Sorption and Desorption of Phosphorus as

Influenced by Corn Stalk Residue, pH, and Ionic Strength in a Gleysol From Quebec, Canada

by

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Abstract

The Pike River watershed has a history of phosphorus (P) pollution due to surface and subsurface leaching, and erosion of agricultural soil rich in P. It is therefore important to consider factors that may change the dynamics of P sorption and desorption behaviours and potentially increase the P concentration in the soil solution. This thesis investigates the effect of corn stalk residue presence and application rate on P sorption and desorption. This thesis also investigates the effect of varying solution pH and ionic strength on P release. Batch experiments were used to investigate P sorption followed by experiments to test the reversibility of the sorption process under different corn stalk residue applications (0.3,5.3,10.3,15.3, and 20.3%) and at different P concentrations (0, 12.9, 27.7, 42.2, 57.0, and 71.8 mg L⁻¹). The quantity of P sorbed to soil was found to decrease significantly as residue application rates increased (p<0.0001). Phosphorus remaining in the soil after desorption decreased significantly as application of residues increased (p<0.0001). Varying the P concentration under a constant dosage of residue (5.3%) showed that the concentration of P sorbed increased with increases in P application; however sorption efficiency decreased with increasing P application. Sorption in the presence of residues was significantly lower (p<0.0001) than sorption in the absence of residues for P treatments higher than 42.2 mg L⁻¹. Percent sorbed P remaining after desorption was similar in the presence (85-91%) and absence (86-91%) of the 5.3% corn stalk residue treatment. A second study was performed to investigate the effect of varying ionic strength and pH on P release into solution and to identify which factor had a greater effect on P release. It was found that at low ionic strengths the pH effects on P release were more pronounced whereas at high ionic strengths the P concentrations were not significantly different regardless of pH level. Since residue incorporation increased the availability of P in this soil, then due to the P pollution history of the area it is suggested that a large scale study be conducted taking into account a temporal component

(including microbial interaction), depth, and a leaching component. A study of such scale would allow for a more conclusive quantification of P loss associated with the incorporation of different residue applications. It is also recommended to evaluate P release under varying pH and ionic strengths at a larger scale. Results from this study can be used to further inform soil chemistry models as well as advise for or against the use of soil amendments that induce long term changes to soil pH and solution ionic strength with respect to the overall effect on P loss from this Gleysol.

Résumé

Le basin versant de la Rivière aux Brochets présente un historique de pollution par le phosphore (P) liée à son lessivage en surface et par voie souterraine, ainsi que suite à l'érosion des sols agricoles. Il est donc important de prendre en considération les facteurs pouvant changer la dynamique de sorption et désorption du phosphore au sol pouvant contribuer à une augmentation du P dans la solution du sol. Les présentes recherches étudièrent les effets de l'amendement (ou non-amendement) d'un sol avec différentes quantités de résidus de tige de mais sur la sorption et désorption du P. Également, l'effet de modifier le pH et la force ionique de la solution du sol sur la libération du phosphore fut évalué. Des essais par agitation servant à évaluer la sorption du P, suivis par des expériences visant à évaluer la réversibilité du processus de sorption, furent entrepris en absence (0%) et présence de différentes fractions massiques de résidus de tige de mais (0.3, 5.3, 10.3, 15.3, et 20.3% à sec) combinés avec différentes concentrations de P (0, 12.9, 27.7, 42.2, 57.0, et 71.8 mg L⁻¹). En un premier volet la quantité de P sorbée au sol, et en second volet le P demeurant dans le sol après désorption, diminuèrent significativement (p<0.0001) avec une augmentation du taux d'application de résidus. L'application de P à des taux croissants sous un niveau de résidus constant (5.3%) augmenta la quantité de P sorbée, mais diminua l'efficacité de la sorption. Pour les apports de P de plus de 42.2 mg L⁻¹, la sorption du P en présence de résidus fut significativement inférieure à celle en absence de résidus. Le pourcentage de P sorbé demeurant après la désorption fut semblable en présence (5.3% résidus - 85-91%) et absence (0% résidus - 86-91%) de résidus. Une seconde étude visa à établir l'effet prédominant sur la libération de P vers la solution du sol entre les variations en pH et la force ionique de la solution du sol. À une force ionique faible, les effets du pH sur la libération du P s'avérèrent plus prononcés qu'à une force ionique élevée, lorsque le P libéré ne montra aucune différence significative entre différents

pH. Comme d'incorporer les résidus dans le sol augmenta la disponibilité du P et donné l'historique régionale de pollution par le P, il est à suggérer qu'une étude à grande échelle soit entreprise prenant en compte un aspect temporel (incluant les interactions microbiennes), la profondeur, et le lessivage. Une étude à une telle échelle permettrait une quantification plus concluante des pertes en P advenant de l'incorporation des divers résidus. Il serait à recommander d'évaluer si le P libéré sous divers pH et forces ioniques demeurent valables à une plus grande échelle. Les résultats de la présente étude peuvent servir à éclairer davantage les modèles de chimie des sols, et aider à se prononcer pour ou contre l'utilisation d'amendements au sol causant des changements à long terme du pH ou de la force ionique du sol, quant à leur effet global sur les pertes en P d'un gleysol.

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Preface and Contribution of Authors

This thesis contains a title page, abstract in both English and French, an acknowledgements section, a table of contents, list of tables, figures, and abbreviations, major contents, and references. The major contents include 5 chapters written and prepared by the candidate (with all contributors and any assistance being acknowledged in the acknowledgements section). The major contents include: Chapter 1: the introduction; Chapter 2: the general review of literature, Chapter 3: Sorption and desorption of phosphorus in the presence of corn stalk residue on a Gleysol from Quebec, Canada, Chapter 4: Investigating the effect of varying solution pH and ionic strength on phosphorus release from a Gleysol, and Chapter 5 a summary and conclusions section. There is a connecting paragraph before Chapters 3 and 4.

Chapter 3 is being prepared for submission to the *Journal of Environmental Quality*, and is coauthored by my supervisor Dr. Zhiming Qi, and Dr. Eman M. ElSayed, and Dr. Shiv O. Prasher.

Dr. Zhiming Qi aided in the editing and shaping of Chapter 4.

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List of Abbreviations

| cm | Centimeter |
|------|--------------------------|
| cmol | Centimole |
| g | Gram |
| mg | Milligram |
| ml | Milliliter |
| Al | Aluminium |
| °C | Degree Celsius |
| Ca | Calcium |
| DOC | Dissolved organic carbon |
| DOM | Dissolved organic matter |
| Fe | Iron |
| L | liter |
| Р | Phosphorus |
| PP | Particulate phosphorus |
| | |
| TOC | Total organic carbon |

Chapter 1: Introduction

Eutrophication of waters has become one of the most pressing issues of our time. Identified as the limiting nutrient for the growth of cyanobacteria and phytoplankton in most aquatic systems, phosphorus (P) has been linked to the presence of massive algal blooms, eutrophication and the unfortunate consequences that follow (Schindler, 1974). The major pathways leading P into surface and subsurface waters from agricultural fields have been identified as: the erosion of soils by runoff, the presence of preferential flow pathways leading to subsurface drainage, the inefficient design of artificial drainage, and prevailing soil management methods (King et al., 2015). Sims et al. (1998) suggested that high Р loads subsurface in drainage may occur when agricultural soils are high in P, when soils have a low sorption capacity for P, or when fields are artificially drained. Risk assessments for P loss must consider both potential sources of P and transport mechanisms. When considering the source of P, understanding the mobility of P between soil solid phase and soil solution is paramount to the understanding of losses of dissolved P (Börling et al., 2004).

The spreading of crop residues on the soil surface followed by their incorporation into the soil is a conservation practice designed to protect soils from erosion and improve their fertility (King et al., 2015). Crop residues (whether fresh or decomposed) release dissolved organic carbon (DOC), as well as other soluble nutrients, into the soil solution. Studies have found that the presence of DOC reduces the sorption of inorganic P to soils (Guppy et al., 2005; Hunt et al., 2007; Kafkafi et al., 1988; Oburger et al., 2011; Ohno and Carnell, 1996: Ohno and Erich, 1997; Wang et al., 2016).

The agricultural field, from which soil samples for this study were collected, is situated within the Pike River watershed, which feeds into Lake Champlain's the Missisquoi Bay. The bay's P loading capacity of 97.2 Mg P yr⁻¹ and has been consistently exceeded since 2001 (Gombault et al., 2015). Poor water quality due to nutrient enrichment has plagued both the Pike River watershed and the Missisquoi Bay for many years (Eastman et al., 2010; Gollamundi et al., 2005, 2007; Gombault et al., 2015; Simard, 2005). The study area has had a history of high P levels in surface and subsurface drainage. This P loss has been attributed to a long and consistent history of fertilizers and organic manure application to meet crops' nitrogen requirements (Boluwade and Madramootoo, 2013; Eastman et al., 2010; Jamieson, 2001). The soil used for this study contains levels of P that exceed critical thresholds for soils of this type (Beauchemin et al., 2003; Pellerin et al., 2006). Upon a recent visit to the site we observed that corn residues were incorporated into the soil. Due to the sensitive nature of the P status of the soil and the history of P pollution in the area we questioned what the impact of corn residue incorporation would be on the sorption behaviour of P in this Gleysol.

Soil solution pH and ionic strength may fluctuate seasonally due to interactions with plant roots, microbial activity, leaching, chemical weathering, fixation and defixation (Wiklander and Andersson, 1974). Anthropogenically induced fluctuations can be achieved through the addition of soil amendments such as lime and fertilizer, which can lead to soil solution pH and salinity conditions that may increase the risk of leaching (Wiklander and Andersson, 1974). Changes to soil solution pH and ionic strength have been shown to result in shifts in a soils ability to retain P (Barrow et al., 1980; Barrow, 1984); however, not all soils respond in the same way to these factors (Barrow et al., 1980). In the present study, no specific amendment was considered, but the effect of changing the soil solution's pH and ionic strength on the desorption of P from the soil was studied at a laboratory scale to gain understanding on their influence on the desorption of P in the field.

Given the importance of studying factors which potentially contribute to heightening P mobility from soil to solution, the effect of corn stalk residue addition, and changes to soil solution pH and ionic strength on P sorption and desorption behaviour were investigated. Following sorption experiments, desorption experiments were conducted to test the reversibility of the sorption process. The level of desorption was expressed as a fraction of the P remaining in the soil after desorption. In a second study, P release as a result of extraction by salt solutions of different concentrations and at different pH values was measured. It should be noted that in the second study P was not added to the soil and so the term 'release' served to describe the movement of P from soil to solution, rather than P desorption which describes the release of a predetermined amount of sorbed P.

Study Objectives:

- Investigate the effect of different corn stalk residue application rates (0.3,5.3,10.3,15.3, and 20.3% [percent residue: soil by wight]) on the sorption of P to the soil followed by a desorption test to evaluate the reversibility of P sorption.
- Investigate the effect of different P applications (0, 12.9, 27.7, 42.2, 57.0, and 71.8 mg L⁻¹) on the sorption of P to the soil followed by a desorption test, in the presence and absence of a constant residue application.
- Investigate the effect of changing solution pH and ionic strength on P release from the soil into the solution.

This research addressed the following questions:

- What is the effect of varying residue application rates (0.3,5.3,10.3,15.3, and 20.3%) on P sorption and desorption?
- What is the effect of residue presence and varying P concentrations (0, 12.9, 27.7, 42.2, 57.0, and 71.8 mg L⁻¹) on P sorption and desorption?
- Does varying solution pH and ionic strength result in higher or lower P release in solution?

