**Changes in Soil Test Phosphorus and Phosphorus Forms with Continuous Phosphorus Fertilizer Addition to Contrasting Prairie Soils**

by

Oluwatoyin Abosede Obikoya

A Thesis submitted to the Faculty of Graduate Studies of

The University of Manitoba

In partial fulfillment of the requirements

of the degree of

MASTER OF SCIENCE

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba

# ABSTRACT

Obikoya, Oluwatoyin Abosede. M.Sc., The University of Manitoba, January 2015. <u>Changes in Soil Test Phosphorus and Phosphorus Forms with Continuous Phosphorus Fertilizer Addition to Contrasting Prairie Soils.</u>
Advisor: Dr. Wole Akinremi.

Application of phosphorus fertilizer can lead to changes in soil test P and increase both labile and non-labile phosphorus pools. Sequential fractionation showed that the labile ($H_2O$-P and $NaHCO_3$-P) fractions significantly ($P < 0.05$) increased with the addition of phosphorus fertilizer across all sites. Significant increase was observed in the non-labile (NaOH-P, HCl-P and Residual-P) fractions during the accumulation phase. During the depletion phase, when no further P was added, the accumulated P in the labile P fractions declined but not to the original level. The rates of P application, soil properties, soil test P methods used and time effect all had significant effects on soil test P changes in the extraction experiment. Mehlich-3 extracted the greatest amount of P from the two depths and Olsen-P was intermediate while the smallest amount was extracted with water. The pattern of the rate of change in extractable P with P addition for the $0 - 7.5$ cm depth was not site dependent as the results obtained at the different sites were similar.

# ACKNOWLEDGEMENT

**TABLE OF CONTENTS**

# LIST OF TABLES

# LIST OF FIGURES

# 1. Introduction

## 1.1. Phosphorus and its effects

Scientists have focused on phosphorus (P) throughout the decades since P is an important macronutrient that can limit plant growth if not available in adequate amounts. One of the ways of augmenting soil supply of phosphorus is through fertilizer application. However, application of P at rates exceeding crop removal leads to P accumulation in the soil and increases the potential for P loss to adjacent environment. There have been many concerns raised about the environmental impact of P especially on its impact on water quality (Chien et al. 2009). Phosphorus exists in the soil in water-soluble forms, which can be easily lost through run-off or in particulate forms, which can be lost through erosion. Within the province of Manitoba, there is an increasing interest in the health of Lake Winnipeg as inappropriate or excessive use of P either from fertilizers or manures has been linked to P runoff, and thereby lake eutrophication. Lake Winnipeg is the $10^{th}$ largest freshwater body in the world and it is one of the most eutrophic as measured by the overabundance of cyanobacteria (LWSB 2006). The increasing overloading of P to Lake Winnipeg's watershed is as a result of human activities such as the use of detergents, fertilizers, livestock manure, septic tanks and municipal wastewater.

Continuous application of P fertilizer in excess of crop removal can lead to P accumulation in the soil due to low fertilizer P recovery by plants, which rarely exceeds 25% in the first year of application (Ciampitti et al. 2011). This build-up of P becomes available to subsequent crops grown on the soil (Roberts 1992; Selles et al. 2007). The residual effects of P can provide positive crop responses, which are dependent on factors such as the rate of P fertilizer added, crop P removal, soil type (precipitation and adsorption effects), immobilization in organic matter

and erosion and leaching losses (Ciampitti et al. 2011).

The plant available P also increases over time with application of P fertilizer at rates exceeding crop removal. Due to the continuum of P forms from soluble to insoluble, there is a need to measure the P status of the soil using appropriate soil testing methods. The environmental risk due to high P levels in soils and its agronomic effect on crop production can now be monitored using appropriate soil test P methods (Kumaragamage et al. 2007). Agronomic soil test methods focus on the extracted P that is available to the crop, as regulated by soil and plant factors.

Some of these soil factors that regulate available P include soil pH, mineralogy, organic matter, adsorption capacity, soil texture, temperature, soil moisture, impedances; and the plant factors include the presence of roots, residues, and micro-organisms (Ciampitti et al. 2011).

## 1.2 Soil Testing

Soil testing is a routine soil analysis carried out to relate the concentration of P in soil to the response of crops to fertilization. The use of soil test methods that do not give an accurate estimate of P-available to plants can result in high variability in P fertilizer response (McKenzie and Bremer 2003). An accurate soil test method extracts a portion of P that relates well with plant uptake, and does not contain significant amount of non-available P (Corey 1987).

Soil test P methods can be categorized into agricultural and environmental. Agronomic soil test P methods such as Olsen, Modified Kelowna and Mehlich-3 have been used to determine plant nutrient availability during the growing season (Olsen et al. 1954; Mehlich 1984; Van Lierop 1988). Different extracting agents have the ability to extract different forms and amounts of P, that are dependent on the soil properties, and the solubility of the P forms common in the region (Ige et al. 2006). Due to the calcareous origin of Manitoba soils, the agronomic soil test P method mostly used in Manitoba is the Olsen method while the Mehlich-3 is used rarely.

Mehlich-3 extractions may not be suitable for calcareous soils because $NH_4F$ reacts with $CaCO_3$ to form $CaF_2$, which may precipitate soluble P (Kleinman and Sharpley, 2002). However, Mehlich-3 is regarded as suitable for a wide range of soils; it is thus considered as a popular soil test extractant especially in acidic to slightly acidic soils. It can extract P and other elements in a wide range of soils (Carter and Gregorich, 2007).

The Kelowna extracting reagent, for example Kelowna-1 (0.25 M acetic acid and 0.015 M ammonium fluoride), is a multi-element extractant (Van Leirop 1988), that is used in some Western Canadian soil testing laboratories to dissolve acid-soluble P such as calcium phosphate and some iron and aluminum phosphate. The dissolved P is maintained in solution by complexing the associated metal ion with acetate. This method is considered suitable for calcareous and non-calcareous soils with neutral to alkaline pH. Kelowna reagent (Kelowna-2) was modified by adding 0.25 M ammonium acetate to the original Kelowna extractant and buffering at pH of 4.9 (Qian et al., 1994). Ashworth and Mrazek (1995) further modified the extraction, creating Kelowna-3 by increasing the concentrations of ammonium acetate to 1.0M and acetic acid to 0.5 M.

Ige et al. (2006) reported the differences in various soil test P methods and how the extracted P differed due to the varying power of the extracting solutions. Although these soil test P methods are classified as agronomic soil test methods, they have nevertheless been shown to effectively predict the risk of P loss from soils (Pote et al. 1996; Pautler and Sims 2000). However, environmental soil P tests such as water-extractable P (Self-Davis et al. 2000) and 0.01 M $CaCl_2$-P (Kuo 1996) extract a portion of soil P that is easily lost by leaching or surface run-off. Water-extractable P is intended to represent runoff during rainfall events or spring season snowmelt. However, deionized water does not occur naturally in the soil environment; thus, $CaCl_2$ solution

becomes a valid representative extractant as it contains a dilute amount of salts that mimics the soil solution.

Along with agronomic and environmental soil tests, other indices have been developed to assess the environmental risk of P loss from soil to water bodies. These include the degree of phosphorus saturation (DPS) (Zhou and Li 2001) and P index (Sharpley et al. 2003). The DPS is an environmental index for assessing the potential for phosphorus loss due to its strong relationship with runoff phosphorus concentration and leaching (Sims et al. 2002). Ige et al. (2005) proposed that DPS is preferred to soil test P in assessing the risk of P loss to runoff because DPS, along with the P intensity factor, also considers the capacity of soils to retain P. Phosphorus sorption capacity (PSC) is a measure that determines the ability of the soil to retain P (Ige et al. 2005). Determination of P sorption status of soils is dependent on the method used to measure STP and PSC, and on the equation used to calculate DPS (Casson et al. 2006). In acid soils, the oxalate extractable Fe and Al are used as an index of the PSC, with the oxalic acid precipitating Ca during oxalate extraction and changing the pH of the acid buffer when it reacts with $CO_3$ (Loeppert and Inskeep 1996). Thus, it is not suitable for alkaline or calcareous soils, which occur widely on the Canadian prairie region.

Ige et al. (2005) suggested that for the DPS to be an effective environmental indicator of P loss potential, a good correlation with the form of soil P most susceptible to runoff and leaching losses is imperative. Good correlations were observed between water extractable P and DPS derived from Mehlich-3 extractable Ca and Mg, designated as $(Ca + Mg)_{M3}$. This may be due to the acid nature of Mehlich-3 extracting agent, which is able to extract Ca and Mg at the exchange sites, as well as other reactive forms of Ca and Mg, which could be important to soil P retention.

Maguire et al. (2005) noted that environmental P thresholds indicate the STP values above which

excessive amounts of P could be lost to run-off. Gartley and Sims (1994) reported that environmental threshold limits for STP were typically between three and six times the value accepted as adequate for optimum crop yields. Using these criteria, the Manitoba Phosphorus Expert Committee (2006) proposed the environmental threshold for Olsen P range as 60-120 mg $kg^{-1}$ and the agronomic optimum as 15 mg $kg^{-1}$. On the other hand, Kumaragamage et al. (2007) suggested the environmental soil P threshold range for Olsen P as 88-118 mg $kg^{-1}$ in Manitoba soils.

### 1.3. Factors affecting changes in soil test P

### 1.3.1. Soil specific

Agronomic soil tests are used as indicators of P availability during a growing season. After initial increases in plant-available P following P amendment, the pool of P extracted by agronomic soil tests gradually decreases with time (Haden et al. 2006), and the magnitude of change with time is soil specific. Kashem et al. (2004b), in a laboratory incubation study showed that Mehlich-3 P, Kelowna-P, Olsen-P, $NH_4Cl$-P and $H_2O$-P declined gradually between week 1 and week 32 after P application. Regardless of extractant and soil, extractable P was small 1 week after adding biosolids (17–93 mg $kg^{-1}$ as Olsen P) and large with MAP (59–672 mg $kg^{-1}$ as Olsen P) while hog and cattle manures were intermediate between biosolids and MAP (20–461 mg $kg^{-1}$ as Olsen P) in their effects on extractable P. In the study by Kashem et al. (2004b), all amendments were added to provide the same total P. Likewise, Agbenin and Tiessen (1994) used anion exchange membranes on five benchmark soils and reported a gradual decline in extractable P with time, with equilibrium ultimately being reached at approximately 50 d after P application. A study performed by Randall et al. (1997) on a Minnesota Webster clay loam soil (initial soil test P measured very high, 22 mg $kg^{-1}$) showed that the addition of 26 kg P $ha^{-1}$ $yr^{-1}$ would raise Bray-1

soil test P by 1 mg P kg$^{-1}$ yr$^{-1}$, where continuous corn was grown for 7 yr followed by 11 yr of a corn–soybean rotation for grain harvest. Dodd and Mallarino (2005) also reported that 23, 28, and 17 kg P ha$^{-1}$ yr$^{-1}$ increased Bray-1 soil test P by 1 mg P kg$^{-1}$ yr$^{-1}$ at Boone (loam), Kanawha (clay loam), and Nashua (loam) soils with the highest annual P rate (44 kg P ha$^{-1}$ yr$^{-1}$) respectively. Zhang et al. (2004) found that 6.3 kg P ha$^{-1}$ of net P surplus was required to increase M-3 P by 1 mg P kg$^{-1}$ with continuous P fertilization at rates from 44 to 132 P ha$^{-1}$ yr$^{-1}$ and 4.2 kg P ha$^{-1}$ of crop P removal decreased soil M-3 P by 1 mg P kg$^{-1}$ in plots previously receiving 132 kg P ha$^{-1}$ yr$^{-1}$. Reddy et al. (1999) stated that the variable effects of manure and fertilizer P on different pools of soil P depend on rates of P applied, P removed by crops, inherent soil properties and climatic conditions. Thus, the amount of fertilizer P required for each milligram of P per kilogram increase of soil test P varies with climatic conditions, soil type, soil test method employed, as well as the rate of fertilizer P applied and the time since P application started.

