantly increased the P adsorption capacity of the soil with a significantly higher efficiency than that of the LKD.

It can be concluded that the LKDFe is a promising soil amendment to increase P adsorption in soil. The simple iron-coating procedure proposed in this study could be optimized and adopted to develop high-efficiency P adsorbing soil amendments to immobilize P in soil and, in turn, to reduce P desorption into surface water bodies to mitigate eutrophication of lake and rivers. Further studies are suggested to optimize the iron-coating procedure in order to achieve a higher material yield and to evaluate the potential to reuse the non-coated iron remaining in the solution as a feed for subsequent coating procedures. It is recommended to evaluate the potential of the LKDFe in adsorbing other chemicals as well as field-scale application of the product.

7-6 Acknowledgement

This study was conducted at the Macdonald Campus of McGill University in collaboration with Graymont to whom we would like to express our sincere thanks. This study was equally funded by NSERC-CRD and Graymont. We would also like to express our special gratitude to Ms. Hélène

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CHAPTER 8: SUMMARY AND CONCLUSION

The ultimate goal of this research was to develop a new lime-based product to offer a phosphorus immobilizing soil amendment that could help retain more phosphorus in soil, and thereby, mitigate rapid eutrophication of lakes and rivers as a result of non-point source P losses from agricultural fields.

This study first focused on the assessment of lime-based products as soil amendments to reduce phosphorus concentration in the leachate from different agricultural soils. Different soil textures, especially in the neutral and alkaline pH ranges, were selected for this study to evaluate the worst-case scenario. Laboratory, intact soil columns, and field lysimeter studies were conducted and compared to evaluate the effect of lime application on different forms of phosphorus with a focus on soluble reactive phosphorus as it is the most readily available form of phosphorus for both plant uptake and rapid algal growth. Later, laboratory adsorption and desorption studies were conducted to find out if sorption is the main mechanism controlling phosphorus retention in soil as influenced by lime. In the end, a new iron-coated lime kiln dust was characterized and developed to improve soil phosphorus adsorption capacity. A summary of results and conclusions is as follows:

8-1 Lime optimum application dose

A study with repacked clay loam soil columns was conducted to find the minimum effective lime application dose for four lime products to reduce soluble reactive phosphorus concentrations in the leachate to below 0.03 mg L^{-1}.

- All four studied lime-based products (high calcium hydrated lime, dolomite hydrated lime, lime kiln dust #1 and #2) were able to reduce soluble reactive phosphorus concentration in the leachate below 0.03 mg L^{-1} at the minimum effective dose of 1, 1.25, 2, and 1% by air-dried soil mass, respectively.

- High calcium hydrated lime and lime kiln dust #2 having lower effective application doses at 1% (w/w) were selected for further studies.
- An indoor runoff study with a rainfall simulator showed that high calcium hydrated lime and lime kiln dust #2 applied and mixed on the top surface can reduce soluble phosphorus concentrations in the runoff from the clay loam soil. However, total phosphorus concentrations in the runoff were increased.

8-2 Effect of soil texture

In order to evaluate the efficiency of lime in reducing phosphorus leaching from different soil textures (sandy loam, loam, and clay loam), intact soil column studies were carried out and compared to that of repacked soil columns. Intact soil columns received natural rainfall from June to October, while the laboratory columns received artificial rainwater.

- The effect of lime on phosphorus mobility varied by soil type.
- Lime application at the top 5 cm of intact soil columns effectively reduced dissolved reactive phosphorus release from sandy loam and loam soil columns; however, no significant difference was observed in the limed clay loam soil column leachates in terms of dissolved reactive phosphorus.
- In laboratory repacked and indoor intact columns, lime did not affect the total dissolved phosphorus in the leachate from the sandy loam column but significantly reduced total

dissolved phosphorus concentrations in the leachate of finer-textured soils (loam and clay loam).

- The laboratory repacked columns and intact soil columns (indoor and outdoor) showed similar results regarding soluble reactive phosphorus concentrations.
- The extent of lime-induced P retention in soil was variable between intact and repacked columns demonstrating the influence of soil structure on lime and P interactions in the soil.

8-3 Field lysimeter study on soybean growth

To study the effect of lime on phosphorus release at larger scale under natural conditions and with the presence of soybean, a lysimeter study with sandy soil was carried out during a full growing season in 2018. Leachate samples were collected at two sampling depths. The following main conclusions were drawn:

- Lime application to the top 5 cm soil reduced soluble reactive phosphorus by 50% in the leachate from the sandy soil lysimeters.
- Soluble reactive phosphorus was lower in the leachate collected from the 30 cm depth compared to the 7 cm depth
- Total dissolved phosphorus was not significantly affected by lime application in the leachate
- The soybean did not significantly affect the soluble reactive phosphorus or total dissolved phosphorus concentration in the soil water. However, it did significantly decrease the Mehlich-3 extractable phosphorus in soil compared to the lysimeters with no plant.

- Application of lime at 1% by soil weight to the topsoil of sandy lysimeters with a neutral pH not only did not reduce soybean nutrient availability, but it also increased soybean yield by 10%.
- Fall application of lime is preferred to spring application as it also reduced total dissolved phosphorus in the leachate and less calcium release was observed.