Chapter 2: General Review of Literature

2.0 Background

Situated near the town of Bedford, Québec, the study area had a long history of intensive agricultural activity (Boluwade and Madramootoo, 2013; Gollamundi et al., 2007). Drainage from agricultural fields in this area feed into the 629 km² Pike River watershed, which spans the Québec-Vermont border and empties into Lake Champlain's Missisquoi Bay (Gollamundi et al., 2007). The bay has suffered from eutrophication due to high loads of nitrogen and P for close to 20 years. High nutrient loadings, especially in the case of P, have been associated with the increased proliferation of cyanobacterial populations in the Missisquoi Bay, which threaten both the health and economy of lakeshore communities (Gombault et al., 2015).

Between 70% and 80% of the 200 Mg P yr⁻¹ of P entering the bay annually can be attributed to non-point source pollution from agricultural activities within the feeder watersheds. This loading rate exceeds the bay's P loading capacity of 97.2 Mg P yr⁻¹(Gombault et al., 2015). Between 2000 and 2003, the Pike River watershed alone contributed roughly 44 Mg P yr⁻¹ to the Missisquoi Bay (Deslandes et al., 2007). Recent studies in the Pike River watershed have found that the majority of the P losses from crop production sites were in the form of Particulate P (PP) bound to sediments, and arose predominantly from high sediment losses from sites with clayey soils (Eastmann et al., 2010; Gollamundi et al., 2007). The high PP losses were also attributed to loss through preferential flow (Eastmann et al., 2010).

During a visit to the site in October 2015, corn residues were observed to have been left after harvest and subsequently incorporated into the soil with the fall tillage. Using residues as a soil coverage followed by their full or partial incorporation into the soil is an established practice that has lead to reductions in nutrient loss and sediment losses through erosion (Seta et al., 1993). However, the potential impact of the corn residue application and presence in the soil solution on the mobility of applied P between soil and solution is not known.

Phosphorus Cycle and Phosphorus Sorption:

Phosphorus occurrence in soils originates from the weathering of the mineral apatite $(3[Ca_3(PO_4)2]\times CaX_2)$, where X can be F⁻, Cl⁺, OH⁻, or CO₃²⁻. As apatite is weathered and during subsequent soil development P is gradually transformed into inorganic and organic forms through precipitation as secondary minerals, plant uptake, or microbial uptake. Under acidic conditions, the secondary minerals that form are predominantly iron (Fe) and Aluminium (Al) phosphates, whereas under neutral to alkaline conditions, calcium(Ca) phosphate minerals predominate (Havlin et al., 2005). Inorganic P adsorption mainly occurs on soil particles including: clay minerals, calcium carbonate(CaCO₃) in calcareous soils, and Al and Fe oxides and hydroxides in acidic soils. This labile inorganic P can also desorb back into soil solution. Soil microorganisms digest plant material and other organic materials over time to form organic P compounds (immobilization) which can then be mineralized as a result of microbial activity and released as inorganic P into the soil solution; immobilization and mineralization occur in tandem (Dodd and Sharpley, 2015; Havlin et al., 2005).

The largest fraction of soil P occurs in a non-labile form as primary minerals, secondary minerals, stabilized soil organic P, and occluded P (P sorbed on the surfaces of Al or Fe minerals that have been encapsulated and rendered less available). These forms of P become labile (available for reaction) through dissolution and mineralization. Phosphorus that is sorbed onto clay minerals, surfaces of oxides, hydroxides, and a portion of the organic P pool contain a labile P portion; however, this portion is smaller than the non-labile portion. Finally, the solution P pool represents the very small portion of P existing in soluble forms (e.g., $H_2PO_4^-$ or HPO_4^{2-}). The P cycle is summarized in Figure 2.1.



Figure 2. 1 Phosphorus cycle in an agricultural soil (adapted from Havlin et al., 2005).

2.1 Phosphorus Sorption and Release

Adsorption/sorption is one of the most important processes governing the transport of nutrients and contaminants in soils. Adsorption refers to the accumulation of a substance at the interface between the solid surface and the solution in contact with the surface (Stumm, 1992). Adsorption also includes the removal of solute from solution and its attachment to the solid surface (Sparks, 2003). Adsorption does not include surface precipitation, though both mechanisms are involved with respect to interactions between solution P and the soil surface. Accordingly, when the mechanism of retention onto the soil surface is not known the phenomenon is referred to as sorption and will be referred to as such throughout the thesis with the exception of this section.

Interactions between P and the surface occur through functional groups on the soil surface which may be present through oxides, hydroxides, and the edges of clay minerals (Sparks, 2003). Adsorption of P occurs mainly through inner sphere complexes. These complexes form as a result of adsorption taking place at specific coordination sites on the oxides or hydroxides where no water molecules are present between the phosphate ion and the site. Adsorption onto the soil surface may occur through ligand exchange on the surfaces of variably charged materials (such as Al and Fe oxides and hydroxides) via the exchange of an OH⁻ from the surface for a phosphate ion, which then results in the formation of a covalent bond between the metal and the phosphate.

Phosphorus retention in acidic soils occurs through the precipitation of Al and Fe phosphates onto the surfaces of Al and Fe oxides and hydroxides, as well as through adsorption via ligand exchange. Phosphate can also be adsorbed to the surfaces of CaCO₃ in calcareous soils, or may react with the Ca and precipitate as calcium phosphate minerals on the surface of CaCO₃.

Sorption can be described using a sorption isotherm which depicts sorption/desorption as a function of equilibrium concentration in solution. Sorption isotherms are created by equilibration of the soil with a solution containing a known amount of P (batch process). After equilibration, the soil and solution are separated by centrifugation and filtration and the P in solution is measured. The difference between the initial P added and the final P remaining in the equilibrium solution is assumed to be the quantity of P sorbed or desorbed by the soil. As isotherms do not act as proof of specific sorption mechanisms (i.e., a sorption isotherm cannot confirm if precipitation or adsorption has occurred), molecular investigations must be used to confirm the mechanisms involved (Sparks, 2003).

As illustrated in Figure 2.2, there are four general categories of sorption isotherms: S-curve, L-curve, H-curve, and C-curve (Sparks 2003; Sposito 2008). The S-curve begins with an

increasing slope as the equilibrium concentration of P in the soil solution increases, but eventually plateaus as vacant sorption sites are filled. The S curve occurs as a result of two opposing mechanisms, where the sorption of a compound is hindered by the presence of other compounds in solution (Limousin et al., 2007; Sposito, 2008). The L-curve or Langmuir isotherm shows a decreasing slope as concentrations increase, this behaviour is explained by the soil surface having a high affinity for the sorptive at low concentrations, but that affinity decreases as concentrations are increased and as saturation of sorption sites is reached (Sparks, 2003). The H-curve or high affinity isotherm, describes a strong relationship between the sorbate (the solid surface where sorption takes place) and sorbtive, such as occurs in the formation of inner sphere complexes. Finally, the C-curve describes a partitioning mechanism whereby the sorptive is partitioned between the interfacial phase and the bulk solution phase and specific bonding between sorbate and sorptive does not occur (Sparks, 2003).



Figure 2.2 Isotherm shapes adapted from Limousin et al., (2007) where Q is the quantity of P sorbed and C is the equilibrium concentration of P. (a) represents the C isotherm where the ratio between concentration in solution and sorbed on the solid surface is the same at any concentration, (b) the L or Langmuir type isotherm shows a decrease in the ratio between concentration in solution and sorbed on the solid surface as the concentration is increased, (c) the H isotherm or high affinity isotherm depicts a very high initial slope, and (d) shows the S isotherm which contains a point of inflection.

Different sorption models have been used to describe P sorption behaviour, some of the wellknown models include:

The Langmuir equation has the form (Sparks, 2003):

$$q_e = \frac{K \cdot C_e \cdot Q_{max}}{1 + (K \cdot C_e)} \tag{2-1}$$

where,

| qe | is the amount of phosphorus sorbed (mg kg ⁻¹), |
|----------------|---|
| C _e | is the equilibrium concentration of phosphorus in solution (mg L ⁻¹), |
| K | is a constant related to the bonding energy (L mg ⁻¹), and |
| Q_{max} | is the maximum P sorption capacity (mg kg ⁻¹). |

The Langmuir equation assumes that sorption occurs as a monolayer on the soil surface, that binding energy is the same for every site on the surface (surface is homogenous), that the adsorption process is reversible, and that there is no lateral movement of molecules on the surface (Sparks, 2003).

The Freundlich equation has the form (Sparks, 2003):

$$q_e = K_f(C_e)^{\frac{1}{n}} \tag{2-2}$$

where,

| n | is the constant related to binding intensity, and |
|-------|--|
| K_f | is a constant related to the sorption capacity (L kg). |

This model takes into account the heterogeneity of surfaces; however, it has the disadvantage that it does not describe a sorption maximum and that K_f implies that the energy of sorption on a homogenous surface is independent of surface coverage.

Another equation used to study the sorption behaviour of P is the Temkin equation, which has the form (Hunt et al., 2007):

$$q_e = [a \cdot log(C_e)] + b \tag{2-3}$$

where,

ais the slope of the linear isotherm, andbis the intercept.

If a plot of q_e against $\log(C_e)$ gives a straight line, this implies that the adsorption energy decreases linearly with increased surface coverage (Mead, 1981).

Phosphorus release in soils can occur through dissolution of phosphate minerals, through desorption of P adsorbed to soil surfaces, and through the mineralization of organic P (Havlin et al., 2005). Desorption occurs through ligand exchange with OH⁻ and is a slower process than the sorption process (Börling et al., 2004). Different types of desorption experiments have been used in order to measure P release. Some have studied P release using resins and Fe impregnated strips which remove desorbed phosphorus from solution and in that way mimic plant P uptake (Daly et al., 2001; Sibbesen, 1978). Desorption and release can be measured via extraction with water or a dilute salt solution (Bhatti and Comerford, 2007; Daly et al., 2001; McDowell and Sharpley, 2001). In the present study, P desorption experiments were used in two ways: (i) desorption by dilution is measured immediately after a sorption experiment in order to test the reversibility of the adsorbed component and to calculate the P fraction remaining in the soil, and (ii) P release into solution was measured under different pH and ionic strengths.

There are many different factors that affect the sorption of P to soils, they range from organic matter content, clay content, clay minerology, presence of secondary minerals of Al and Fe, exchangeable Al and Fe content, calcium content, pH and ionic strength of the soil solution, current P status of the soil, and Dissolved Organic Carbon (DOC) in the soil solution (Barrow, 2015; Guppy et al., 2005; Tisdale et al., 1993). This review mainly focuses on water soluble DOC derived from residues, soil solution pH and soil solution ionic strength.

2.2 Dissolved Organic Carbon and Phosphorus Sorption in Soils

Traditionally defined as the organic material small enough to pass through a 0.45 µm filter, DOC is a measurement used to quantify dissolved organic matter (DOM). The main sources of DOC in soils originate from throughfall, leaf litter, root exudates, decaying fine roots, and leaching or decomposition of older microbial-processed soil organic matter (McDowell, 2003). Other sources of DOC in soils include decomposition of soil animals and the lysed contents of microbial cells. Chemically, the DOC consists of low molecular weight organic acids (LOA), aromatic acids, amines, polysaccharides and many other carbon-bearing compounds (Guppy et al., 2005).

Many studies support that P and DOC interact in such a way that the sorption behaviour of P in soil is altered (Guppy et al., 2005; Kafkafi et al., 1988; Oburger et al., 2011; Ohno and Carnell, 1996; Ohno and Erich, 1997; Wang et al., 2016). A review by Guppy et al. (2005) mentions different mechanisms involved in soil-borne P and DOC interactions, including: (i) competitive relationships between DOC and P for sorption sites such as metal complexation and dissolution reactions that may result in reduction of P sorption sites, (ii) lowering of the point of zero charge on sesquinoxides, making it more difficult for P to bind to them, or (iii) formation of metal bridges which may increase sites for P sorption (Figure 2.3).