### 1.3.2. Source of P applied

A number of researchers have observed that P from various fertilizer and manure sources can have differential effects on the chemistry of P sorption and availability (McDowell and Sharpley 2004). Kumaragamage et al. (2011) found that the amount of P required to raise Olsen-P by 1 mg kg$^{-1}$ in Newdale clay loam soil was 11.4, 3.7 and 1.5 mg kg$^{-1}$ 6 wk. after the application of solid cattle manure (SCM), liquid swine manure (LSM) and synthetic fertilizer (MAP) respectively. For the Lone sand soil, the values were 7.0, 2.1 and 1.7 mg kg$^{-1}$ for SCM, LSM and MAP, respectively. According to Haden et al. (2006), $NH_4HPO_4$ was approximately two times more effective at raising Morgan-P (M-P) and M3-P concentrations than either triple super phosphate [$Ca(H_2PO4)_2$] or liquid dairy manure on a per-unit-P-added basis. These differences have been

6

linked to a combination of soil test P methods used and inherent chemical differences among the three P sources. Griffin et al. (2003) found significant differences in the efficiency by which $KH_2PO_4$, beef, dairy, poultry, and swine manure raised modified Morgan-P and Mehlich-3 P, and argued that a significantly greater fraction of P from $KH_2PO_4$ remains soluble during a 90-d period relative to P from manure sources.

Reddy et al. (1999) showed that the level of Olsen P increased linearly with regular application of fertilizer P to each crop from 1992-1995 in both manured and unmanured plots. They reported that the mean P balance (addition in excess of crop removal) required to increase the level of Olsen P by 1 mg kg$^{-1}$ was 17.9 kg ha$^{-1}$ of fertilizer P in unmanured plots which was greater than 5.6 kg ha$^{-1}$ of manure plus fertilizer P in manured plots. This value of surplus fertilizer P required to increase the level of Olsen P by 1 mg kg$^{-1}$ is comparable to the 16–17 kg P ha$^{-1}$ of fertilizer P reported by Richards et al. (1995). The lower requirement for P in the manured plots suggests that manure application increases the soil's ability to retain added P in the form that can be extracted using Olsen P. This is because manure's organic matter and its decomposition products are known to reduce P sorption/fixation (Sharpley et al. 1984; Hue 1990) thereby enhancing the level of Olsen P. Conversely, Zhou et al. (1997) suggested that P sorption might increase when sufficient amounts of organic matter are present and in association with Al, Fe, and Ca compounds. In particular, the significant amount of $CaCO_3$ and organic carboxylate functional groups contained in poultry litter are thought to increase P sorption and reduce P availability by providing additional sorption sites (Brock et al. 2007; Siddique and Robinson 2003, 2004; Pote et al. 2003; Sato et al. 2005). Other studies, however, have suggested that the amounts of $CaCO_3$ contained in liquid dairy manure are insufficient to cause significant reductions in P availability (Siddique and Robinson, 2003).

### 1.3.3. Initial amount of P in soil

Another factor that could influence STP increase following the addition of fertilizer or manure is the initial amount of P in the soil. Studies by Pote et al. (2003) and Griffin et al. (2003) suggested that changes in STP might increase as initial P levels approach P saturation (Psat) thresholds. In several studies on naturally acidic soils, Psat was estimated as the ratio of M3-P over the molar sum of M3-Al and Mehlich-3 extractable Fe (Maguire and Sims 2002a, 2002b; Kleinman and Sharpley 2002). Whereas, on alkaline soils, P saturation can be estimated using $(Ca + Mg)_{M3}$, this may be due to the acid nature of Mehlich-3 extracting agent, which is able to extract other reactive forms of Ca and Mg, which could be important to soil P retention in addition to Ca and Mg on the exchange sites (Ige et al. 2005). Zhang et al. (1995) reported an increase in Mehlich-3 extractable P levels from an initial level of 104 and 120 kg P ha$^{-1}$, to 366 and 229 kg P ha$^{-1}$ when fertilizer was applied for 6 years at rates of 132 kg ha$^{-1}$ and 44 kg P ha$^{-1}$ respectively. In contrast, the initial Mehlich-3 P value of a Ste. Rosalie clay soil (32 mg P kg$^{-1}$) increased after 10 yr fertilizer application by 39 mg P kg$^{-1}$ in the normal rate plots receiving 44 kg P ha$^{-1}$ of P fertilizer and by 157 mg P kg$^{-1}$ in the high rate plots receiving 132 kg ha$^{-1}$ of P fertilizer (Zhang et al. 2004).

### 1.3.4. Rate of P application

Rate of P applied can also affect changes in soil test P. Continuous addition of amendments (organic and inorganic P sources) and the rates of application have residual effects on chernozemic soils for several years (Read et al. 1977; Bailey et al. 1977; Spratt et al. 1980). After a single large application of monocalcium phosphate fertilizer at the first year on the Waskada soil at rates of 100, 200 and 400 kg P ha$^{-1}$, Olsen-P increased from 5 mg P kg$^{-1}$ with no P applied to 45, 85 and 200 mg P kg$^{-1}$ respectively (Spratt et al. 1980). This indicates the short-

term effect of P over time. A sharp decline in Olsen-P concentration was reported for the largest rate of application over a period of 8 years, which shows the stabilization of P with time (long-term effect) and this was attributed to the interaction of the soil and fertilizer-P reaction products (Spratt et al. 1980). The Ca- and Mg-saturated soil in the Canadian prairies reacts rapidly with fertilizer-P to form a series of products with varying solubilities (with time) going from moderately soluble and plant-available forms (such as di-calcium phosphate dehydrate) to sparingly soluble octa-calcium phosphate, and to relatively insoluble and unavailable forms such as apatite (Racz and Soper 1967). It is also likely that the addition of a single large concentration of fertilizer- P (200 to 400 kg/ha) to these soils accelerated the rate of the reaction for soluble forms going to insoluble forms initially, and later these were partially released (Spratt et al. 1980). These results are similar to those of Laboski and Lamb (2003) and Kashem et al. (2004b), who also observed that available-P was reduced with time in P amended soils.

### 1.3.5. Time of P application

Influence of time on soil test P is dependent on the type of amendment, soil type and rate of application as stated by Kashem et al. (2004a). In an incubation study by Kashem et al. (2004a), phosphorus was added at rates of 0, 110, 220, 440 and 880 mg P $kg^{-1}$ for the Osborne soil and 0, 123, 307 and 614 mg P $kg^{-1}$ for the Lakeland soil in different amendments of biosolids, hog manure, cattle manure and mono-ammonium phosphate (MAP). The soils were incubated for 1, 4, 16 and 32 wk and extracted using $H_2O$, $NH_4Cl$, $NaHCO_3$ (Olsen P), and the Kelowna and Mehlich–3 extracts. Extractable P increased with increase in the rate of application for all amendments. It was found that extractable P (regardless of the extractant) slightly increased with increasing incubation time in the biosolid-amended soil. In the Osborne soil, extractable P with

MAP amendment decreased from 672 mg kg$^{-1}$ after 1 wk to 157 mg kg$^{-1}$ after 16 wk of incubation at the highest P application rate. In the Lakeland soil, the decrease in extractable P with MAP was small (from 398 to 332 mg kg$^{-1}$ for 1 wk to 16 wk respectively); this was similar to the changes with cattle manure P with incubation time. No change with incubation time was observed for extractable P with cattle manure in the Osborne soil and with hog manure in the Lakeland soil.

### 1.4. Forms of available-P

The forms of residual fertilizer P in soil can be studied using the modified Hedley's sequential extraction procedure (Hedley et al. 1982). This procedure fractionates soil P into the various P forms, starting with the labile P to the more stable P forms. This method has been used to study changes in P form in slightly weathered soils (Hedley et al. 1982; Tiessen et al. 1983; Richards et al. 1995) to highly weathered soils (Beck and Sanchez, 1994; Schmidt et al. 1996). Amidst soil P fractions, the water and bicarbonate extractable P can be related to the plant available P, while the hydroxide and acid extractable P fractions are considered as sparingly available for plant uptake. Past studies also suggested that the acid-extractable P could be an important source of P replenishment subsequent to the dissolution of Ca-P compounds, thereby, adding to the labile P pools over a long period of time (Vu et al. 2008; Wang et al. 2008).

Following the application of fertilizer to the soil, it must be converted to orthophosphate forms before plants can utilize it. Orthophosphate may exist as $H_2PO_4^-$ or $HPO_4^{2-}$ in soils depending on pH. When the soil pH is near 7.0, two orthophosphate forms can be found readily available for plant uptake. But when the pH increases above 7.0, $HPO_4^{2-}$ becomes the dominant form of available-P. Apart from soil pH, P form also depends on other soil factors such as temperature,

moisture, texture, organic matter content and crop residue incorporation.

In the soil, P can also exist as labile P, non-labile P or residual P. Labile-P ($H_2O$-P and $NaHCO_3$-P) usually occur as readily soluble or desorbable orthophosphate forms, which are available for plant uptake. As the plant takes up water soluble orthophosphate from the soil, the concentration of phosphate in solution declines and is replenished from the labile pool (Busman et al. 2009). The labile pool is the main source of available P for crops because the water-soluble P pool is very small and phosphate concentration becomes reduced as a plant takes it up. The labile and non-labile pools consist in part, of inorganic phosphate that is adsorbed to soil surfaces or precipitated in increasing amounts as the amount of phosphate in solution increases. The adsorbed phosphate ions are held on active sites on the soil surfaces. In alkaline soils (soil pH greater than 7), Ca is the dominant cation that will react with phosphate to form precipitates such as di-calcium phosphate dihydrate, octocalcium phosphate, and hydroxyapatite. Wagar et al. (1986) reported that octa-calcium phosphate (OCP), a fertilizer P reaction product, has been shown to react slowly and remain moderately available in calcareous soils for a long period. In contrast, in acidic soils (soil pH less than 5.5), Al and Fe are the dominant ions that will react with phosphate and amorphous Al and Fe phosphates often form. The amorphous Al and Fe phosphates slowly change into crystalline variscite (Al phosphate) and strengite (Fe phosphate) compounds. These processes lead to a decrease in solubility and availability of phosphate to plants.