8-4 Adsorption and desorption studies

Sorption studies were performed to evaluate and compare hydrated lime and lime kiln dust as soil amendments to increase soil phosphorus adsorption capacity in four different soil textures with neutral to alkaline pH. The following outcomes were concluded:

- At lower phosphate concentrations, adsorption is the dominant mechanism involved in the lime-induced increase in phosphorus retention in the studied soils
- Soil phosphorus adsorption in limed soil can be best described by the Freundlich isotherm, where sorption happens on a heterogenous or multilayer surface and it can continuously increase.
- Lime-induced increase in the soil phosphorus adsorption capacity is dependent on soil type at a fixed pH
- Both hydrated lime and lime kiln dust significantly increased the Freundlich adsorption coefficient by 3.2, 2.4, 2.0 and 1.6 times in loam, sandy, sandy loam, and clay loam soils, respectively.

- Lime kiln dust preforms similarly to high calcium hydrated lime, especially at lower phosphorus concentrations, making it a promising cost-effective phosphorus-immobilizing amendment.
- Lime amendment reduced the cumulative phosphorus desorption after ten days for all soils by more than ten times.
- The average desorbed phosphorus in mg kg^{-1} for the ten desorption events negatively correlated with the Langmuir adsorption affinity parameter (R^2=0.929).

8-5 New iron-coated lime kiln dust development

At the final stage of the research, given the promising potential of lime products in retaining phosphorus in the soil, lime kiln dust as a cost-effective material was selected as the base for the novel material development. The study intended to modify the lime kiln dust in a manner that would improve its efficiency. The following outcomes were found:

- A novel iron-coated lime kiln dust was developed through thermo-hydrolysis of hexahydride iron chloride in a lime kiln dust suspension solution.
- The new iron-coated lime kiln dust had a surface area of 34.87 $m^2 g^{-1}$ (30 times more than the original lime kiln dust at 1.168 $m^2 g^{-1}$) and an increased pore volume by 36 times.
- The new product had a neutral pH of 7.65, making it easily applicable to any soil regardless of the initial soil pH.
- Both chemical and image analysis confirmed the presence of iron load (16% of total mass) on the lime kiln dust surface.

- Iron coating the lime kiln dust led to the creation of more micro and smaller size mesopores, which is favorable in the phosphorus adsorption, especially in the lower phosphorus concentration ranges.
- Clay loam soil amended with 1% (w/w) iron-coated lime kiln dust had an increased soil phosphorus adsorption capacity by 2.65 times while the Langmuir adsorption coefficient was increased by 5.25 times compared to the non-amended soil.
- Langmuir maximum adsorption capacity was increased by 10% in the soil amended with the iron-coated lime kiln dust, while the adsorption affinity was increased by 4.65 times. Therefore, the product performs better at lower phosphorus concentrations similar to the soil solution ranges.
- The modified lime kiln dust showed an improved performance in increasing soil phosphorus adsorption capacity in comparison with the unmodified lime kiln dust at a fixed pH.
- The phosphorus removal efficiency of the original lime kiln dust was recorded in the range of 16 - 35%, while for the iron-coated lime kiln dust, this range was 62 - 99%.
- Iron-coated lime kiln dust can be a cost-effective product in terms of increasing soil phosphorus adsorption capacity as well as removing phosphorus from solutions as an adsorbent.

In the end, it can be concluded the novel iron-coated lime kiln dust can be a promising soil amendment to increase soil phosphorus adsorption capacity that would lead to less soluble phosphorus release into downstream water bodies and mitigate rapid eutrophication.

CHAPTER 9: CONTRIBUTIONS TO KNOWLEDGE AND RECOMMENDATIONS

9-1 Contributions to knowledge

This research has resulted in the following contributions to knowledge:

- ✓ This study evaluated both the high-quality lime products and a lime by-product (lime kiln dust) as soil phosphorus immobilizing amendments in several neutral and alkaline soils, which led to valuable insights in this area of knowledge where limited studies are available.
- ✓ Minimum effective lime application rate of 1% by air-dried soil mass to the top 5 cm of soil can reduce soluble reactive phosphorus loss from the studied soils without having negative effects for crop growth.
- ✓ The extent and form of phosphorus retention in limed soils varies by soil type.
- ✓ Lime products can reduce soluble reactive phosphorus release from the studied neutral and alkaline soils by increasing soil phosphorus adsorption capacity.
- ✓ Adsorption is the main mechanism responsible for retaining phosphorus in lime amended soils in the neutral and alkaline pH ranges.
- ✓ A novel iron-coated lime kiln dust was developed, having a neutral pH and an increased adsorption capacity as a result of increased pore volume and surface area.
- ✓ The novel iron-coated lime kiln dust offers a promising cost-effective soil phosphorus immobilizing amendment that can be applied to any soil regardless of the soil pH and can increase soil phosphorus adsorption capacity by up to 50%. The application of this new product can help mitigate the rapid eutrophication of our precious surface bodies.

9-2 Recommendations for future work

Based on the current research and the outcomes, the following recommendations are made for future work to further contribute to knowledge in this field of research:

- To study the effect of the lime kiln dust as well as the iron-coated lime kiln dust on phosphorus retention in several other soil types with different properties.
- Study the effect of soil properties such as initial soil phosphorus content, soil organic matter, and cation concentrations on the lime-induced phosphorus retention in soils.
- Field-scale application of the iron-coated lime kiln dust to evaluate its effectiveness on phosphorus retention under natural weather conditions.
- A multi-year study of the lime products at a field scale to understand the long-term effect of lime on phosphorus leaching, crop yield, and other soil properties.
- Industry-level optimization of the iron-coating procedure to minimize the use of hexahydride iron chloride and to reuse the solution of this product in several coating cycles.
- Study the potential of the iron-coated lime kiln dust in removing phosphorus from water at the lake scale.
- Testing the iron coating procedure for other low-cost lime by-products

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