Figure 2. 3 Effect of DOC on the sorption-release of P (adapted from Guppy et al., 2005). [LOA: low molecular weight organic acids. M: metal. P: phosphate].

Containing compounds bearing carboxylic and phenolic groups and varying widely in sizes, DOC tends to behave as a weak acid when in soil solution (Tisdale et al., 1993). Some of the more extensively studied of these compounds belong to the group of LOA which includes citrate, malate, and oxalate. A discussion of studies that have evaluated P sorption in the presence of LOA is included in the literature review of the present study on the effect of crop residues on P binding to soil, because LOA concentrations in plant materials, where they participate actively in cell metabolic processes (*e.g.*, TCA cycle), are 10- to 100-fold greater than those found in the soil (Jones, 1998). Soil LOAs typically account for 2-10% of total DOC in the soil (Guppy et al.,2005).

Phosphorus and LOAs are both multi-protic and have accordingly been shown to be affected by changes to pH. It is thought that the competition between LOA and P for sorption sites may occur in two ways:

- i. both cause the overall surface charge to become more negative and may then discourage (via electrostatic repulsion) further sorption of P or LOA,
- ii. physical competition for sorption sites when the pka of the organic ligand is reached (Guppy et al., 2005).

Oburger et al., (2011) studied P solubilisation mechanisms by exposing 4 well-studied organic acids to non-calcareous soils at high and low rates of saturation of P sorption sites. Although this study was mainly directed towards achieving a better understanding of root exudate solubilisation of P, it can be included in the discussion on DOC effect on phosphorus sorption. One of their main conclusions was that phosphorus solubilisation by the organic acids studied was mainly dependent on soil type, soil sorption sites, and P loading. At a low P saturation rates a soil exposed to organic acids demonstrated ligand promoted mineral dissolution as the main inorganic P solubilizing mechanism. In contrast, ligand exchange was found to be more prominent in soils with high P saturation rates. The organic acids were found to solubilize Fe and Al sites in soils (although the impact varied depending on the acid used). It was also found that soils with high amounts of exchangeable calcium had reduced soluble P levels due to proton-induced Ca solubilisation, which increased solution ionic strength, altered the soil particles' surface potential and thereby suppressed P release.

Wang et al.,(2016) showed that LOA added to three agricultural soils (Calcareous, neutral, and acidic) reduced the adsorption of phosphorus. The LOA were said to alter P sorption sites through ligand exchange and chelation with Fe and Al. The authors reasoned that the chelating ability of LOA's may be discriminated into two pathways:

i. LOA ligands may directly compete with added P for space on surface exchange sites, and

ii. LOA ligands may chelate the soil Ca, Fe, and Al through the formation of organo-metal complexes and thereby reduce adsorption of P to Fe, Al, and Ca-P compounds.

They also found that all LOAs added acidified the soil solution, which resulted in a small decrease in P sorption; however, this was insignificant in comparison with ligand exchange and chelation.

2.2.1 Water Extractable Dissolved Organic Carbon and Sorption-Desorption of Phosphorus

Emphasizing the need for further research in the area of water soluble DOC derived from residue or green manures, Guppy et al., (2005) mentioned that DOC molecules' negative charge density may deter their ability to effectively compete for sorption sites with phosphorus. However, Ohno and Cranell, (1996) demonstrated that DOC derived from green manures was able to release Al from soil into solution, resulting in a decrease in the precipitation of Al-P complexes, leaving more P in solution. Ohno and Erich, (1997) studied the sorption kinetics of P as effected by crop residue derived DOC and demonstrated that DOC derived from corn (Zea mays L.) and wheat (Triticum aestivum L.) decreased the rate of phosphorus sorption, providing further evidence for inhibition of P sorption by surface ligand complexation of Al. Both studies were able to demonstrate that the presence of water extractable DOC from residues and green manure resulted in the reduced sorption of applied P to an acidic, coarse silty soil. Fernandez-Perez et al., (2005) evaluated P sorption in the presence of peat-borne water extractable DOC in two calcareous soils from Spain; a loam and a clay soil. They showed the quantity of P sorbed in soils receiving DOC concentrations of 15, 35, 70, 100 mg L⁻¹ (vs. no DOC amendment) decreased by 15.6-19.9% for the loam and 14.6-17.3% for the clay soil. They concluded that a DOC-induced drop in soil solution pH may have disturbed the formation of calcium phosphate minerals.

Hunt et al., (2007) found that DOC derived from decomposed corn residue and crimson clover (*Trifolium incarnatum* L.) residue at 50 mg L⁻¹ total carbon concentration (C_T) significantly inhibited P sorption to goethite and gibbsite, whereas fresh residue at the same rate did not significantly inhibition P sorption. However at 200 mg L⁻¹ C_T both fresh and decomposed residue derived DOC showed significant sorption inhibition on goethite and gibbsite surfaces. Dissolved organic carbon was not found to affect sorption of P on kaolin; however, hydrophobic partitioning of DOC onto the kaolin surface was consistent with the lack of P inhibition by DOC on kaolin. While they demonstrated that DOC can inhibit P sorption to metal hydrous oxide minerals, they were unable to conclude that it was the direct effect of competitive inhibition, or that the extent of inhibition depended upon the chemical structure of both the DOC and the sorbing surface.

The incorporation of native shrub residues to acidic sandy soils in Senegal was also found to reduce the sorption of P and increase its desorption (Dossa et al., 2008). Used batch techniques, they demonstrated that soils amended with the residues of the two dominant shrub species in the area, showed a reduced capacity of the soil for P sorption based on Freundlich and Langmuir parameters. Having conducted a desorption experiment during which they evaluated P desorption (quantified relative to P remaining bound after desorption) under sequential leaf, leaf + stem, and manure amendments, Dossa et al., (2008) reported P desorption under all organic amendments to generally exceed that for a non-amended soil.

In all studies, regardless of soil texture, the effects of water extractable DOC amendments on the sorption of P led to an impairment of the soils' ability to retain P. Ohno et al., (2007) suggested that P inhibition due to water extractable DOC may be due to a fractionation and preferential sorption of higher molecular weight compounds.

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2.4 pH, Ionic Strength, and Surface Charge

Many suspended solids or colloidal solids in soil solution may bear a surface charge, and this charge may be heavily influenced by pH. The way in which charge has been theoretically represented within the soil solution includes a fixed surface charge on the soil surface, with further contributions to the surface's electric state perhaps arising through a diffuse charge from the liquid in contact with the surface. These two layers shape the electric state of the soil surface (Stumm, 1992). Changes to soil solution pH introduce positive or negative ions (H⁺ and OH⁻) which may then interact directly with ions on the soil surface and thus reshape the distribution of charge. In addition, electrolyte additions to the solution may affect the diffuse charge contributed by the liquid to the surface.

Reporting several issues in considering the effects of pH on P sorption, Barrow (1984) found that performing sorption experiments at a wide range of pH values made the detection of changes to sorption dynamics more obvious. In some soils at high pH, further increasing the pH increased P sorption rather than decreased it, and that at low pH increases in pH resulted in decreased P sorption, whereas, as an anion, increasing the positive surface charge should rather increase its likelihood of sorption. A second factor was that different soils behaved differently in terms of their response to changes in solution pH (which builds on the above observations), and that the primary contributing factors were Fe and Al oxides in soils. Iron and Al oxides bear their own charge, and that charge has been found to change along with changes in pH (Barrow et al., 1980). Depending on the predominant forms present and the quantity of these oxides present in soil, their response to pH effects may be significant enough to likewise change the sorption behaviour of P. Moreover, P desorption from the soil may affect the effect of pH on sorption of

added P. Finally, the effect of pH on the retention of P in the soil also depends on the ionic medium within which the soil was immersed. Should the surface charge be positive, decreasing the ionic strength increased the retention of P through an increase in the electrostatic potential in the plane of adsorption. If the predominant surface charge was negative, decreasing the ionic strength allowed the electrostatic potential in the plane of adsorption to become more negative, resulting in decreased P retention.

In conclusion, pH affects the surface charge, ionic strength affects the diffuse charge, and the presence of variable charged materials as well as deeper penetration of charge imparting constituents, may result in variable P sorption behaviour at the soil surface.

2.5 Conclusions

The Pike River watershed and the Mississquoi Bay suffer from water quality degradation attributable to P pollution originating from agricultural drainage. Incorporation of corn stalk residues may aid in reducing P losses due to erosion; however, it is not known in what way this incorporation may affect the sorption-desorption behaviour of P in the soil. It is important to consider and understand the interaction between P sorption-desorption as affected by residue incorporation as many have found that water extractable DOC from plant matter can increase P availability into the soil solution and this may have implications on the soil's behaviour as a source of P. Important and constantly fluctuating factors such as soil solution pH and ionic strength were also discussed and the effects of both may vary with respect to different soils with different P status and the charge of P binding constituents. The literature demonstrates the different ways in which varying pH and ionic strength separately can influence the sorption of P. It was therefore considered important to also study the effect of varying soil solution pH and ionic strength on the release of P from the soil, as this may have implications on the soil behaving as a source of P. This thesis does not explore transport mechanisms but endeavors to shed light on P sorption-desorption and interactions between P and soil as affected by residue incorporation, and P release as affected by pH and ionic strength.

Chapter 3: Sorption and desorption of phosphorus in the presence of corn stalk residue on a Gleysol from Quebec Canada

Abstract:

The addition of organic matter to soils has been shown to increase phosphorus (P) availability in the soil solution. For agricultural fields with a history of P pollution, the incorporation of residues may increase the risk of the soil behaving as a source of P. The objectives of this study were to investigate the sorption and desorption behaviour of P as affected by different corn stalk residue (Zea mays L.) application rates and at different P concentrations. Two batch sorption experiments were conducted to evaluate P sorption in response to application of corn stalk residue at different rates (0, 0.3, 5.3, 10.3, 15.3, and 20.3% [residue:soil percent by weight]) and at different P concentrations (0, 12.9, 27.7, 42.2, 57.0, and 71.8 mg L^{-1}). This was followed by desorption experiments. Corn residue application rates exceeding 10.3% resulted in significant reductions in P sorption (p < 0.0001). Under the highest residue amendment rate P sorption was reduced by 50% to 30% compared to the non-amended soil. Compared to the non-amended soil, P remaining in the soil after desorption was significantly reduced at residue application rates exceeding 10.3% (p < 0.0001), this reduction being on the order of 90% to 70% under the highest residue amendment rate. In a second sorption experiment, concentrations of P were varied in the presence and absence of a 5.3% residue application. Phosphorus sorption decreased with increasing P concentrations; however, sorption in the presence of residues was generally lower, but only significantly (p <0.0001) so at P concentrations of 57 mg L^{-1} and 71.8 mg L^{-1} . Percent sorbed P remaining after desorption was similar in the presence (85-91%) and absence (86-91%) of residues. This study demonstrates that P sorption inhibition occurred when corn stalk residue was incorporated into a Bedford Gleysol. Given the P pollution history of the area from which the soil

originated and the observation that residue incorporation may increase the soil's P availability, a large-scale study should be conducted to take into account plant growth, microbial interaction, soil depth effects, along with including a leaching component. A study of such scale would allow for a more conclusive quantification of P loss associated with the incorporation of different residue applications.

3.0 Introduction

To protect soils from erosion and to strengthen their integrity (aggregate stability), conservation practices such as covering the soil surface with crop residues, and later incorporating them into the soil has become quite common (King., 2015). Crop residues added to soil leaches dissolved organic matter which is measured as dissolved organic carbon (DOC). Many studies support the idea that phosphorus (P) and DOC interact in such a way that alters the sorption behaviour of P to soil particles (Kafkafi et al., 1988; Oburger et al., 2011; Ohno and Carnell, 1996: Ohno and Erich, 1997; Guppy et al., 2005; Wang et al., 2016). Describing processes by which P is retained by the soil, P sorption includes adsorption (which involves the accumulation of P at the interface between the soil surface and solution), as well as precipitation reactions (Sparks, 2003).