Adding to the non-labile soil P fractions (NaOH-P and HCl-P) through fertilization increases the amount of remaining P, because the crop will not utilize most of the P fertilizer applied to the soil in the first season. The residual P fraction is made up of inorganic phosphate compounds that are sparingly soluble and organic compounds that are resistant to mineralization by

microorganisms in the soil. Continuous application of more P than crop removal increases phosphate in this pool, which may remain in soils for years without being made available to plants (Busman et al. 2009).

## 1.5. Transformation of P added to soils

Treating mined rock phosphate with acid to aid its solubility led to the majority of phosphate fertilizers produced. When phosphate fertilizers come in contact with the soil, they are initially quite soluble and available until the occurrence of different reactions that reduce the P solubility and availability. These reactions are governed by soil factors such as pH, moisture or water content, temperature and soil minerals present. Phosphate fertilizers begin dissolving on contact with the soil moisture, and there is a slow movement of phosphate ions in solution away from the fertilizer particles. The phosphate ions are mainly adsorbed on surfaces of soil particles or can be precipitated by soil cations such as Ca, Al, Mg and Fe. The adsorbed phosphate gradually forms more insoluble compounds over time, causing the phosphate to become fixed and unavailable (Busman et al. 2002).

On calcareous soils, long-term application of fertilizer in excess of P removal by crops increases both the labile ($H_2O$-P and $NaHCO_3$-P) and non-labile P (NaOH-P and HCl-P) forms as well as residual P (Vu et al. 2008). Previous findings also reported increase in these P pools after long-term application of P fertilizers in other soil types (McKenzie et al. 1992; Tiessen and Moir 1993; Linquist et al. 1997). It has also been found that long-term application of cattle manure increases the $P_i$ forms in the labile, moderately labile and total soil P content (MnKeni and McKenzie 1985; Dormaar and Chang 1995; Tran and N'dayegamiye 1995). Zhang et al. (2004) found that addition of fertilizer either annually at high rates, or with accumulated time, increased

NaOH-$P_i$ at a rate of 6.9 mg P $kg^{-1}$ $yr^{-1}$ and 34.3 mg P $kg^{-1}$ $yr^{-1}$ during the first 6 yr and the following 4 yr respectively. Zhang et al. (2004) also found that increased fertilizer addition linearly increased NaHCO$_3$-$P_i$ at a rate of 15.7 mg P $kg^{-1}$ $yr^{-1}$ and 18.1 mg P $kg^{-1}$ $yr^{-1}$ for the first 6 yr and the following 4 yr. The great rate of increase during the later part of the study was attributed in NaHCO$_3$-P and NaOH-P fractions to the saturation of the sorption sites on the soil particles. Kashem et al. (2004b) reported that an increase in the application rate of P fertilizer to the soil in a laboratory incubation study resulted in a proportionate increase of the NaHCO$_3$-P fraction, indicating the short-term effect of P addition. The increase in the labile P fraction indicates that as the capacity of the soil to retain added P in stable fractions diminishes, so does the strength of retention, which can lead to increased risk of P losses to surface waters.

Vu et al. (2008) found that long-term application of P fertilizer resulted in increases in the inorganic fractions of H$_2$O-, NaHCO$_3$-, NaOH-, HCl-P as well as the residual P. Significant increase in the residual P fraction suggested that the applied P was increasingly precipitated at higher rates of P application. This was consistent with the findings of Bertrand et al. (2003) that the applied P was mainly precipitated in highly calcareous soils in South Australia but was dissolved by NaHCO$_3$ extractant.

According to Qian et al. (2004), repeated addition of manure in black chernozemic soil results in a significant increase in labile inorganic P, which accounted for 15% of the total soil P. The P forms loosely sorbed on the soil surface relates to the labile inorganic P, resin-P & NaHCO$_3$-$P_i$ (Chauhan et al. 1981) and NaHCO$_3$-$P_o$ corresponds to the easily mineralizable organic P (Bowman and Cole 1978).

The moderately labile P (NaOH-P fraction) can replenish the soil labile P for plant uptake when the labile P pool is diminished (Tiessen et al. 1984; Ivarsson 1990). It was also reported that soil

NaOH-$P_i$ is held strongly by chemisorption to Fe and Al components of soil surfaces which is considered as moderately labile soil P (Ryden et al. 1977; McLaughlin et al. 1977). Addition and depletion of P fertilizer has no significant effect on HCl-$P_i$, moderately stable fraction (Zhang et al. 2004). It has been suggested that HCl-$P_i$ represents the primary mineral P (apatite) and it's not readily available to plants (William et al. 1980). In a long-term winter wheat experiment carried out on a calcareous soil, path coefficients showed that a labile P pool, octa-calcium phosphate ($Ca_8$-P), accumulated due to the transformation from other fractions ($Ca_2$-P and Al-P) after continuous inorganic fertilizer application, thereby contributing to soil available P (Wang et al. 2010). Shen et al. (2004) found that labile P ($Ca_2$-P, $Ca_8$-P, and Al-P) could be readily fixed into non-labile P (Fe-P, occluded P, and $Ca_{10}$-P) due to its association with hydrous Fe oxides and calcareous compounds in calcareous soils. Path analysis technique suggests that transformation between P fractions is dependent on the nutrient sources, soil developmental stage, management systems and soil properties (Zheng et al., 2002; Tiessen et al., 1984). Zheng et al. (2002) reported that 86% of the resin-P originated from inorganic P fertilizer addition but in the dairy manure system, added organic P was transformed into NaOH-$P_o$ and $NaHCO_3$-$P_o$. Thus, moderately labile NaOH-$P_o$ acted as the source of labile $NaHCO_3$-$P_o$ and $P_i$ in this system. This shows that the labile $P_i$ pools resulted from the mineralization of the moderately labile NaOH-$P_o$ pool. Therefore, transformations of P fractions are dependent on factors like P uptake by plants, soil microbial activities, root exudation, and other rhizosphere processes (Negassa and Leinweber, 2009).

In order to regulate P concentration in agricultural soils and reduce P losses to the environment, the climatic conditions, soil type, soil test P method used, as well as the rate of fertilizer P applied to soil has to be taken into consideration. The new regulations for agricultural P

management in Manitoba require different P management strategies for different soil test P values. The regulatory thresholds are based on Olsen-P test owing to its agronomic popularity in the province and the strong relationship between runoff P and Olsen-P (Sawka 2009). Soil phosphorus (Olsen-P) test values of 0-5, 5-10, 10-15, 15-20, 20 and above 20 ppm has been rated in Manitoba as very agronomically low, low, medium, high, very high and very high plus, respectively (MAFRI 2007). These soil test values go together with the recommended fertilizer placement rates either as seed-placed, side banded, banded or broadcasted for each crop type. Knowing the rate at which soil test P values change with fertilizer surpluses and deficits for each soil type will be valuable for P management by Manitoba farmers.

Therefore, there's need to determine the method for estimating changes in soil test P values with fertilizer addition or depletion on several soils. The hypotheses of this research are that (i) labile P fractions will increase more than the non-labile P fractions with continuous application of P fertilizer in excess of crop removal and P fractions that increase substantially during the accumulation stage will decline substantially during the depletion stage (chapter 2; the fractionation study), (ii) Soil test P will increase with time under continuous P application in excess of crop removal for different soil types and it will decrease during P depletion stage for different soil types (chapter 3; the extraction study).

### 1.6. References

Agbenin, J.O. and H. Tiessen. 1994. P transformations in a topo-sequence of Lithosols and Cambisols from semi-arid northern Brazil. Geoderma 62:345–362.

Alberta Agriculture and Rural Development. 2008. Agronomic thresholds for soil phosphorus in Alberta: Basis for fertilizer recommendations in Alberta. [Online] Available: http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/sag6746 [February 2012].

Alloway, B. J. and E. Steinnes. 1999. Anthropogenic additions of cadmium to soils. In:

McLaughlin MJ, Singh BR (eds) Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, pp 97–123.

Ashworth, J. and K. Mrazek. 1995. "Modified Kelowna" test for available phosphorus and potassium in soil. Commun. Soil Sci. Plant Anal. 26: 731–739.

Bailey, L. D., E. D. Spratt, D. W. L. Read, F. G. Warder and W. S. Ferguson. 1977. Residual effects of phosphorus fertilizer. II. For wheat and flax grown on Chernozemic soils in Manitoba. Can. J. Soil Sci. 57:263-270.

Barber, S.A. 1979. Soil phosphorus after 25 years of cropping with five rates of phosphorus application. Commun. Soil Sci. Plant Anal. 10: 1459–1468.

Beck, M.A., and P.A. Sanchez. 1994. Soil phosphorus fraction dynamics during 18 years of cultivation on a Typic Paleudult. Soil Sci. Soc. Am. J. 34:1424–1431.

Bertrand, I., R. E. Holloway, R. D. Armstrong and M. J. McLaughlin. 2003. Chemical characteristics of phosphorus in alkaline soils from southern Australia. Aust. J. Soil Res 41:61-76.

Bowman, R. A. and C. V. Cole. 1978. An exploratory method for fractionation of organic phosphorus from grassland soils. Soil Sci. 125: 95–101.

Brock, E.H., Q.M. Ketterings and P.J.A. Kleinman. 2007. Measuring and predicting P sorption capacity of manure amended soils. Soil Sci. 172:266–278.

Busman, L., J. Lamb, G. Randall, G. Rehm and M. Schmitt. 2009. The nature of phosphorus in soils. University of Minnesota, Minnesota Extension Service. WW-06795-GO.

Cai, T. T., T. W. Olsen, R. S. Yost and J. A. Silva. 1997. Performance indices for tests of soil nutrient status: Extractable phosphorus, Commun. Soil Sci. Plant Anal. 28:3-5, 329-339.

Casson, J.P., D.R. Bennett, S.C. Nolan, B.M. Olson and G.R. Ontkean. 2006. Degree of phosphorus saturation thresholds in manure-amended soils of Alberta. J. Environ Qual. 35: 2212-2221.

Chang, C., T. G. Sommerfeldt and T. Entz. 1991. Soil chemistry after eleven annual application of cattle feedlot manure. J. Environ. Qual. 20: 475–480.

Chauhan, B. S., J. W. B. Stewart and E. A. Paul. 1981. Effect of labile inorganic phosphate status and organic carbon additions in the microbial uptake of phosphorus in soil. Can. J. Soil Sci. 61: 373–385.

Ciampitti, I.A., F.O. García, L.I. Picone, and G. Rubio. 2011. Phosphorus budget and soil extractable dynamics in field crop rotations in Mollisols. Soil Sci. Soc. Am. J. 75:131–142.

Cope, J.T., Jr. 1981. Eff ects of 50 years of fertilization with phosphorus and potassium on soil test levels and yields at six locations. Soil Sci. Soc. Am. J. 45:342–347.

Corey, R. B. 1987. Soil testing procedures: Correlation, pp. 15-21. In: J.R. Brown (ed.), Soil Testing: Sampling, Correlation, Calibration, and Interpretation. Spec. Publ. 21. Soil Sci. Soc. Am. Madison, WI.

Dormaar, J. F. and C. Chang. 1995. Effect of 20 annual applications of excess feedlot manure on labile soil phosphorus. Can. J. Soil Sci. 75: 507–512.

Eghball, B. and J. F. Power. 1995. Composted and non-composted beef feedlot manure effects on corn production and soil properties under conventional and no-till systems. Pages 557–563 *in* C. C. Ross, ed. Seventh International Symposium on Agricultural and Food Proceeding Wastes. American Association of Agric. Engineers, St. Joseph, MI.

Fixen, P.E. and J. H. Grove. 1990. Testing soils for phosphorus, pp. 141-180. In: R.L. Westerman (ed.), Soil Testing and Plant Analysis. 3rd ed. SSSA Book Series 3. Soil Science Society of America, Madison, WI.

Gartley, K.L. and J. T. Sims. 1994. Phosphorus soil testing: Environmental uses and implications. Commun. Soil Sci. Plant Anal. 25: 1565–1582.

Griffin, T. S., C. W. Honeycutt and Z. He. 2003. Changes in soil phosphorus from manure application. Soil Sci. Soc. Am. J. 67: 645–653. 15.

Haden, V.R., Q. M. Ketterings and J.E. Kahabka. 2006. Factors affecting change in soil test phosphorous following manure and fertilizer application. Soil Sci. Soc. Am. J. 71:1225–1232.

Hedley M. and M. McLaughlin. 2005. Reactions of phosphate fertilizers and by-products in soils. In: Sims JT, Sharpley AN (ed) Phosphorus: agriculture and the environment. Agronomy Monograph no 46, ASA-CSSA-SSSA, Madison, WI, USA, pp 181–252.

Hue, N.V. 1990. Interaction of Ca(H2PO4)2 applied to an Oxisol and previous sludge amendment: Soil and crop response. Commun. Soil Sci. Plant Anal. 21:61–73.

Ige, D. V., O. O. Akinremi and D. N. Flaten. 2005. Environmental index for estimating the risk of P loss in calcareous soils of Manitoba. J. Environ. Qual. 34: 1944–1951.

Ige, D. V., O. O. Akinremi, D. N. Flaten and M. A. Kashem. 2006. Comparison of soil test phosphorus methods in neutral to calcareous Manitoba soils. Can. J. Soil Sci. 86: 691–699.

Ivarsson, K. 1990. The long-term soil fertility experiments in southern Sweden. IV. Changes in inorganic and organic soil phosphorus after a pot trial. Acta Agric. Scand. 40: 205–215.

Kashem, M.A., O.O. Akinremi, and G.J. Racz. 2004a. Extractable phosphorus in alkaline soils amended with high rates of organic and inorganic phosphorus. Can. J. Soil Sci. 84(4): 459–467.

Kashem, M.A., O.O. Akinremi, and G.J. Racz. 2004b. Phosphorus fractions in soil amended with organic and inorganic phosphorus sources. Can. J. Soil Sci. 84(1): 83–90.

Kleinman, P.J.A. and A.N. Sharpley. 2002. Estimating soil phosphorus sorption saturation from Mehlich-3 data. Commun. Soil Sci. Plant Anal. 33:1825–1839.

Kumaragamage, D., D. Flaten, O.O. Akinremi, C. Sawka, and F. Zvomuya. 2011. Soil test phosphorus changes and phosphorus runoff losses in incubated soils treated with livestock manures and synthetic fertilizer. Can. J. Soil Sci. 91(3): 375–384.

Laboski, C. A. M. and J. A. Lamb. 2003. Changes in soil test phosphorus concentration after application of manure or fertilizer. Soil Sci. Soc. Am. J. 67: 544–554.

Linquist, B. A., P. W. Singleton, R. S. Yost and K. G. Cassman. 1997b. Aggregate size effects on the sorption and release of phosphorus in an Ultisol. Soil Sci. Soc. Am. J. 61:160–166.

Linquist, B.A., P.W. Singleton and K.G. Cassman. 1997. Inorganic and organic phosphorus dynamics during a build-up and decline of available phosphorus in an Ultisol. Soil Sci. 162:254-264.

Maguire, R.O. and J.T. Sims. 2002a. Measuring agronomic and environmental soil phosphorus saturation and predicting phosphorus leaching with Mehlich 3. Soil Sci. Soc. Am. J. 66:2033–2039.

Maguire, R.O., and J.T. Sims. 2002b. Soil testing to predict phosphorus leaching. J. Environ. Qual. 31:1601–1609.

Maguire, R.O., W.J. Chardon and R.R. Simard. 2005. Assessing potential environmental impacts

of soil phosphorus by soil testing. *In* Phosphorus: Agriculture and the Environment. J.T. Sims and A.N. Sharpley (eds) Pp. 145-180.

MAFRI. 2007. Manitoba soil fertility guide. Manitoba Agriculture, Food, and Rural Initiatives. Winnipeg, MB. Available: http://www.gov.mb.ca/agriculture/crops/soil-fertility/soil-fertility-guide/fertilizer-guidelines-for-soil-tests.html.

Manitoba Phosphorus Expert Committee. 2006. Recommendations for regulating phosphorus from livestock operations in Manitoba. Final report by the Manitoba Phosphorus Expert Committee to the Manitoba Minister of Conservation. 32 pp.

McDowell, R.W. and A.N. Sharpley. 2004. Variation of phosphorus leached from Pennsylvanian soils amended with manures, composts or inorganic fertilizer. Agric. Ecosyst. Environ. 102:17–27. 16.

McKenzie, R. H. and E. Bremer. 2003. Relationship of soil phosphorus fractions to phosphorus soil tests and fertilizer response. Can. J. Soil Sci. 83:443-449.

McKenzie, R. H., J. W. B. Stewart, J. F. Dormaar and G. B. Schaalje. 1992. Long-term crop rotation and fertilizer effects on phosphorus transformations. II. In a Luvisolic soil. Can. J. Soil Sci. 72:581-589.

McLaughlin, J. R., J. C. Reyden and G. K. Syers. 1977. Development and evaluation of a kinetic model to describe phosphate sorption by hydrous ferric oxide gels. Geoderma 18:295-307.

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15: 1409–1416.

MnKeni, P. N. S. and A. F. McKenzie. 1985. Retention of ortho- and polyphosphates in some Quebec soils as affected by added organic residues and calcium carbonate. Can. J. Soil Sci. 65: 575–585.

O'Halloran, I.P., J.W.B. Stewart and R.G. Kachanoski. 1987. Influence of texture and management practices on forms and distribution of soil phosphorus. Can. J. Soil Sci. 67:147–163.

Olsen, S. R., C. V. Cole, F. S. Watanabe and L. A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA circular 939. U.S. Government Printing Office, Washington, DC.

Pautler, M.C. and J.T. Sims. 2000. Relationship between soil test phosphorus, soluble phosphorus, and phosphorus saturation in Delaware soils. Soil Sci. Soc. Am. J. 64: 765-773.

Pote, D.H., J.A. Lory and H. Zhang. 2003. Does initial P level affect water extractable P response to applied P? Adv. Environ. Res. 7:503–509.

Qian, P., J. J. Schoenau and J. J. Karamanos. 1994. Simultaneous extraction of available phosphorus and potassium with a new soil test: a modification of the Kelowna extraction. Commun. Soil Sci. Plant Anal. 25: 627–635.

Qian, P., J. J. Schoenau, T. Wu and P. Mooleki. 2004. Phosphorus amounts and distribution in a Saskatchewan soil after five years of swine and cattle manure application. Can. J. Soil Sci. 84: 275–281.

Racz, G. J. 1979. Release of P in organic soils under aerobic and anaerobic conditions. Can. J. Soil Sci. 59: 337–339.

Racz, G. J. and R. J. Soper.1967. Reaction products of orthophosphates in soils containing varying amounts of calcium and magnesium. Can. J. Soil Sci. 47:223–230.

Randall, G.W., T.K. Iragavarapu, and S.D. Evans. 1997. Long-term P and K applications: I. Effect on soil test incline and decline rates and critical soil test levels. J. Prod. Agric. 10:565–571.

Read, D. W. L., E. D. Spratt, L. D. Bailey and F. G. Warder. 1977. Residual effects of phosphorus fertilizer.I. For wheat grown on four Chernozemic soil types of Saskatchewan and Manitoba. Can. J. Soil Sci. 57:255-262.

Read, D. W. L., E. D. Spratt, F. G. Bailey, F. G. Warder and W. S. Ferguson. 1973. Residual value of phosphatic fertilizer on Chernozemic soil. Can. J. Soil Sci. 53:389 -398.

Reddy, D. D., A. S. Rao and P. N. Takkar. 1999. Effects of repeated manure and fertilizer phosphorus additions on soil phosphorus dynamics under a soybean-wheat rotation. Biol Fertil Soils 28 :150–155.

Richards, J. E., T. E. Bates and S. C. Shepherd. 1995. Changes in forms and distribution of soil phosphorus due to long term corn production. Can. J. Soil Sci. 75:311–318.

Roberts, T. L. 1992. Phosphate management for small grains in western Canada. Proc. 35th Ann. Man. Soil Sci. Soc. Proc., Winnipeg, MB. Jan. 06-07.

Ryden, J. C., J. R. McLaughlin and J. K. Syers. 1977. Mechanisms of phosphate sorption of soils

and hydrous ferric oxide gel. J. Sci. 28:72–92. 17.

Sawka, C.A.D. 2009. Relationship between chemical analyses of P in soil and P loss in simulated runoff. Available at http://mspace.lib.umanitoba.ca/xmlui/bitstream/handle/1993/21586/Sawka_Relationship_between.pdf?sequence=1&isAllowed=y (verified 10 August 2016).

Schmidt, J.P., S.W. Buol and E.J. Kamprath.1996. Soil phosphorus dynamics during seventeen years of continuous cultivation: fractionation analyses. Soil Sci. Soc. Am. J. 60: 1168–1172.

Self-Davis, M. L., P. A. Moore, Jr. and B. C. Joern. 2000. Determination of water or dilute salt extractable phosphorus in soils. Pages 24–26 in G. M. Pierzynski, ed. Methods of phosphorus analysis for soils, sediments, residuals and waters. Southern Cooperative Series Bull. No 396. Kansas State University, Manhattan, KS.

Selles, F., C. A. Campbell, R. P. Zentner, D. James, and P. Basnyat. 2007. Withholding phosphorus after long-term additions -soil & crop responses. Better Crops with Plant Food 91 (4): 19-21.

Sharpley, A.N., J.L. Weld, D.B. Beegle, P.J.A. Kleinman, W.J. Gburek, P.A. Moore, Jr., and G. Mullins. 2003. Development of phosphorus indices for nutrient management planning strategies in the United States. J. Soil Water Conserv. 58:137–152.

Sharpley, A.N., S.J. Smith, J.W.B. Stewart, and A.C. Mathers. 1984. Phosphorus forms in soil receiving cattle feedlot waste. J. Environ. Qual. 13:211–215.

Siddique, M.T. and J.S. Robinson. 2003. Phosphorus sorption and availability in soils amended with animal manures and sewage sludge. J. Environ. Qual. 32:1114–1121.

Sims, J. T., R. O. Maguire, A. B. Leytem, K. L. Gartley, and M. C. Pautler. 2002. Evaluation of Mehlich 3 as an agri-environ- mental soil phosphorus test for the mid Atlantic Unites States of America. Soil Sci. Soc. Am. J. 66: 2016–2032.