Dissolved organic carbon from green manures was found to inhibit P fixation by way of precipitation in acidic soils (Ohno and Crannell, 1996). Similarly, DOC from corn and wheat residues was shown to reduce P sorption kinetics on acidic soil (Ohno and Erich, 1997). Incorporation of native shrub residues was found to reduce the sorption of P onto highly weathered calcareous soils from the tropics and desorption of P was greater in soils amended with residues than non-amended soils (Dossa et al., 2008). Hunt et al, (2007) reported that DOC derived from decomposed corn residue or clover residue applied at a rate of 50 mg $L^{-1}C_T$ significantly inhibited P sorption to goethite and gibbsite whereas fresh residue at the same rate did not significantly

affect P sorption. They also found that DOC derived from either fresh or decomposed residues applied at a rate of 200 mg $L^{-1}C_T$ both significantly inhibited P sorption on goethite and gibbsite surface. In addition, they examined the molecular weight of the organic compounds and found that preferential adsorption was generally given to more aromatic and higher molecular weight organic compounds. Moreover, this preferential adsorption decreased in the presence of P. Fernández-Pérez et al., (2005) performed batch experiments to evaluate the effect of DOC on P retention by two calcareous soils, one of high permeability and one of low-permeability. They found that for both soils DOC at concentrations from 15-100 mg $L^{-1}C_T$ all resulted in a decreased retention of P.

Enumerating the different mechanisms proposed to account for P-DOC interactions in soil, the review by Guppy et al., (2005) described: (i) a competitive relationship between DOC and P for sorption sites, metal complexation, (ii) dissolution reactions that may result in reduction of sorption sites for P, (iii) decreasing the point of zero charge on sesquinoxides making it more difficult for P to bind, or (iv) formation of metal bridges which may increase sites for P sorption. Guppy et al., (2005) recommended further research in the area of water soluble DOC derived from residue or green manures. Ohno and Carnell (1996) reported that at low concentrations dissolved organic matter (DOM[DOC is a measure used to quantify DOM]) derived from green manures could participate in ligand exchange with aluminium (Al), whereas at high concentrations, it inhibited P sorption through complexation. Moreover, green manure derived DOM had a lesser inhibitory effect on P sorption the presence of citric acid. Investigating the chemical properties of water extractable DOM from residue and manure sources, Ohno et al., 2007 demonstrated that DOM fractionation resulted from preferential sorption of the higher weight molecules onto goethite and that this was weakly related to the DOM's carboxyl group content.

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An additional mechanism proposed to explain a DOC-induced reduction P sorption is that DOC alters soil solution pH. Fernández-Pérez et al., (2005) proposed that the main mechanism responsible for reduced phosphorus retention by calcareous soils was DOC-induced pH effects that interfered with the growth of calcium phosphate precipitates. Wang et al., (2016) showed that low molecular weight organic acids (LOAs) added to three agricultural soils (Calcareous, neutral, and acidic) acidified the soil solution and reduced the sorption of P. However, this effect on P sorption behaviour was deemed insignificant compared to that of ligand exchange and chelation. It could be that DOC induced pH effects are more significant in calcareous soils as opposed to other soils.

The water quality of the Pike River watershed and Missisquoi Bay suffered as a result of several years of nutrient enrichment (Eastman et al., 2010; Gollamundi et al., 2005, 2007; Gombault et al., 2015; Simard, 2005). The Missisquoi Bay's P loading capacity of 97.2 Mg P y⁻¹ and has been consistently exceeded since 2001(Gombault et al., 2015). The regions' history of high surface and subsurface drainage P loads and associated P losses to waterways can be attributed to a long history of inorganic fertilizer and manure application, which were originally applied to meet crop nitrogen requirements, with little concern for the P contributed (Jamieson, 2001; Eastman et al., 2010; Boluwade and Madramootoo, 2013). The soil used for this study bears a level of P that exceed critical P saturation (P/AI) thresholds for soils of this type (Beauchemin et al., 2003; Pellerin et al., 2006). Upon a recent visit to the field site, corn residues (*Zea mays* L.) were seen to have been incorporated into the soil. This raised the question as to what the impact of residue incorporation might be on the sorption and desorption behaviour of P on a soil that exceeds P saturation thresholds and may be at risk of behaving as a source of P to the soil solution.

Based on the relationship between DOC derived from residues and P sorption as confirmed in the literature, we expect that the application of residues will result in decreased P sorption. Accordingly, the main objectives of this study are to: (i) investigate the effect of corn stalk residue application rate on P sorption and (ii) investigate the effect of residue presence on the sorption of P at different P concentrations. Both studies are to be followed by desorption experiments to test the soil's ability to retain sorbed P.

3.1 Materials and Methods:

3.1.1 Soil and Corn Residue

Soil samples were gathered from an agricultural field near Bedford, Quebec (Lat: 45° 7' 34", Long: 73° 3' 44"). The Bedford area is situated within the Pike River watershed; a watershed that feeds into the Missisquoi Bay of Lake Champlain. According to the soil survey of Shefford, Brome, and Missisquoi counties in the province of Québec, the predominant soil type in the Bedford region is a Gleysol (Cann, Lajoie, and Stobbe, 1947). This field site was previously found to encompass 3 clay loam units: Suffield, St. Rosalie, and Bedford sandy clay loam (Simard, 2005). Detailed soil characteristics are listed in Table 3.1.

| Soil properties | Value | |
|---|-------|--|
| Clay (%) | >40 | |
| CEC (cmol kg ⁻¹) | 29.51 | |
| pH (1:1) | 7.81 | |
| $P(MIII) (mg kg^{-1})$ | 44.9 | |
| Total Phosphorus (mg kg ⁻¹) | 859 | |
| Water extractable P w/o electrolyte* (mg L^{-1}) | 0.124 | |
| Water extractable P with electrolyte*(mg L^{-1}) | 0.032 | |
| Ca (mg kg ⁻¹) | 5042 | |
| Al (mg kg ⁻¹) | 468 | |
| Mg (mg kg ⁻¹) | 359 | |
| P saturation P/Al (%) | 10.8 | |
| Bulk Density $(g \text{ cm}^{-3})$ | 1.45 | |

| Carbonate Content (mg kg ⁻¹) | 3190 |
|--|------|
| Organic Matter Content (%) | 2.71 |

*It was calculated as 3 g of soil mixed with 30 ml of double deionized water in the presence and absence of 0.01M KCl.

Soil samples bearing some post-harvest crop residues were collected from the surface layer (0-30 cm). The soil was air dried, ground, and sieved through a 2mm sieve, with any crop residues also being removed. Phosphorus, aluminium, potassium, calcium, and Magnesium were extracted using Melhich III extraction (Ziadi and Sen Tran, 2007). Organic matter content was analyzed by loss on ignition (400 °C for 4 hours). Soil pH was measured at a 1:1 ratio of soil to distilled water. Particle size distribution was determined using the hydrometer method. Soil carbonate content was measured using the method of Bundy and Bremner (1971). Lastly, cation exchange capacity was estimated using BaCl₂, following the method of Hendershot et al., (2007).

Corn stalk residues were collected from agricultural fields in St. Emmanuel (Côteau-du-Lac, QC) and from the Macdonald campus farms of McGill University (Sainte-Anne-de-Bellevue, QC). The residues were dried, shredded, and ground to less than 2 mm in size. Soil and corn stalk residue were digested for total phosphorus using the method of Parkinson and Allen (2008).

3.1.2 Effect of the residue application rates on sorption and retention of inorganic phosphorus

In this experiment, the solid mass of soil was fixed at 3g; however, the residue application rates were varied on a weight by weight basis: 0, 0.3, 5.3, 10.3, 15.3, and 20.3% of residue to soil by weight, respectively. The percentage of residues were chosen to reflect low to high residue applications, where 6 Mg ha⁻¹ was considered a typical corn residue application rate (Sharpley et al., 1989). Further information on percent application rate and corresponding large-scale
application rates can be found in Table 1.2. Each treatment consisted of 4 replicates and each sample received two drops of toluene (American Chemical, LTD, Montreal, CA) to suppress microbial activity.

Table 3. 2 Corn stalk residues application rates of $(R_0 - R_{20.3})$, corresponding mass and large scale application rate, and pH

| Treatment | Percent (%) | Mass (mg) | Mass of dissolved P from residues | Concentration of total P in residue ^a (mg g ⁻¹) | Corresponding application rate (kg ha ⁻¹) | P in stalk residues (kg ha ⁻¹) | DOC ^{b, c} (mg L ⁻¹) | pHc |
|--------------------------|-------------|--------------|--|---|--|---|--|-----|
| R ₀ | 0 | - | - - | - | - | - | 12.36 | 7.6 |
| <i>R</i> _{0.3} | 0.3 | 9 | 1.2 | 0.902 | 127 | 0.114 | 43.55 | 7.7 |
| R _{5.3} | 5.3 | 159 | 1.3 | 0.902 | 2249 | 2.05 | 114.0 | 6.8 |
| <i>R</i> _{10.3} | 10.3 | 309 | 1.4 | 0.902 | 4371 | 3.98 | 186.5 | 6.5 |
| <i>R</i> _{15.3} | 15.3 | 459 | 1.5 | 0.902 | 6492 | 5.91 | 228.5 | 6.4 |
| <i>R</i> _{20.3} | 20.3 | 609 | 1.5 | 0.902 | 8614 | 7.84 | 273.5 | 6.4 |
| | | | | | | | | |

^aTotal P was calculated by digesting fresh residue, then estimating total P (mg P g^{-1}) in each residue application.

^bCorn residue DOC was analyzed using a TOC analyzer (Sievers InnovOx, GE Power and Water) and the samples were placed in a dark refrigerator at 4° C.

^cCorn stalk residue DOC and pH were measured in 30 ml of deionized water.

In the sorption test the constant phosphorus concentration was chosen based on fertilizer requirements (CRAAQ, 2003) for an agricultural soil of the texture and P saturation presented in this soil, namely 35 kg ha⁻¹ of P₂O₅, then scaled down to represent the small surface area of the conical centrifuge tubes used in this experiment. A solution of P (39 mg L⁻¹) derived from

Potassium Phosphate Dibasic (K₂HPO₄) (anhydrous, ACS grade, Bishop, Burlington, Ontario, CA) was added to each treatment (R_0 , $R_{0.3}$, $R_{5.3}$, $R_{10.3}$, $R_{15.3}$, $R_{20.3}$)

Samples were then mixed using a vortex mixer, 30 seconds each and then left to shake at 160 rpm for 24 hours. After the 24-hour period, samples were then centrifuged at 3000 rpm[1,931xg] for 15 minutes. The supernatants were filtered using 0.5/47 µm/mm fiber glass filter paper (Maine Manufacturing, LLC, USA), and inorganic phosphorus was analyzed colorimetrically by the molybdenum blue method of Murphy and Riley (1962) using a flow injection autoanalyzer (Lachat QuickChem series 8000, Lachat, Milwaukee, WI).

To assess P desorption, 30 ml of double deionized water were added to soil and residue samples after the sorption experiment. Two drops of toluene were also added to the samples. The samples then followed the same procedure as the previous test. A one way- ANOVA test was preformed on both sorption and desorption data, followed by Tukey Kramer post hoc test. All statistical analyses for this paper were generated using SAS[®] 9.4 (Copyright © 2013 SAS Institute Inc)¹.

¹ SAS and all other SAS Institute Inc. product or service names are registered trademarks or trademarks of SAS Institute Inc. in the USA and other countries. ® indicates USA registration.