Spratt, E. D., F. G. Warder, L. D. Bailey, and D. W. L. Read. 1980. Measurement of fertilizer phosphorus residues and its utilization. Soil Sci. Soc. Am. J. 44: l2OO-1204.

Syers, J. K., A. E. Johnston, and D. Curtin. 2008. Efficiency of soil and fertilizer phosphorus use. FAO Fertilizer and Plant Nutrition Bulletin 18, FAO, Rome, Italy.

Tiessen H. and J.O. Moir. 1993. Characterisation of available P by sequential extraction. In: Carter MR (ed) Soil sampling and methods of analysis. Lewis, London, pp 75–86.

Tiessen, H., J.W.B. Stewart, and J.O. Moir. 1983. Changes in organic and inorganic phosphorus composition of two grassland soils and their particle size fractions during 60–90 years of cultivation. J. Soil Sci. 34:815–823.

Tiessen, H., J. W. B. Stewart, and C. V. Cole. 1984. Pathways of phosphorus transformations in soils of differing pedogenesis. Soil Sci. Soc. Am. J. 48: 853–858.

Tran, T. S. and A. N'dayegamiye. 1995. Long-term effects of fertilizers and manure application on the forms and availability of soil phosphorus. Can. J. Soil Sci. 75: 281–285.

Van Leirop, W. 1988. Determination of available phosphorus in acid and calcareous soils with Kelowna multiple element extractant. Soil Sci. 146: 284–291.

Vu, D. T., C. Tang, and R. D. Armstrong. 2008. Changes and availability of P fractions following 65 years of P application to a calcareous soil in a Mediterranean climate. Plant Soil 304:21–33.

Wagar, B. I., J. W. B. Stewart, and J. L. Henry. 1986. Comparison of single large broadcast and small annual seed-placed phosphorus treatments on yield, and phosphorus and zinc contents of wheat on chernozemic soils. Can. J. Soil Sci. 66: (in press).

Webb, J.R., A.P. Mallarino, and A.M. Blackmer. 1992. Effects of residual and annually applied phosphorus on soil test values and yields of corn and soybean. J. Prod. Agric. 5:148–152.

Zhang, T. Q., A. F. MacKenzie and B. C. Liang. 1995. Long-term changes in Mehlich-3 extractable P and K in a sandy clay loam soil under continuous corn (*Zea mays* L.). Can. J. Soil Sci. 75: 361–367.

Zhang, T. Q., A. F. Mackenzie, B. C. Liang and C. F. Drury. 2004. Soil test phosphorus and phosphorus fractions with long-term phosphorus addition and depletion. Soil Sci. Soc. Am. J. 68:519–528.

Zhou, M., and Y. Li. 2001. Phosphorus-sorption characteristics of soils and limestone from the Southern Everglades and adjacent farmlands. Soil Sci. Soc. Am. J. 65:1404–1412.

Zhou, M., R.D. Rhue and W.G. Harris.1997. Phosphorus sorption characteristics of Bh and Bt horizons from sandy Coastal Plain soils. Soil Sci. Soc. Am. J. 61:1364–1369.

## 2. CHANGES IN PHOSPHORUS FORMS AND FRACTIONS FOLLOWING CONTINUOUS ADDITION OF PHOSPHORUS FERTILIZER IN CONTRASTING PRAIRIE SOILS

### 2.1. Abstract

Continuous application of phosphorus fertilizer can lead to an increase in both labile and non-labile phosphorus pools. A laboratory experiment was carried out to determine the effect of continuous P application, in excess of crop removal on the labile and non-labile P fractions of the soils and how these fractions changed once the P addition has stopped. Phosphorus was added at a rate of 80 kg P ha$^{-1}$ at five different sites under durum wheat-flax cropping sequence for 6 years followed by a 3-year P depletion phase during which no more P fertilizer was added. Five P fractions were measured in the 0 – 7.5 cm depth of these soils, using a modified Hedley's P fractionation procedure. Results, presented as proportion of total P, showed that during P accumulation phase, $H_2O$-P and $NaHCO_3$-P increased significantly at all the sites. Cropping these soils for 3 years without P resulted in a significant decline in the $H_2O$-P fraction whereas no significant difference was observed in the $NaHCO_3$-P fraction. In contrast, the recalcitrant or non-labile P (HCl-P and Residual-P) showed a significant decrease in the accumulation phase except NaOH-P fraction. In the depletion phase, NaOH-P significantly declined but HCl-P and Residual-P fractions increased significantly. This shows that most of the added P ended up in the labile P fraction, which was the fraction that was also depleted during the depletion phase.

The results indicate that there was a significant increase in labile-P and non-labile P fractions with continuous P fertilizer addition.

### 2.2. Introduction

One of the major nutrients limiting plant growth is phosphorus (P). Availability of soil P can be augmented by addition of P fertilizer to the soil. However, continuous addition of fertilizer in

excess of crop removal can lead to P loading thus increasing the possibility for P loss to surface waters with the potential to cause eutrophication (McDowell et al. 2001). Phosphorus availability in the soil is regulated by geochemical and biological processes (Cross and Schlesinger 1995). The geochemical processes of P cycle are initially governed by soil parent material and gradually by soil properties, and in turn, climate and parent material determine the overall weathering rate (Cross and Schlesinger 1995). As the soil develops, the proportion of the total P in various forms changes (Walker and Syers 1976). When plants and microbes take up the P required for their growth, the immobilized P is returned to the soil through mineralization following the death of organisms. Both decomposition and mineralization process makes inorganic phosphorus available in the soil solution. Transformation of inorganic P into stable forms of organic and inorganic P in soil happens through biological and geochemical processes over time (Cross and Schlesinger 1995; Soinne 2009).

The P cycle is controlled by reactions such as precipitation, sorption, desorption, solubilization, leaching, mineralization and immobilization. Solubilization of apatite P, the primary mineral source of P in soils, occurs through weathering processes. However, the pH of the soil solution determines the ionic form of the solubilized P; $H_2PO_4^-$ being the predominant form in acidic soils and $HPO_4^{2-}$ in alkaline soils. This solubilized P can either be leached from the soil, sorbed and geochemically fixed unto iron (Fe) and aluminium (Al) oxides and edges of clay particles, precipitated as calcium (Ca), Fe-, or Al- minerals or absorbed by living organisms. Desorption of P from the sorption sites can occur following a decrease in soil solution P concentration or by an increase in pH. Thus, P sorption and desorption is determined by soil temperature, pH, P concentration and ionic strength of the soil solution (Soinne 2009).

Soil P fractions are important in determining the availability of P in soil. The soil P pool is made

up of the inorganic and organic P fractions but the latter is often the most dominant pool. The soil P fractions also include the non-occluded labile fractions ($H_2O$- and $NaHCO_3$-P), the non-occluded Fe- and Al- bound P (NaOH-P), the occluded Ca-bound P (HCl-P) and stable occluded P (Residual P). Sequential fractionation techniques can be used to separate and characterize soil P fractions using different extraction solutions of varying strengths. The fractionated P can generally be classified into two forms, the labile P and the recalcitrant P. There are different fractionation methods for determining available P in different soil types (Wang et al. 2010). The modified Hedley procedure has been used to study changes in P form in soils ranging from slightly weathered (Hedley et al. 1982; Tiessen et al. 1983; Richards et al. 1995) to highly weathered (Beck and Sanchez 1994; Schmidt et al. 1996). In the modified Hedley fractionation technique, the labile P is the sum of $H_2O$- and $NaHCO_3$- P, which represents the short-term plant available P that is rapidly dissolved and desorbed from the surface of soil particles. Non-labile or recalcitrant P represents the NaOH-, HCl-, and residual P fractions that are in the mineral, organic or organo-mineral complexes that are not readily available to plants. The NaOH-P is noted to be of lower plant availability and HCl-P fractions are considered biologically and chemically inactive and not readily available because of their low solubility in mild extractants. The non-occluded P ($H_2O$-, $NaHCO_3$- and NaOH-P) is considered to be biologically available, and occluded P (HCl- and residual P) is thought to be available only on a long-term basis (Cross and Schlesinger 1995).

A recent study by Vu et al. (2008) reported that long term fertilizer application on calcareous soil increased both the labile ($H_2O$-P and $NaHCO_3$-P) and non-labile P (NaOH-P and HCl-P) forms as well as residual P. The authors reported that 43 % of fertilizer P applied to a calcareous sandy soil was in the labile P fraction. The stable HCl-$P_i$ fraction was not significantly affected by P

25

application rates but residual P was found to increase significantly with increased P application rates. Past studies by Wang et al. (2007) showed that the addition of triple super phosphate (TSP) fertilizer at a rate of 20 kg P ha$^{-1}$ to a black Vertisol soil in south-east Queensland resulted in a two-fold increase in resin-P and $NaHCO_3$-$P_i$ fractions at 0-0.10 m depth. A 25 % and 10 % increase in NaOH- and HCl-$P_i$, respectively, was also reported but a 15 % decrease in the residual P occurred at the 0-0.10 m depth. The predominant fraction, HCl-P and residual P, constituted about 75 % of the soil P fractions after P addition. In a laboratory study with Manitoba soils, Kashem et al. (2004b) reported a significant increase in the various P fractions ($H_2O$-, $NaHCO_3$-, NaOH- and HCl-P) except the residual P with rates of P addition from fertilizer P and other amendments. The authors also found that the proportion of labile P fractions increased from 10 % of total P in the control soils to 37 % of total P when 614 mg kg$^{-1}$ fertilizer P was added. While many studies have been conducted elsewhere on the effect of continuous application of P fertilizer on soil P fractions, very few studies have been carried out under field conditions in the Canadian prairies. Better understanding of the fate of fertilizer P in soils of the prairies will help to improve nutrient sustainability and P utilization for long-term benefits of crops.

The hypothesis of this research is that labile P fraction will increase more than the non-labile P fractions with continuous addition of P fertilizer and also that the P fractions that increased during the addition stage will decline during the P depletion stage. Therefore the objective of this study is to determine the effect of continuous P addition in excess of crop removal on the labile and non-labile P fractions of the soils and to determine what happens to these P fractions during the P depletion years.

## 2.3. Materials and Methods

### 2.3.1. Site description, treatments and experimental design

This study was carried out at seven locations across the three prairies provinces of Alberta (Ellerslie, Fort Saskatchewan and Carstairs), Saskatchewan (Sylvania) and Manitoba (Carman, East of Spruce, and Forrest), Canada from 2003 to 2009 with a focus on P accumulation. Starting from 2010, P addition was stopped and the study was continued until 2012 to focus on P depletion. During the P accumulation stage, four rates of P, namely 0, 20, 40 and 80 kg P ha$^{-1}$ were applied each year, using three sources of granular commercial mono-ammonium phosphate (MAP) fertilizers containing low (4 ppm), moderate (70 ppm) or high (230 ppm) concentrations of cadmium (Cd), for a total of 10 treatments with four replications at each site in a randomized complete block design (RCBD). The low Cd MAP fertilizer originated from Kapuskasing (Ontario), the moderate Cd level was from North Carolina (USA), while the high Cd MAP was from Idaho (USA). The plot size was approximately 5m by 2m with some variability across sites, depending on the local equipment that was used to manage the plots. The first 20 kg P ha$^{-1}$ of MAP fertilizer was side-banded during seeding. The remaining MAP and Urea-N were broadcast and incorporated prior to seeding. Urea fertilizer (46-0-0) was applied to supplement the N supplied by MAP treatments and to meet crop N requirements (90 kg N ha$^{-1}$ for durum wheat, 50 kg N ha$^{-1}$ for flax). The sites were cropped annually using a durum wheat-flax cropping sequence. Durum wheat (AC Avonlea cultivar) was seeded at a rate of 136 kg ha$^{-1}$ in even years and flax (AC Lightning cultivar) at a rate of 40 kg ha$^{-1}$ in odd years. Herbicides were applied to control weeds such as lamb's-quarters, volunteer canola, smartweed, wild buckwheat, redroot pigweed, green foxtail, and wild oat. Due to poor weather conditions, the experiment at Carstairs was not established in 2003 while in 2009, the Sylvania site was affected by flooding; thus, there

was no data available for these years and these two sites were not included in our analysis.

## 2.3.2. Soil sampling

Soil samples were collected at 0 - 7.5 cm depth in fall of 2003, 2009 and 2012. The samples were air-dried and ground to pass through a 2-mm size sieve. The chemical properties such as pH, organic carbon and cation exchange capacity were adapted from Grant et al. (2013) as seen in Table 2.1. Mehlich-3 P was extracted using Mehlich-3 extracting reagent and analyzed for Mehlich-3 extractable phosphorus, iron, calcium and magnesium using the inductively coupled plasma (ICP) emission spectroscopy. The particle size distribution was determined using the pipette method (Carter and Gregorich 2008).

**Table 2.1 Physicochemical properties of research sites (0 – 7.5 cm depth)**

| Site | Soil Type | pH[a] | CEC[a] cmol kg$^{-1}$ | Organic C[a] mg kg$^{-1}$ | Clay[c] % | Silt[c] % | Sand[c] % | M3-Fe[b] mg kg$^{-1}$ | M3-Ca[b] mg kg$^{-1}$ | M3-Mg[b] mg kg$^{-1}$ | M3-P[b] mg kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| East of Spruce | Orthic Black Chernozem | 7.4 | 34 | 28 | 36 | 38 | 26 | 8 | 499 | 26 | 4 |
| Carman | Orthic Black Chernozem | 5.0 | 16 | 37 | 19 | 14 | 67 | 29 | 204 | 11 | 7 |
| Forrest | Orthic Black Chernozem | 7.4 | 35 | 38 | 22 | 32 | 46 | 10 | 478 | 20 | 3 |
| Ellerslie | Eluviated Black Chernozem | 6.2 | 42 | 40 | 43 | 42 | 15 | 29 | 538 | 19 | 4 |
| Fort Sask. | Eluviated Black Chernozem | 7.3 | 42 | 51 | 35 | 43 | 22 | 17 | 620 | 22 | 6 |

[a] pH, CEC, Organic C: sampled at 0 -15 cm depth in year 2003, adapted from Grant et al. (2013)

[b] M3-Fe, Mehlich-3 extractable Fe; M3-Ca, Mehlich-3 extractable Ca; M3-Mg, Mehlich-3 extractable Mg; M3-P, Mehlich-3 extractable P (values obtained at 0 - 7.5cm depth interval from samples taken in 2012)

[c] Clay, Silt, Sand (values obtained at 0 – 7.5 cm depth interval from samples taken in 2012)
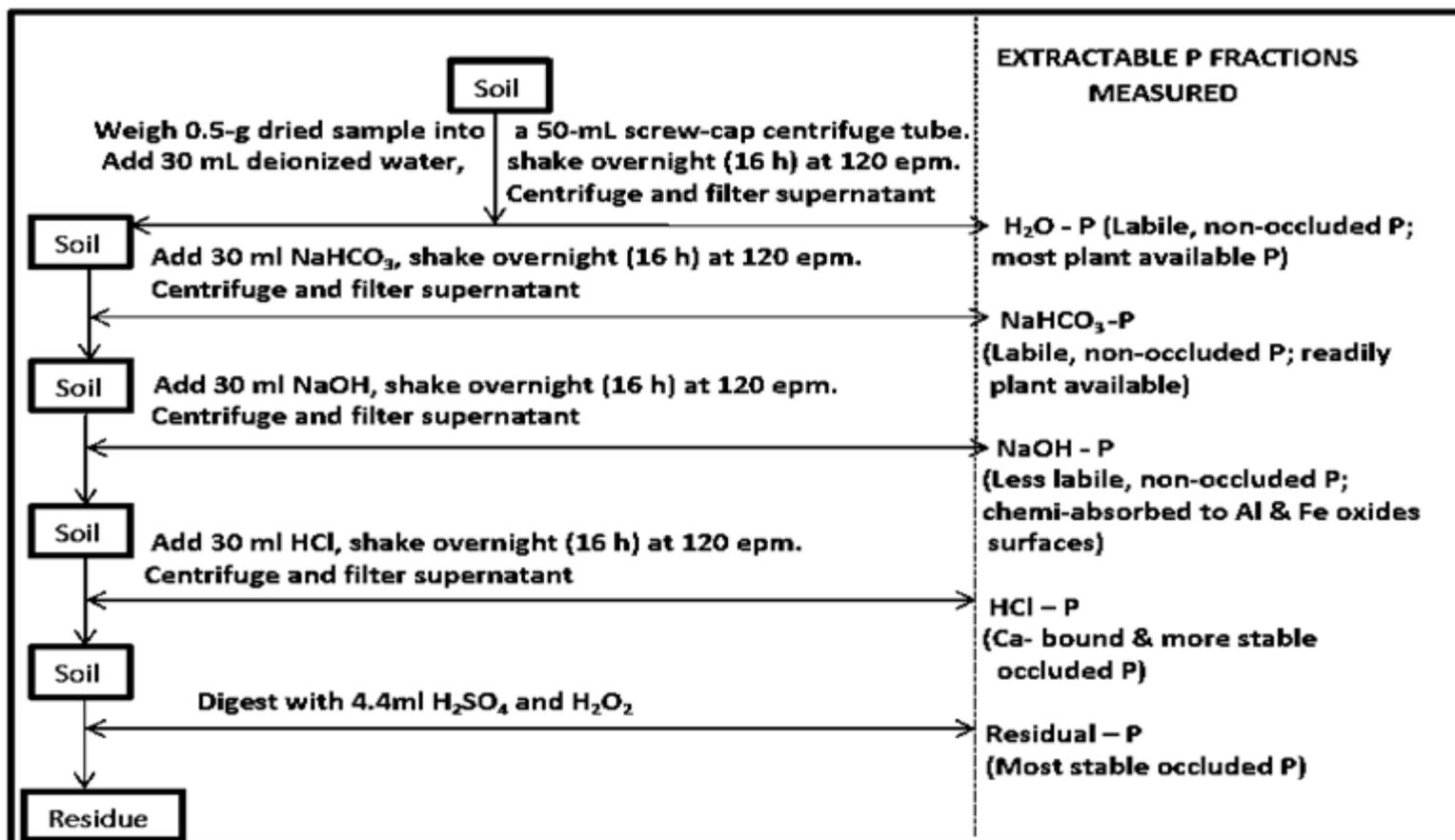
**Figure 2.1** Modified Hedley sequential fractionation procedure

### 2.3.3. Sequential extraction of phosphorus

A modified Hedley procedure was used in this sequential extraction experiment (Hedley et al. 1982). A 0.5-g soil sample was weighed into a 50 mL centrifuge tube and extracted sequentially with 30 mL deionized water, 0.5 M NaHCO$_3$ (pH = 8.5), 0.1 M NaOH, and 1 M HCl. The soil together with the extractant was shaken for 16 h on an end-to-end shaker (at 120 excursions per minute) after which the tube was centrifuged at 12,500 g for 10 min at room temperature. The supernatant was filtered under suction using a 0.45-µm cellulose membrane filter (Figure 2.1). The total P in each extract was determined by analyzing the filtrate using inductively coupled plasma (ICP) emission spectroscopy. The residual P was determined using the wet oxidation method of Akinremi et al. (2003). Certified reference material from AgroMAT (compost SC0063619) and in-house laboratory reference soil material were used in assessing the reliability of the analytical procedures by digesting them with the soil samples. Values for total P concentration were within the confidence intervals given in the standard and reference material.

### 2.3.4. Statistical analysis

The PROC UNIVARIATE procedure carried out on all the soil P fractions showed that they were normally distributed (i.e. the Shapiro-Wilk statistic was greater than 0.9). Analysis was then performed using the PROC Mixed procedure of SAS Version 9.3 (SAS Institute 2011) on all soil P fractions with two factors, experimental sites and years being represented as fixed effects and blocks as random effect. The mean comparison method used was the least significant difference (LSD). Effects were considered significant if $P < 0.05$.

## 2.4. RESULTS AND DISCUSSION
### 2.4.1. Soil phosphorus ($P_t$) fractions

In all five sites, the application of 80 kg P $ha^{-1}$ $yr^{-1}$ for 6 years significantly increased the absolute value of soil P present in the labile ($H_2O$-$P_t$ and $NaHCO_3$-$P_t$) and moderately labile $P_t$ forms ($NaOH$-$P_t$) (Figure 2.2, 2.3 & 2.4). Similar results were obtained by Wagar et al. (1986) who reported that there was a significant increase in resin-, $NaHCO_3$- and $NaOH$-$P_t$, 5 and 8 years after high rates fertilizer were applied on Sutherland and Waskada soils, respectively.

In the P accumulation and P depletion plots, significant differences (P < 0.05) were observed in the main effects of year and site, in all soil $P_t$ fractions except Res-$P_t$ for which the year effect was non-significant (Table 2.2). Also, the two-way interaction was significant in $H_2O$-$P_t$ and $NaHCO_3$-$P_t$ fractions but non-significant in $NaOH$-$P_t$, $HCl$-$P_t$ and Res- $P_t$ fractions. Similarly, the two-way year × site interactions and main effects of year and site were significant on soil total P. In the fertilized plots, total soil P fractions ranged from 502 to 1021 mg $kg^{-1}$ and 446 to 863 mg $kg^{-1}$ across all sites for the end of the addition and depletion phases respectively (Appendix 2A).

At the 80 kg P $ha^{-1}$ rate, soil $H_2O$-$P_t$ increased at a rate of 9.3, 6.9, 13.0, 19.2, 6.3 mg P $kg^{-1}$ $yr^{-1}$ at Carman, East of Spruce, Ellerslie, Fort Saskatchewan and Forrest sites, respectively, during the 6 years (Figure 2.2). The $NaHCO_3$-$P_t$ also increased at a rate that was similar to that of $H_2O$-$P_i$ with increases of 10.6, 8.6, 15.8, 24.5, 9.6 mg P $kg^{-1}$ $yr^{-1}$ in Carman, East of Spruce, Ellerslie, Fort Saskatchewan and Forrest sites, respectively (Figure 2.3). The $NaOH$-$P_t$ fraction increased at a lower rate of 4.3, 6.1, 4.1 mg P $kg^{-1}$ $yr^{-1}$ in Carman, Ellerslie, Fort Saskatchewan sites in comparison to the $H_2O$-$P_t$ and $NaHCO_3$-$P_t$ fractions; however, the $NaOH$-$P_t$ fraction did not increase at East of Spruce and Forrest sites (Figure 2.4). Also, the $HC1$-$P_t$ fraction increased significantly only at Fort Saskatchewan site at a rate of 13.0 mg P $kg^{-1}$ $yr^{-1}$ but no significant

increase was observed at Carman, East of Spruce, Ellerslie, and Forrest sites (Figure 2.5).