3.1.3 Effect of phosphorus concentration and residue presence on the sorption and desorption of inorganic phosphorus

The residue application rate of 5.3% was chosen as the constant application rate for this batch experiment as it was the highest residue application rate which showed sorption of P that was not significantly different from the control in the previous batch experiment. In this study, we analyzed 2 factors:

- corn residues (2 levels)
 - presence, $R_{5.3}$, and
 - absence, R_0
- P concentration applied (6 levels)
 - 0 mg L⁻¹ (control, P_0)
 - 12.9 mg $L^{-1}(P_{12.9})$
 - 27.7 mg $L^{-1}(P_{27.7})$
 - 42.2 mg $L^{-1}(P_{42.2})$
 - 57.0 mg L⁻¹ ($P_{57.0}$)
 - 71.8 mg L⁻¹ ($P_{71.8}$)

Each treatment combination was done in triplicate. In this study we investigated. The effects of residue and P concentration on P sorption and desorption were tested in a thrice replicated 2×6 factorial design. Statistical hypotheses were tested using 2-way ANOVA using the glimmix procedure. Data transformation was not needed as data followed a normal distribution and variance between treatments appeared to be homogeneous. All statistical analyses for this paper were generated using SAS[®] 9.4 (Copyright © 2013 SAS Institute Inc, Cary, NC)².No background electrolyte was used for this experiment and two drops of toluene were applied to

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suppress microbial activity. Each of the treatment solutions were shaken in a vortex mixer for 30 seconds, then placed on an orbital shaker at 160 rpm for 24 hours, followed by centrifugation at 3000 rpm [1,931xg] for 15 minutes, and filtration using 0.5 µm fiber glass filter paper. Inorganic P was analyzed with a Lachat MicroDist system using the molybdate blue method (Murphy and Riley, 1962). Phosphorus desorption followed the same procedure as in the previous section.

3.1.4 Sorption and Desorption Calculations and Fitting

Sorption was calculated as:

$$q_e = \frac{m_{P-}m_{P_{eq}}}{m_s + m_{res}} \tag{3-1}$$

where,

| m_P | is the mass of P administered for each treatment (mg) |
|------------------|--|
| $m_{P_{eq}}$ | is the mass of P in solution after 24 hours (mg), |
| m _{res} | is the mass of corn residue (kg) |
| m_s | is the mass of the soil (kg), and |
| q_e | is the concentration of P adsorbed to soil (mg kg ⁻¹). |

The quantity of P remaining in the soil after desorption was calculated as:

$$D = \frac{m_{P_{ads}} - m_{P_{deq}}}{m_s + m_{res}} \tag{3-2}$$

where,

| D | is the concentration of P remaining in soil after desorption |
|---------------|---|
| $m_{P_{ads}}$ | is the mass of P sorbed to soil $(= m_{P-}m_{P_{eq}})$, |
| $m_{P_{deq}}$ | is the mass of P in solution after the 24-hour desorption period. |

Percent sorption and percent remaining after desorption were calculated as:

$$S_{\%} = 100 \cdot \frac{q_e}{m_P} \tag{3-3}$$

$$D_{\%} = 100 \cdot \frac{m_{rem}}{m_{P}}$$
where,
 m_{rem} is the mass of P remaining in soil after desorption (mg kg⁻¹),
 $D_{\%}$ is the percent of P remaining in to the soil after desorption
 $S_{\%}$ is the percent P sorption.
(3-4)

Using MATLAB (MATLAB 9.0, the Math Works Inc., Natick, MA, 2016), data were fitted to linear Freundlich (Eq. 3-5), Langmuir (Eq. 3-6), and Temkin (Eq. 3-7) equations (Hunt et al.,2007; Mehmood et al.,2010):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{3-5}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_m \cdot K} + \frac{C_e}{Q_m} \tag{3-6}$$

$$q_e = [a \cdot \log C_e] + b \tag{3-7}$$

where,

| a | is the slope of the linear isotherm, |
|----------------|---|
| b | is the intercept of the linear isotherm, |
| n | is a constant related to binding intensity, |
| k _f | is a constant related to the sorption capacity (L kg ⁻¹), |
| q_e | is the amount of P sorbed (mg kg ⁻¹), |
| C _e | is the equilibrium concentration of P in solution (mg L^{-1}), and |
| Κ | is a constant related to binding strength. |
| Q_m | is the sorption maximum of P(mg kg ⁻¹) |

For each treatment combination Visual MINTEQ (v3.0) (Gustafsson, 2012) was used to check the solubility of the various aluminum and calcium phosphate species that would be present under the experimental conditions and at the measured pH. For $6.9 \le pH \le 7.4$ and at the different P concentrations associated with each measured solution pH, the sample solutions were saturated with AIPO₄.1.5H₂O and Varscite (AIPO₄.2H₂O). The sample solutions were also found to contain

calcium phosphate species such as hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2)$, calcium monohydro gen phosphate (CaHPO₄), and amorphous calcium phosphate (CaPO₄-1), all of which were in saturated solutions.

3.2 Results and Discussion:

3.2.1 Soil and Soil Phosphorus

The soil used in this study was a Gleysol with a clay exceeding 40% (Table 3.1). The effective cation exchange capacity fells within the range of those found in clay and clay loams (Tisdale et al., 1993), which concurred with the particle size distribution. According to the Clay Minerology of Canada, the predominant clay types matching the latitude and longitude of our sampling site were micaceous and 2:1 clays (vermiculite and smectite) (Kodama et al., 1993). The soil used in the present study was alkaline and calcium-rich. The soil contained a Mehlich (III) P extract of 44.9 mg kg⁻¹. The Mehlic III P/Al saturation ratio was found to be 0.108. According to the findings of Pellerin et al., (2006), the critical P/Al (M III) ratios for top soils containing > 300 g clay kg⁻¹ was 0.076; these values were representative of a soil at high risk for water extractable P release. Their results were supported by Beauchemin et al., (2003) who noted that topsoils with critical values of Mehlic P/Al between 0.064-0.131 maintained a mean annual total tile drainage P loss of between 0.02-0.04 mg L⁻¹. The P/Al saturation ratio for the Bedford soil was 0.108 and the soil was found to release 0.032 mg L⁻¹ of phosphorus into solution; both values fall within the range listed by Beauchemin et al., (2003). Beauchemin et al., (2003) monitored tile drainage water quality in 10 tile drained gleyed soils of the St. Lawrence Lowlands.

The critical P/Al for gleyed soils that would result in a total tile drainage P of 0.03mg L^{-1} was 0.094. Similarly, Pellerin et al., (2006) found a critical P/Al of 0.092 for gleyed soils. The Bedford site was recorded as having a P saturation of 0.07 in a previous study (Eastman et al.,

2010) which falls below critical values stated earlier; however, the site still experienced substantial P loss through surface and subsurface drainage. The Bedford site experienced average sediment losses of 1.96 Mg ha⁻¹ y⁻¹ and resulting high particulate P losses (Gollamundi et al., 2005; Eastman et al., 2010). In outflow from 2004-2006, total P loss was 2.9 kg ha⁻¹ y⁻¹, of which 20% was dissolved and 80% in particulate form (Eastman et al., 2010). It was reasoned that preferential flow could be responsible for greater PP loss since the clay loam soil from this site was found to develop deep vertical cracks (Eastman et al. 2010; Gombalt et al., 2015). In terms of fertilization history, the site received roughly 46 kg ha⁻¹ of P fertilizer at planting in 2005, and the topsoil had a P/AI ratio of 7% (Eastman et al., 2010). According to CRAAQ (2003) a saturation ratio between 5.1-7.5% for a soil with clay content greater than 30% should receive P fertilizer at rates 35-50 kg ha⁻¹ in the case where soil Mehlic III P is less than 150 kg ha⁻¹. For a soil with a P/AI saturation ratio between 7.6-10.0 and greater than 30% clay content, the recommended amount for corn crop production would be 35 kg ha⁻¹.

3.2.2 Effect of application rates on sorption and desorption of applied phosphorus

Sorption

Residue application had a significant effect on equilibrium P concentration (p <0.001). The equilibrium P concentration at different residue application rates of showed that $R_{20.3}$ contained significantly higher P in solution (i.e. less sorption to soil) than all other treatments but $R_{15.3}$ (Figure 3.1). There was no significant difference in equilibrium P concentration between the $R_0, R_{0.3}, R_{5.3}, R_{10.3}$, and $R_{15.3}$ treatments. The main effect of residue application rate was found to be significant for P sorption (Eq. 3-1; p \leq 0.0001) and multiple comparisons of means can be found in Table 3.3, which also shows percent sorption (Eq. 3-3) values. Results of the concentration of P remaining in the soil after desorption under different residue application rates showed a decreasing trend in the quantity of P sorbed to soil with increasing residue application. The P

sorption was significantly lower (1.4 and 1.8 fold lower, respectively) for $R_{15.3}$ and $R_{20.3}$ treatments than the control, R_0 . No significant differences were found between the $R_0, R_{0.3}$, and $R_{5.3}$ treatments, the $R_{20.3}$ and $R_{15.3}$ treatments, the $R_{15.3}$ and $R_{10.3}$ treatments, or the $R_{10.3}$ and $R_{5.3}$ treatments (Figure 3.2).



Figure 3. 1 Phosphorus equilibrium concentration with increasing residue addition. Significant differences were found (p<0.05). Treatments represented by the same letter were not significantly different.

| Table 3.3 | Sorption | and P r | remaining | after | desorptio | n as | effected | by | v residue | application | rate |
|-----------|----------|---------|-----------|-------|-----------|------|----------|----|-----------|-------------|------|
| | 1 | | 0 | | 1 | | | ~ | | 11 | |

| Treatments | MeanP | Sorption | MeanP | P Remaining |
|------------|--------------------|-------------------|------------------------|---------------|
| | sorbed | (S _%) | Remaining | (D %) |
| | concentration (mg | | (mg kg ⁻¹) | |
| | kg ⁻¹) | | | |
| | | | | |

| R ₀ | 203.9 ^a | 51.35 | 183.5 ^a | 89.99 |
|--------------------------|---------------------|-------|---------------------|-------|
| <i>R</i> _{0.3} | 203.5 ^a | 51.28 | 184.1ª | 90.41 |
| R _{5.3} | 198.1 ^a | 49.90 | 178.0 ^{ab} | 89.78 |
| <i>R</i> _{10.3} | 170.2 ^{ab} | 42.88 | 141.2 ^{bc} | 82.88 |
| <i>R</i> _{15.3} | 145.6 ^{bc} | 36.68 | 84.97 ^{dc} | 75.86 |
| R _{20.3} | 115.3 ^c | 29.03 | 58.15 ^d | 69.25 |

The amount of P added to each sample was 397 mg kg⁻¹. Each column was analyzed independently of each other. Means with the same letters are not significantly different from each other.

Overall, as residue application was increased P sorption was found to decrease. The presence of DOC from organic matter has been found to result in a decreased sorption of P (Guppy et al. 2005; Hunt et al. 2006; Ohno and Carnell 1996; Ohno and Erich 1997). The $R_{0.3}$ and $R_{5.3}$ resulted in a negligible decrease in P sorption compared to R_0 , and the corresponding concentrations of DOC as total C in solution were 43.5 and 114 mg L⁻¹. Sorption of P was significantly reduced (p<0.05) starting with $R_{10.3}$ which bore total C concentrations of 228.5 mg L⁻¹. Hunt et al., (2007) found that DOC extracted from fresh residues of corn and clover at total carbon concentrations of 50 mg L⁻¹ did not result in reductions in P sorption; however, concentrations of 200 mg L⁻¹ resulted in significant reductions in P sorption. Their experiment was conducted using the minerals Geothite, Gibbsite, and Kaolin, where it was suggested that P interaction with DOC on the surfaces of Geothite and Gibbsite might be controlled by competitive inhibition and negative surface charge effects; however, no such observations were made for DOC-P interactions on Kaolin. Overall, our findings concur with other studies with respect to the inhibitory effect of DOC on P sorption at concentrations exceeding 200 mg L⁻¹.