During the depletion phase, soil $H_2O$-$P_t$ decreased at a rate of 13.0, 11.0, 9.6, 27.7, 11.9 mg P $kg^{-1}$ $yr^{-1}$ in Carman, East of Spruce, Ellerslie, Fort Saskatchewan and Forrest sites, respectively (Figure 2.2). The $NaHCO_3$-$P_t$ decreased only at the Fort Saskatchewan site at a rate of 21.1 mg P $kg^{-1}$ $yr^{-1}$ after 3 years of durum wheat-flax crop rotation from 2009 to 2012; changes were not significant at Carman, East of Spruce, Ellerslie, and Forrest sites (Figure 2.3). The soil $NaOH$-$P_t$ decreased only at Carman site at a rate of 7.1 mg P $kg^{-1}$ $yr^{-1}$ but changes were not significant at East of Spruce, Ellerslie, Fort Saskatchewan and Forrest sites (Figure 2.4). In the $HC1$-$P_t$ fraction, there were no significant changes at any site during the depletion phase from 2009 to 2012 (Figure 2.5).

$H_2O$-$P_t$ and $NaHCO_3$-$P_t$ were significantly affected by the two-way year × site interaction. The Fort Saskatchewan soil had the greatest rate of increase (16.4 and 21.0 mg P $kg^{-1}$ $yr^{-1}$ for $H_2O$-$P_t$ and $NaHCO_3$-$P_t$ respectively) during the accumulation phase whereas the Forrest soil had the smallest rate of increase (5.4 mg P $kg^{-1}$ $yr^{-1}$) for $H_2O$-$P_t$ and East of Spruce had the smallest rate of increase (7.4 mg P $kg^{-1}$ $yr^{-1}$) for $NaHCO_3$-$P_t$.
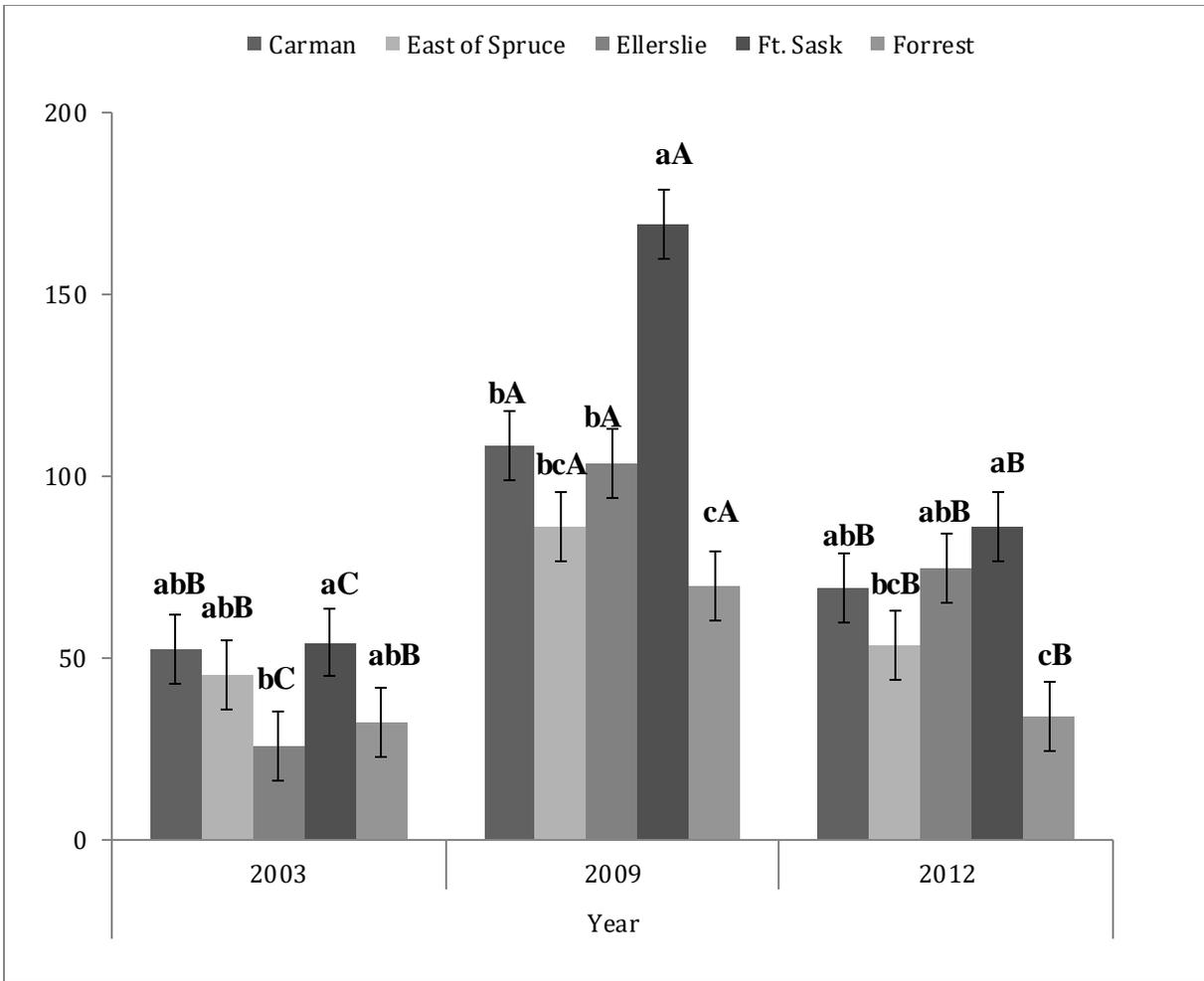
**Figure 2.2 Concentrations of H₂O - P fraction across all soils that received P fertilizer at 80 kg ha⁻¹ for 6 years and P depletion for 3 years. Means groupings indicated by lowercase letters are used to compare between different sites within each year. Means groupings indicated by uppercase letters are used to compare between different years at each site. Means followed by the same letter are not significantly different.**
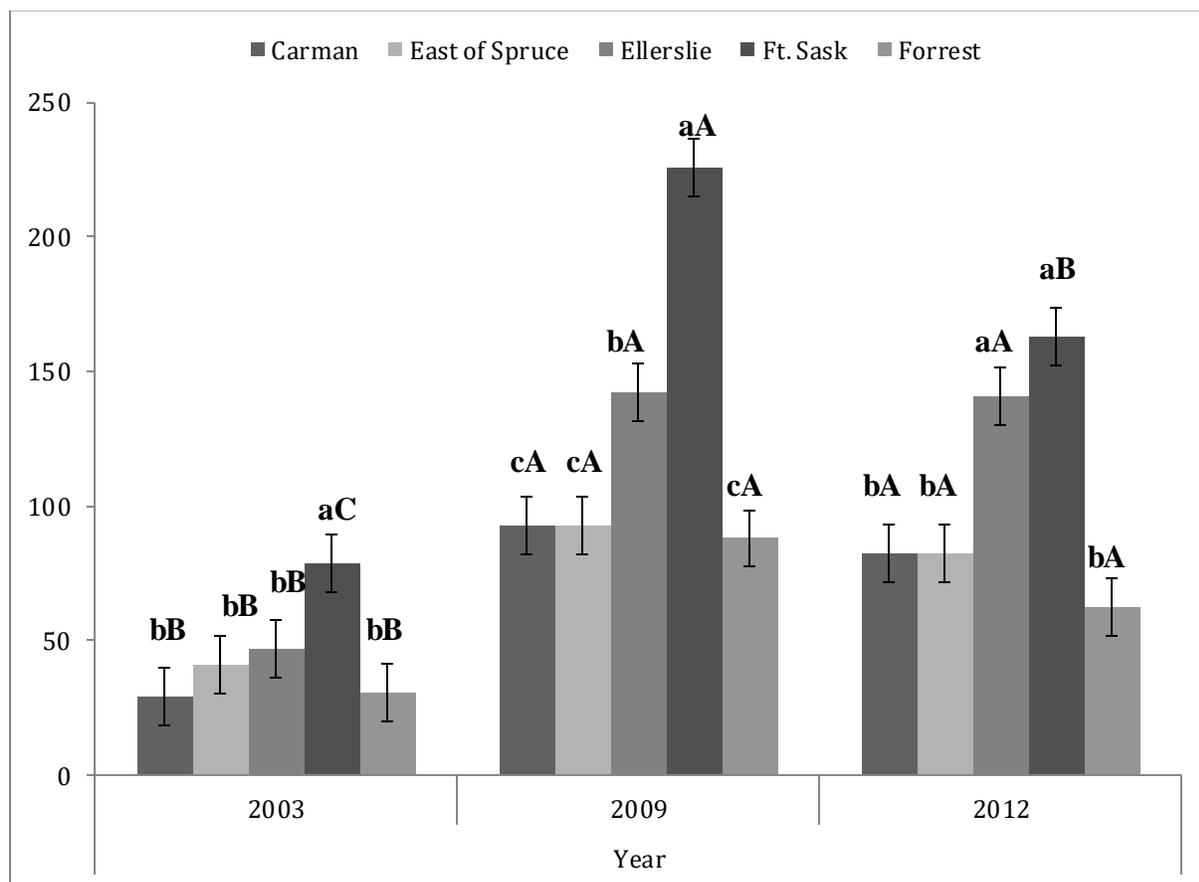