The literature suggests that many mechanisms affect the behaviour of DOC and P in the soil solution (Guppy et al., 2005). The general agreement is that DOC may interact with P via an exchange reaction, and may complex with P sorption sites and draw the P into solution. The DOC

may also create metal linkages with the soil surface, thus creating more sorption sites for P, and/or the presence of high quantities of DOC (the majority of which have a net negative charge) may repel P anions from the soil surface.

In the present study, the addition of corn residue in the absence of soil, after sorption or after desorption, resulted in a decrease in solution pH (Table 3.4). Dissolved organic carbon compounds behave as weak acids when in soil solution due to the presence of their carboxylic and phenolic groups (Tisdale et al., 1993). Soil constituents do buffer to some extent against decreases to pH induced by the presence of DOC from residue leachate. An increased resistance to the lowering of pH may be attributed to the buffering of Al(OH)₃ or Al(OH)₂⁺ as DOC reacts with H⁺ resulting in the liberation of Al³⁺ and water. Hydroxy-aluminium complexes can behave as both acids and bases given the right conditions (Tisdale et al., 1993). In this case the soils ability to buffer against pH changes was stronger than water extractable DOC induced pH changes.

| Treatment | pH Sorption Test | pH Desorption Test |
|--------------------------|------------------|--------------------|
| R ₀ | 7.58 | 7.13 |
| <i>R</i> _{0.3} | 7.28 | 7.58 |
| R _{5.3} | 7.03 | 7.50 |
| $R_{10.3}$ | 6.98 | 7.38 |
| <i>R</i> _{15.3} | 7.00 | 7.15 |
| <i>R</i> _{20.3} | 7.20 | 7.20 |

Table 3. 4 Average pH of soil solution (1:10) for each treatment with different residue additions.

Desorption

The desorption experiment tested the soil's ability to retain the P sorbed in the presence of residues. The equilibrium P concentration was found to be significantly higher when larger

applications of residues were made and the quantity of P remaining in soil after desorption was significantly lower with an increasing application of residues (Figure 3.3). The Equilibrium P was found to be significantly higher than the control at and beyond the $R_{10.3}$ treatment. The percent of P remaining bound to the soil after desorption was calculated using Eq. 3-4 (Table 3.3). A one-way ANOVA of the desorption data showed that there was a significant difference among treatments ($p \le 0.0001$). Phosphorus remaining in the residue-amended soil after desorption was significantly lower as the residue application rate rose. The concentrations of P remaining in the $R_{10.3}$, $R_{15.3}$, and $R_{20.3}$ soils were, respectively, 1.3-, 2.2- and 3.2-fold times lower than in the non-amended soil (R_0). The percentage of P remaining in the soil declined reduced from 90% at R_0 to 70% at $R_{15.3}$ (Table 3.3). This suggests that the sorption that occurs in the presence of residues is more reversible than that which occurs in the absence of residues. This concurs with the observations of Dossa et al., (2008).



Figure 3. 2 Phosphorus Equilibrium Concentration after desorption experiment. A one-way ANOVA was run and significant differences were found (p value <0.0001). Tukey-Kramer

multiple comparison of means was applied. Means with the same letters are not significantly different.

3.2.2 Effect of phosphorus concentration on the sorption and desorption of phosphorus in the presence and absence of residues

Sorption

The shape of the residue-amended and non-amended sorption isotherms (Fig. 3.4) appear slightly different:

- i. in the absence of residues the isotherm resembles an L-type isotherm without a strict plateau, that is the slope of the curve begins to decrease at higher concentrations as sorption sites become filled and saturation is approached (Sparks 2003).
- In the presence of residue, the isotherm appears to follow more of an S-type shape, which may suggest that other species in solution are hindering sorption of the primary sorbate through competition (Sposito, 2008).

Loumisen et al., (2007) suggests that the latter curve is typical for sorption in the presence of soluble ligands which inhibit the sorption of the sorbate due to complexation. Phosphorus sorption inhibition due to complexation may be occurring during this process; however, it is only distinguishable at the higher P concentrations ($P_{57.0}$ and $P_{71.8}$). It is important to note that these conclusions are based on a 6-point isotherm and that more points would provide a more complete image-based conclusion.



Figure 3. 3 Concentration of P sorbed by soil at different concentrations of applied P in the presence $(R_{5,3})$ and absence (R_0) of corn residues.

Main effects of residue presence and P concentrations on P sorption were significant $(p \le 0.0001)$ as were their interaction $(p \le 0.0001)$. Measurements of P sorption in the presence and absence of corn stalk residues at varying P concentrations (Table 3.5) shows that at higher P concentrations $(P_{57.0} \text{ and } P_{71.8})$ P sorption is significantly diminished (p<0.001) by the presence of residue. The concentration of sorbed P increased with increasing rate of P application; however, the sorption percentage or efficiency was found to decrease (Table 3.5). Though not tested

statistically, percent sorption ($S_{\%}$) in the presence of residues was generally lower than in the absence of residues. The general decrease in percent sorption as P concentrations were increased may be attributed to the soil approaching saturation. Moreover, in the presence of large concentrations of P, the soil surface may have become negatively charged, resulting in electrostatic repulsion and a reduced ability of the soil to bind more P (Barrow, 2014). The roughly 1.2-1.3 times lower percent sorption that occurred in the presence (*vs.* absence) of residues, further support the idea that the presence of organic compounds from corn stalk residue may result in the inhibition of P sorption.

| | L | S Mean P | sorption | | LS Mean sorbed P remaining | | | | |
|-------------------|---|-----------------------|----------------|-----------------------|----------------------------|--------------------------------------|----------------|--------------------------------|--|
| Treatment | Absolute q _e (mg kg ⁻¹) | | Rela S% | Relative $S_{\%}$ (%) | | Absolute D (mg kg ⁻¹) | | Relative D _% (%) | |
| [P]\Residue | R ₀ | R _{5.3} | R ₀ | R _{5.3} | R ₀ | R _{5.3} | R ₀ | R _{5.3} | |
| P ₀ | -0.386 ^a * | -0.217 ^a * | - | - | -0.499ª* | -0.497 ^a * | - | - | |
| P _{12.9} | 80.68 ^b | 61.13 ^b | 62.54 | 47.39 | 74.22 ^b | 55.89 ^b | 91.99 | 91.43 | |
| P _{27.7} | 139.2° | 136.9° | 50.25 | 49.42 | 126.1° | 125.8 ^c | 90.57 | 91.94 | |
| P _{42.2} | 198.7 ^d | 179.1 ^d | 47.09 | 42.43 | 177.6 ^d | 159.1 ^d | 89.40 | 88.81 | |
| $P_{57.0}$ | 280.6 ^e | 191.7 ^{de} | 49.23 | 33.62 | 250.6 ^{ef} | 167.8 ^{de} | 89.32 | 87.53 | |
| $P_{71,8}$ | 307.6^{f} | 264.5^{f} | 42.84 | 36.83 | 264.9^{f} | 226.6^{f} | 86.12 | 85.67 | |

Table 3. 5 Phosphorus sorption and P remaining after desorption as affected by P concentrations in the presence or absence of residues.

*Column-wise (between P concentration) means with the same letter are not significantly different (p > 0.05). Rowwise means are significantly different (i.e., $R_0 \neq R_{5.3}$, $p \le 0.05$) if $R_{5.3}$ value is italicized. A negative value of q_e or D for the treatment without additional P (P_0) represents a net P release. The value for mean absolute P sorption at P_0 - R_0 was based on duplicate rather than triplicate samples as one sample was designated as an outlier.

The sorption models were fit to data (Tables 3.6). In general the Freundlich and Langmuir equations fit the data well ($R^2 > 0.75$), with the former fitting the data exceptionally well ($R^2 > 0.9$). In contrast, in the presence of residues the Temkin model's fit for P sorption resulted in a lower R^2 than that of Langmuir and Freundlich equations.

| | Sorption Model | | | | | | | | |
|-------------------------|---|-------|-----------------------|-----------------------------------|--------------------------------|-----------------------|--------|------|-----------------------|
| Residue | Freundlich | | Ι | angmuir | |] | Temkin | | |
| level | <i>K_f</i> (L kg ⁻¹) | n | R ² | <i>K</i> (L mg ⁻¹) | Qmax (mg kg ⁻¹) | R ² | a | b | R ² |
| <i>R</i> _{5.3} | 20.20 | 1.495 | 0.93 | 80.6 | 285.7 | 0.79 | 66.17 | 85.2 | 0.73 |
| R_0 | 27.42 | 1.529 | 0.97 | 80.0 | 357.0 | 0.80 | 103.9 | 75.4 | 0.78 |

Table 3. 6 Sorption models coefficients, and R^2 for sorption of P in the presence and absence of corn stalk residues.

The goodness of fit of the Freundlich equation in describing P sorption in soils (over a limited range) had been previously reported (Barrow, 1978), and is attributed to the model's assumption that binding affinity decreases with increased P sorption, which reflects reality better than the assumption of constant binding energy implied by the Langmuir equation (Sparks, 2003; Dosa et al., 2008). The Freundlich model parameters, K_f and n, the sorption capacity and the binding intensity respectively, were reduced in the presence of residues which concurred with the findings of others (Dossa et al., 2008) Wang et al., (2016) also reported reductions to K_f and n parameters for treatments in the presence of DOC.

The Langmuir model fit was also acceptable. The binding strength (K) of P was not affected by the presence of residues. The sorption maximum was found to be 1.25-fold greater for the residue-free treatment than for residue-amended treatments, thereby concurring with the findings of Dossa et al., (2008) who also reported decreased Qmax values for samples with shrub residue incorporation. A study by Jiao et al. (2007) looked at the influence of fertilizer source on the sorption of P on a sandy soil and found that Qmax for manured soil was lower than for a triple

superphosphate fertilized soil. They explained that organic acids from manured soil likely blocked sorption sites in topsoil, which may also be the case for the corn residues in the present samples.

On the other hand, treatments with residues show a change in Temkin model parameters from treatments in which residues were absent. Residue absent treatments show a decrease in slope (a) and an increase in the intercept (b) when residues were incorporated. Changes to the slope are interpreted as transformations in the P affinity of mineral sorption sites. A decrease in the slope of the Temkin model may be interpreted as the blocking of sorption sites and an increase in the intercept may be interpreted as an addition of sorption sites (Hunt et al., 2007; Guppy et al., 2005a). According to Temkin model parameters opposing effects were involved, concurring with the findings of Hunt et al., (2007) who also found that soil amendment with fresh corn residue resulted in small reductions in the y intercept and an increase in the slope in the presence of goethite and kaolin. Hunt et al., (2007) also found opposing effects for the Temkin parameters, representing sorption of P in the presence of decomposed dairy manure. This was used to explain the lack of P sorption inhibition experienced by samples since opposing effects may have balanced out. In the case of corn residues, it may be that site blocking by DOC or complexation of P (Loumisen et al., 2007) and the formation of new sorption sites may be occurring in tandem and that is why differences in P sorption behaviour were small between treatments with and without residues. According to Setia et al., (2013) and Rashad et al., (2010), DOC sorption has been found to be strongly affected by cation bridging, and DOC binding strength was found to be influenced by the presence of divalent cations, *i.e.*, bonds formed between DOC and Ca^{2+} . The soil used in this study contained high amounts of calcium, along with DOC from residues. The latter may have bound to the calcium in the soil, resulting in the formation of new sorption sites, which may explain the opposing effects detected by the Temkin model.

Residue-amended treatments showed a slight decrease in pH as P concentrations were increased (Table 3.7). The quantity of residues for each treatment was kept constant and therefore DOC-induced pH effects should be similar throughout. The solution pH may have continued to decrease due to reactions with Al species to form aluminium phosphate and by extension release H+(Havlin et al., 2005). Table 3.7 lists the pH for samples after sorption and desorption equilibration time. There were minor changes to pH of the sample solutions.

| | Sol | ption | Desor | ption |
|-------------------|-------------------------------|-----------------------------|-------------------------------|-----------------------------|
| Treatments | R _{5.3} pH | R ₀ pH | R _{5.3} pH | R ₀ pH |
| P_0 | 7.10 | 6.90 | 6.35 | 6.65 |
| P _{12.9} | 6.47 | 6.83 | 6.87 | 7.03 |
| P _{27.7} | 6.77 | 7.20 | 7.23 | 6.87 |
| P _{42.2} | 6.63 | 7.25 | 7.25 | 6.98 |
| P _{57.0} | 6.27 | 7.13 | 7.23 | 7.00 |
| P _{71.8} | 6.50 | 7.40 | 7.10 | 7.00 |

Table 3.7 pH for sorption (left) and desorption (right) experiments.

Desorption

Desorption was represented as the concentration of sorbed P remaining after desorption by dilution (Fig. 3.5). The desorption isotherms closely follow the behaviour of the sorption isotherms. The range of P sorption that occurred was between 60-307 mg kg⁻¹ whereas after desorption by dilution the range was reduced to 55-264 mg kg⁻¹ (including presence and absence of residues).



Figure 3.4 Concentration of P remaining after the desorption experiment.

Main effects of residue presence/absence and P concentrations on P desorption were significant ($p \le 0.0001$) as were their interactions ($p \le 0.001$). Phosphorus remaining after desorption in the presence and absence of corn stalk residues, as affected by P concentrations, as well as P remaining after desorption as affected by residue presence/absence at different P concentrations is shown in Table 3.5. The percentage of P remaining in the soil after desorption decreased with increased P concentrations both in the presence and absence of residues. The percent P remaining for the different P concentrations was similar in the absence (between 86-91%) and presence (85-91%) of residues. The concentration of P remaining after desorption was generally lower for residue present treatments but was significantly lower(p<0.005) for $P_{57.0}$ and $P_{71.8}$. The presence of residues at 5.3% application did not appear to affect the reversibility of the sorption process since the percentage of sorbed P remaining in the soil after desorption was very similar for residue present and absent treatments. Thus, the generally lower concentration of P remaining in the soil after desorption in the presence of residues may be attributed to the lower sorption of P that occurred in the presence of residues.

In this study, in order to demonstrate the magnitude of the effect that residue incorporation has on the sorption behaviour of P, residue application rates tended to exceed those that what would typically be found on fields. For the sake of simplicity this study does not consider the effect of the microbial community on the interaction between residues, P, and the soil. Microbial decomposition results in the release of inorganic P and DOC compounds with different properties than those released by fresh residues. It is therefore important to consider further the potential effect of microbial decomposition on DOC and P sorption. The inhibition of microbial activity using toluene may result in cell lysis and the release of subsequent DOC and P from microbial cells, this would be expected to be a small contribution, however in future it may be useful to use other forms of microbial inhibition.

3.3 Conclusions

This laboratory study did not consider microbial contributions such as decomposition effects and mineralization, and finely ground corn stalk residues were used as a source of DOC. Although the results do not quantitatively reflect a field situation, important conclusions can still be drawn. Phosphorus sorption decreased as residue application rates increased and P remaining in soil after desorption was lower with increased residue application. Sorption of P was significantly lower than the control at residue applications higher than 10.3% where $R_{15.3}$ and $R_{20.3}$ were 1.4 and 1.8 times lower than the control (R_0). Percent P remaining in the soil after desorption declined from 90% at $R_{0.3}$ to 70% at $R_{20.3}$. The presence of a constant ($R_{5.3}$) residue application resulted in generally lower sorption of P at each P concentration but was significantly lower (p<0.001) for $P_{57.0}$ and $P_{71.8}$. The three equations, Freundlich, Langmuir, and Temkin adequately described the data and demonstrated an inhibitory effect on P sorption in the presence

of corn residues. Percent P remaining after desorption was similar in the presence (range of 85-91%) and absence (86-91%) of residues and it was concluded that the application of 5.3% residue did not increase the reversibility of the sorption process. This study demonstrated that P sorption was inhibited in the presence of corn stalk residues from this Bedford Gleysol; however, on a small scale with residue applications and DOC concentrations more concentrated than what is typically encountered. It is therefore suggested that larger scale studies be conducted, taking into account microbial interactions, and including depth as well as a leaching component in order to quantitatively determine the risk of P loss associated with the incorporation of different residue application.

Connecting Paragraph

In the previous chapter residue application rate was varied at a constant concentration of phosphorus (P) and it was found that beyond the application of 10.3% significantly (p<0.0001) less P sorbed to soil. Phosphorus concentrations were then varied in the presence and absence of a constant application rate of residue. As P concentrations increased greater quantities of P sorbed to soil for treatments with residues and treatments without residues. Residue presence resulted in generally lower sorption results but significantly lower P sorption at P concentrations of 57.0 mg L^{-1} and 71.8 mg L^{-1} (p<0.001) as compared to residue absent treatments. The implications were

that high concentrations of P in the presence of residue will result in a reduced ability of the soil to sorb P. It was proposed that dissolved organic carbon (DOC) from residue may be contributing to reduced sorption of P as this was observed in many studies before this and because as the residue application rate was increased the concentration of residue derived DOC increased in solution(table 3.2). In the next chapter we explore the effects of varying solution pH and ionic strength on the release of P. A batch experiment was initially conducted for the next section with 16 samples followed by digestion of the samples however results were inconclusive and so another experiment was conducted and will be the focus of the next chapter. In the next chapter, Ionic strength effects and pH effects on soil P release were investigated in order to better understand which factor may have a stronger effect on P release from this Gleysol.

Chapter 4: Investigating the effect of varying solution pH and ionic strength on phosphorus release from a Gleysol in Quebec Canada

Abstract:

Phosphorus (P) enrichment of surface waters and subsurface waters result in massive algal blooms, hypoxia, and aquatic habitat devastation. This problem has resulted in greater drive to understand the contribution of different factors on the mobility of P from soil to solution. Solution pH and solution ionic strength have been shown to affect the sorption of P, however it is unclear as to their effect on P release from a soil with a long history of P application. The objective of this study was to investigate whether pH effects or ionic strength effects may result in greater release of P. A batch experiment was used varying three levels of pH (5,7, and 8) and three levels of ionic strength (0,0.01, and 0.05 M) on P release. Varying pH and ionic strength significantly affected P release (p<0.0001) and their interaction was significant (p < 0.0001). Phosphorus release was found to increase with increasing pH at all levels. Phosphorus released at pH 8 was 2.3 (p<0.0001) times higher than at pH 5 for 0 M of ionic strength, but not significantly higher at ionic strength 0.01 M and 0.05 M. Phosphorus release was found to be significantly higher at low ionic strength (0M) but not for medium and high ionic strength (0.01 and 0.05M). Phosphorus release at 0.05M was 2.9 (p<0.005) and between 4.6 (p<0.0001)-4.9 (p<0.0001) times lower than at 0 M for pH 5, 8, and 7 respectively. Mean electric conductivity (EC) measurements were generally highest for pH 5 treatments at all ionic strengths. This small-scale study shows that increasing the solution pH at low ionic strengths will result in high release of inorganic P, however increases in ionic strength of the soil solution may reduce the likelihood of this soil acting as a source of P.

4.0 Introduction

Changes to pH and solution ionic strength have been shown to result in shifts in a soil's ability to retain P (Barrow et al., 1980; Barrow, 1984). Many suspended solids or colloidal solids in soil solution bear a surface charge, and this charge may be heavily influenced by pH (Stumm, 1992). Changes to soil solution pH introduce potential changing ions (H⁺ and OH⁻) which may

then interact directly with ions on the soil surface and thus reshape the distribution of charge. In addition, electrolyte additions to the solution affect the diffuse charge contributed by the liquid to the surface (Barrow et al., 1980; Stumm, 1992).

According to the literature, the phenomenon of sorption and desorption depend heavily on electrochemical dynamics between the solution and the surface. In the case of P, the existence of a relationship between P retention and the presence of variably charged materials in soil is well known (Barrow et al., 1980). These materials (such as Fe and Al hydroxides and oxyhydroxides) have a high P sorption capacity under certain conditions. The sorption ability of materials such as Goethite (FeO(OH)) and Gibbsite (AlOH₃) have been shown to be affected by pH and electrolyte concentration (ionic strength) (Barrow et al., 1980; Hunt et al., 2007). Other factors such as pH and ionic strength may also influence the predominant sorption mechanisms to ensue with respect to surface material (Arnarson and Keil, 2000).

For several years, the Pike River watershed and the Missisquoi Bay have experienced water quality degradation due to nutrient enrichment (Eastman et al., 2010; Gollamundi et al., 2005, 2007; Gombault et al., 2015; Simard, 2005). The area has had a history of high P in surface and subsurface drainage and this P loss has been attributed to a history of consistent application of fertilizers and organic manures over many years. These were initially applied to meet crops' nitrogen requirements, as the misconception at the time was that the soil was a sink for P (Boluwade and Madramootoo, 2013; Eastman et al., 2010; Jamieson, 2001). The history of P loss from the area reinforces the importance of studying factors that may potentially influence the interaction/movement of P between soil to solution.

In the present study we investigate the effects of pH and ionic strength on inorganic P release into solution in order to better understand which factor has the greater effect on P release

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from this soil. It should be noted that in this study P was not added to the soil and so the term 'release' was used to describe the movement of P from soil to solution because the term desorption describes the release of a predetermined amount of sorbed P.

4.1 Materials and Methods

4.1.1 Effect of ionic strength and pH on phosphorus release

Two factors were studied, each including 3 levels, complete with four replicates. The factors were pH (5,7,8) and ionic strength was (0 M, 0.01 M, and 0.05 M). The different ionic strength solutions were created using equivalent concentrations of the KCl. The pH adjustment of the soil solution was performed by adding dilute HCl and KOH to individual samples until the desired pH was reached. The solution's Electric Conductivity (EC) was also measured. The experiment was set up such that the solid to solution ratio was held at 1:10, where 3 g of soil were added to 30 ml of liquid. The ionic strength was adjusted using KCl and the adjusted solution was added to each sample and pH of the solution was adjusted. Samples were left on an orbital shaker for 24 hours at 160 rpm. After the 24-hour period samples were then centrifuged at 3000 rpm [1,931xg] for 15 minutes. The samples were filtered using a 0.5 µm fiberglass filter. The supernatants were then analyzed for P using a Lechat MicroDist system. The analysis for phosphate used the molybdenum blue method (Murphey and Riley, 1962).

A 2-way ANOVA using the Glimmix procedure and a comparison of differences by LSmeans was performed with respect to the effects of pH and ionic strength on P release. A two-way ANOVA was run using the GLM procedure, evaluating the factors pH and ionic strength on solution EC. Treatment effects were analyzed and grouped using the Tukey Kramer test. All statistical analyses were performed using SAS[®] 9.4 (Copyright © 2013 SAS Institute Inc)³.

4.2 Results and Discussion

Refer to the Chapter 3 and Table 3.1 for a discussion of soil physical and chemical characteristics.

4.2.1 Effect of ionic strength and pH on inorganic phosphorus release

A 2-way ANOVA was run and treatment effects of pH and ionic strength were found to be significant (p<0.0001) and an interaction effect between pH and ionic strength on P release was significant (p<0.0001). Changes in P release as a result of changes in pH at the different levels of ionic strength (or vice-versa) are presented in Table 4.1. Under the 0 M ionic strength treatment (I_0), the P concentration in solution increased with increasing pH. Phosphorus release at pH 8 was 2.3 (p<0.0001) and 1.3 (p<0.0042) times greater than at pH 5 and 7 respectively. Phosphorus release continued to increase with increasing pH at ionic strength 0.01 and 0.05 ($I_{0.01}$, and $I_{0.05}$); however, the magnitude of P released was lower and differences in P concentrations in solution were not significant.

Phosphorus solubility is lowest at pH values between 5.5 and 6.0, then increases to a pH of 8-9, at which point calcium phosphate precipitation reduces soluble P concentrations (Murrmann and Peech, 1969). At low pH, P would be primarily present as precipitated iron-phosphate (Fe-P) and aluminium-phosphate (Al-P) minerals on the soil surface. As the pH rises concentrations of dissolved inorganic P originating from the dissolution of Al-P and Fe-P, can begin to be measured in solution (Havlin et al., 2005). Another possible reason for the increase in

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P in solution is the release of P from variably charged materials in the soil that approach or surpass their point of zero charge as pH is increased (Barrow 1984).

| pH levels | Ionic Strength | Ionic Strength | Ionic Strength |
|-----------|----------------------|----------------------|----------------------|
| | (0 M) | (0.01 M) | (0.05 M) |
| рН 5 | 0.0733 ^{cA} | 0.0370 ^{cB} | 0.0253 ^{cB} |
| pH 7 | 0.133 ^{bA} | 0.0315 ^{cB} | 0.0268 ^{cB} |
| pH 8 | 0.171 ^{aA} | 0.0335 ^{cB} | 0.0368 ^{cB} |

Table 4. 1 Phosphorus release (mg L^{-1}) as affected by pH and ionic strength

Means with the same lowercase letter are not significantly (p > 0.05) different column-wise (by pH), and means with the same UPPERCASE letter are not significantly different row-wise (by ionic strength).

Under the pH 5 treatment, the P concentration in solution decreased as ionic strength increased. On average, P release at pH 5 and I_0 was 0.0363 mg L⁻¹ (p<0.0057) and 0.0480 mg L⁻¹ (p<0.0005) higher than at pH 5 and $I_{0.01}$ and $I_{0.05}$, respectively. At pH=7 the concentration of P in solution at I_0 was 0.102 mg L⁻¹ (p<0.0001) and 0.096 mg L⁻¹ (p<0.0001) higher, than at $I_{0.01}$ and $I_{0.05}$, respectively. Similarly, at pH 8 the concentration of P in solution at I_0 was 0.138 mg L⁻¹ and 0.134 mg L⁻¹ higher than at $I_{0.01}$ and $I_{0.05}$, respectively.

As ionic strength increased, the concentration of P released declined. These results concurred with the findings of Hartikainen and Yli-Halla (1982) who found that increases in ionic strength depressed the extractability of P regardless of the type of salt solution used. Barrow (1984) noted that the ionic medium in which the soil was immersed could influence pH and the retention of P. He explained that should the soil surface be predominantly negatively charged, decreasing ionic strength would result in a decrease in the electrostatic potential in the plane of adsorption, which would, in turn, decrease the retention of P. This explanation concurred with our experimental findings that at lower ionic strength values there was a greater release of P. On the other hand, increasing the ionic strength value of a solution increases the electrostatic potential (Barrow et al., 1980; Bolan et al., 1986). For a soil, which may contain a predominantly negative

surface charge, introduction of cations from the addition of electrolytes would increase the surface charge, and, in turn, increase the electrostatic potential in favour of P retention (Barrow, 1984).

For all the ionic strength treatments, as ionic strength was increased so too was the conductivity of the sample (due to the presence of higher concentrations of ions in solution (electrolyte)). Figure 4.1 shows that for every level of ionic strength, when the pH was increased, the conductivity of the solution decreased, however as ionic strength increased the variance in the EC between each pH treatment decreased. The conductivity of the electrolyte masked the resultant pH effect on solution EC.



Figure 4. 1 Electric conductivity of the soil solution under different pH and ionic strength treatments.

To investigate the effect of varying pH and ionic strength on solution EC a 2-way ANOVA was run using the GLM procedure. The effects of pH and ionic strength were significant (p<0.0001). There was no interaction between the two factors (p > 0.5). Varying pH was found to significantly affect solution EC (p<0.001). Likewise, varying ionic strength significantly affected solution EC (p<0.001). Table 4.2 shows Tukey groupings for pH and ionic strength effects. The EC at pH 5 was 1.2 times greater (p < 0.05), than at pH 7 or 8. The EC increased significantly with increasing ionic strength. A strong linear relationship is known to exist between ionic strength and EC (Lindsay, 1979). In the present case, it may be that the conductivity of the electrolyte masked the resultant pH effect on solution EC. It is likely that the low pH resulted in cation exchange between H⁺ and Ca²⁺ which may be a reason why pH 5 treatments displayed higher EC levels. Table 4. 2 Multiple comparison of means for pH and ionic strength effect on solution EC

| Treatment | Mean EC (mS cm ⁻¹) | | |
|----------------|--------------------------------|--|--|
| pH | | | |
| 5 | 2.46^{a} | | |
| 7 | 2.14 ^b | | |
| 8 | 2.11 ^b | | |
| Ionic strength | | | |
| 0 | 0.260 ^c | | |
| 0.01 | 1.25 ^b | | |
| 0.05 | 5.20 ^a | | |

Each treatment grouping was analyzed independently. Means with the same letter are not significantly different.

4.3 Conclusions

This study was conducted to better understand the effects of varying pH and ionic strength on P release from a Geysol collected from an agricultural field in the Pike River watershed, which has a history of P pollution. Phosphorus release was found to increase with exposure to higher solution pH; however, the effect was most pronounced at low ionic strength values. Phosphorus release was found to be significantly lower at higher ionic strength values than at lower ionic strength values. Mean EC was generally highest for pH 5 treatments at all ionic strengths. Overall for this soil, P release dynamics were more influenced by pH when ionic strength was low, but the magnitude of P release was greatly reduced at higher ionic strength values, regardless of pH. It would be interesting to conduct a larger scale study where the effects of varying solution pH and ionic strength on P leaching from soil columns could be studied. A larger scale study would allow for the quantification of P release under conditions where the natural buffering ability of the soil can be taken into account. If the same wide ranges of pH and ionic strength are used then the larger scale study may be used to inform models.

Chapter 5: Summary and Conclusion

The sorption and desorption behaviour of phosphorus (P) was studied in the presence of different corn stalk residue application rates and at different concentrations of P. Phosphorus sorption decreased as residue application rate was increased and P remaining in the soil after desorption also decreased with increasing application rate. Phosphorus sorption efficiency decreased with increasing P concentration and sorption in the presence of corn stalk residues was generally lower but only significantly lower (p < 0.0001) for the two highest P concentrations. The quantity of P remaining in the soil after desorption was not affected by residue presence at the 5.3% application rate as percent P remaining were similar for both residue-present and residueabsent treatments. These findings show, at a laboratory scale, that corn stalk residue incorporation decreased P sorption to this Gleysol. The scale of these experiments limits us from asserting any broad scale conclusions about the efficacy of this management practice for this area; however, given due to the history of P pollution in the region it is our recommendation that a larger scale experiment be conducted. This experiment should include different residue application rates at ranges closer to typical field applications, as well as a depth and leaching component to effectively monitor where DOC and P are accumulating and how far they traveled. The presence of P and DOC in the soil solution are also regulated by microbial interactions therefore we encourage the larger scale study to include a temporal aspect so that microbial interactions with residues may be included. It may also be of interest to study the sorption-desorption dynamics of P on agriculturally cultivated organic soils (such as those in southwestern Quebec and Ontario). Such soils will contain high concentrations of DOC in the soil solution, which will affect the sorption and desorption of inorganic P; for such an experiment inclusion of microbial interactions is essential for the accurate quantification of P loss.

This thesis also investigated the effect of varying pH and ionic strength on P release. Increasing the pH (until 8) resulted in an increase in P release at low ionic strength treatments. Phosphorus release was depressed at higher ionic strengths regardless of pH level. This experiment demonstrated, at a laboratory scale, the magnitude of effect pH and ionic strength had on P release over a wide range of pH and ionic strengths. The range of these treatment levels may be representative of discrete temporary circumstances and not the generally stable buffered soil solution.

It is our recommendation that any future studies with the aim of reducing P leaching through the use of soil amendments (organic or inorganic: including but not limited to limes, iron and aluminium bearing amendments, and types of biochar) to control P fate and transport in this soil, regularly characterize and monitor soil solution pH and ionic strength as a result of amendment addition. Amendments that increase the ionic strength of the soil solution may well reduce the risk of P leaching into the soil solution, however it is unclear for how long this process may last and also what effect it may have on plant-soil and microorganism-soil interactions.

It would be interesting to conduct a laboratory experiment determining the effect of water extractable DOC from residues on solution pH, as well as the effects of DOC induced pH changes on P sorption and desorption. This experiment may also seek to identify mechanisms behind water soluble DOC (derived from residues) induced pH effects on sorption and desorption, whether it is by the dissolution of Al-P and Ca-P minerals, or by other alterations to surface chemistry. It may also be pertinent to study the effect of residue addition on soil solution ionic strength. The experiment could demonstrate how much residue addition would be required to change the ionic strength of the soil solution in a farm soil such that it would affect sorption and desorption of P, and whether this process temporarily or permanently alters the sorption characteristics of the soil.

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Appendix:

| ANOVA table for P equilibrium concentration | at R_0 - $R_{20.3}$ after sorption a | and desorption |
|---|--|----------------|
|---|--|----------------|

| Source | DF | ANOVA SS | Mean Square | F Value | Pr>F |
|------------|----|----------|-------------|---------|----------|
| Model | 5 | 231.7 | 46.347 | 6.99 | 0.0009 |
| Sorption | | | | | |
| Model | 5 | 1039 | 207.8 | 16.31 | < 0.0001 |
| Desorption | | | | | |

ANOVA table for Sorption (mg kg⁻¹) and P remaining after desorption(mg kg⁻¹) as effected by residue application rate R_0 - $R_{20.3}$

| Source | DF | ANOVA SS | Mean Square | F Value | Pr>F |
|------------|----|----------|-------------|---------|----------|
| Model | 5 | 1678.1 | 335.6 | 14.7 | < 0.0001 |
| Sorption | | | | | |
| Model | 5 | 1559.0 | 311.8 | 19.5 | <.0001 |
| Desorption | | | | | |

ANOVA table for phosphorus sorption and P remaining after desorption as affected by P concentrations in the presence or absence of residues.

| Effect | Num DF | Den DF | F Value | $\mathbf{Pr} > \mathbf{F}$ |
|---|--------|--------|---------|----------------------------|
| Residue $(R_0/R_{5.3})$ | 1 | 24 | 36.18 | <.0001 |
| Trt(P ₀ -P _{71.8}) | 5 | 24 | 327.72 | <.0001 |
| Residue*Trt | 5 | 24 | 8.08 | 0.0001 |

ANOVA table for the effect of ionic strength and pH on inorganic phosphorus release

| Effect | Num DF | Den DF | F Value | $\mathbf{Pr} > \mathbf{F}$ |
|----------------------|--------|--------|---------|----------------------------|
| pH | 2 | 27 | 12.69 | 0.0001 |
| Ionic Strength | 2 | 27 | 120.82 | <.0001 |
| pH*Ionic Strength | 4 | 27 | 10.48 | <.0001 |
| Source | DF | ANOVA SS | Mean Square | F Value | Pr > F |
|----------------|----|----------|-------------|---------|----------------------|
| Model | 8 | 164.9 | 20.6 | 746.7 | <.0001 |
| pH | 2 | 0.930 | 0.465 | 16.8 | <.0001 |
| Ionic Strength | 2 | 163.98 | 81.9 | 2968.8 | <.0001 |
| pH*Ionic | 4 | 0.0631 | 0.0157 | 0.57 | 0.6857 |
| Strength | | | | | |

ANOVA table for the effect of pH and ionic strength on solution electric conductivity