**Figure 2.3 Concentrations of NaHCO₃ - P fraction across all soils that received P fertilizer at 80 kg ha⁻¹ for 6 years and P depletion for 3 years. Means groupings indicated by lowercase letters are used to compare between different sites within each year. Means groupings indicated by uppercase letters are used to compare between different years at each site. Means followed by the same letter are not significantly different.**
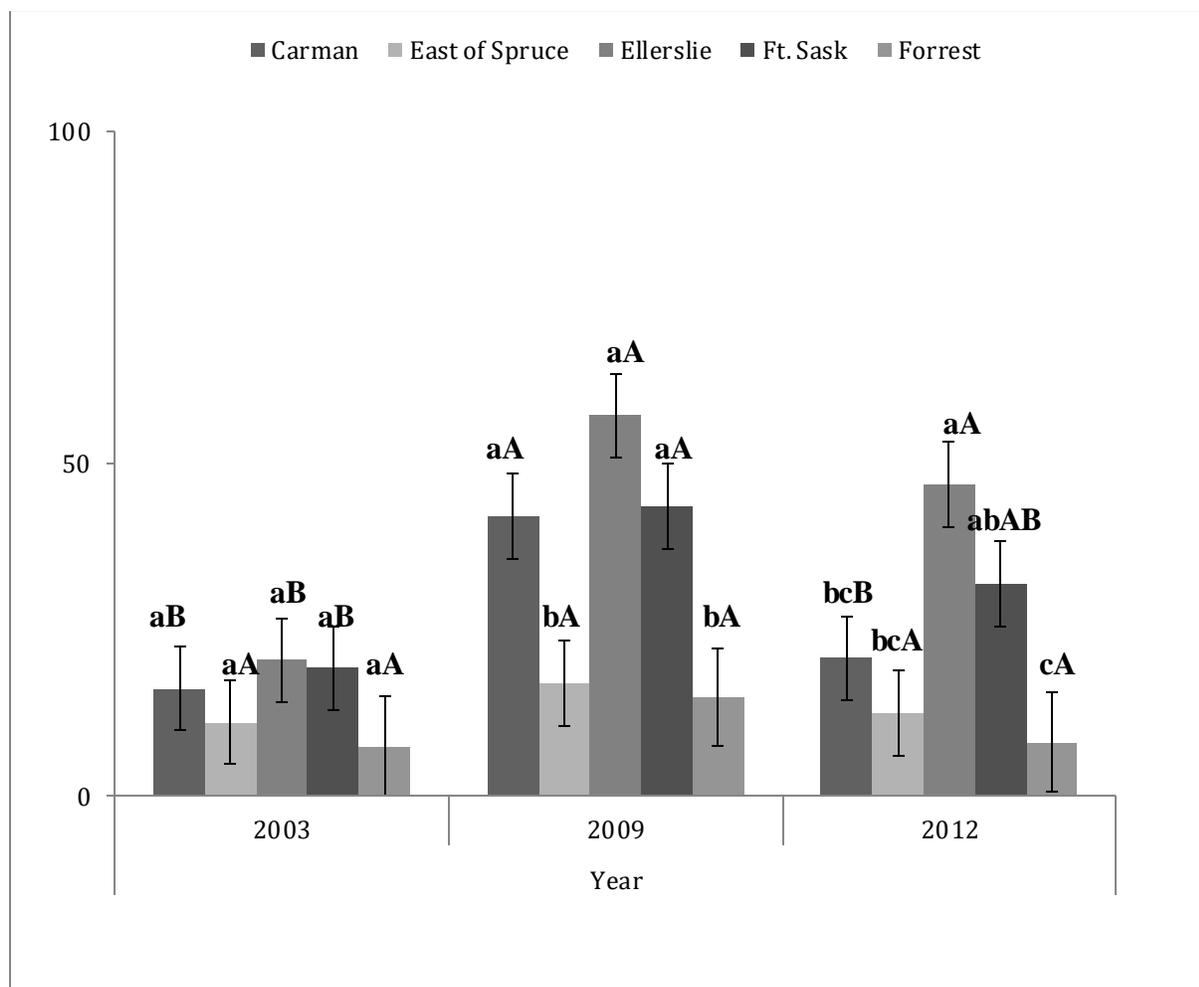
**Figure 2.4 Concentrations of NaOH - P fraction across all soils that received P fertilizer at 80 kg ha$^{-1}$ for 6 years and P depletion for 3 years. Means groupings indicated by lowercase letters are used to compare between different sites within each year. Means groupings indicated by uppercase letters are used to compare between different years at each site. Means followed by the same letter are not significantly different.**
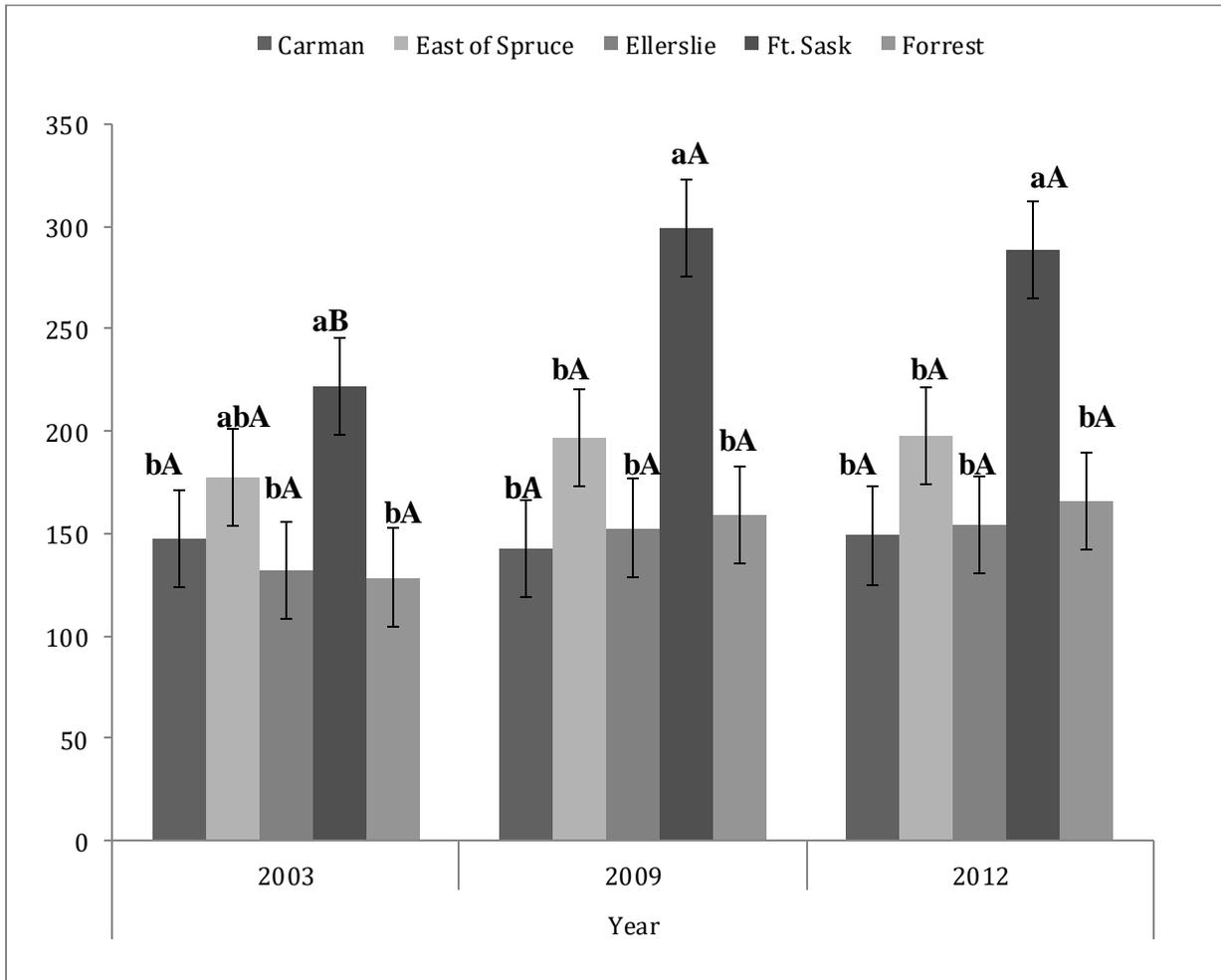
**Figure 2.5 Concentrations of HCl - P fraction across all soils that received P fertilizer at 80 kg ha$^{-1}$ for 6 years and P depletion for 3 years. Means groupings indicated by lowercase letters are used to compare between different sites within each year. Means groupings indicated by uppercase letters are used to compare between different years at each site. Means followed by the same letter are not significantly different.**
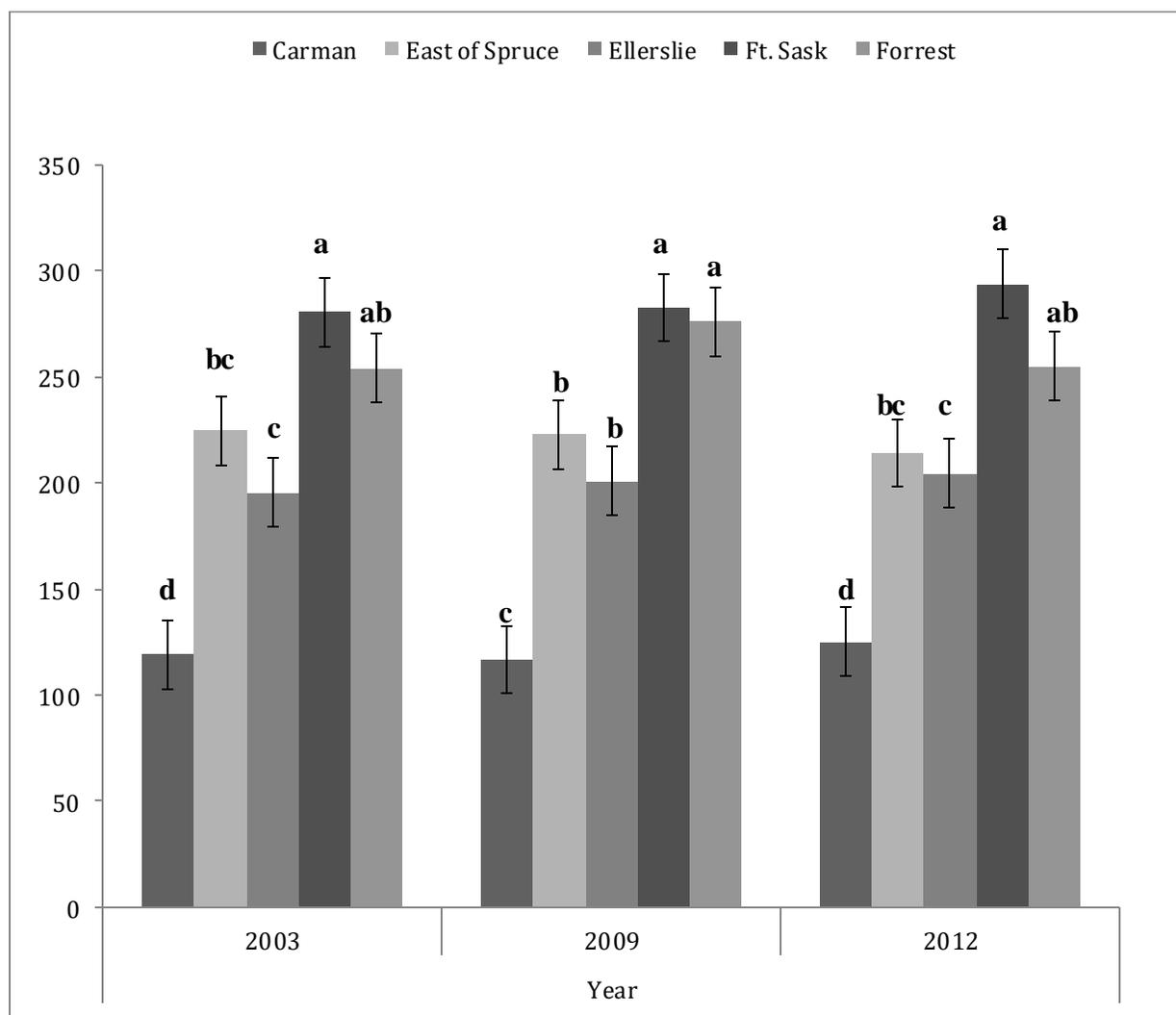
**Figure 2.6 Concentrations of Residual P fraction across all soils that received P fertilizer at 80 kg ha$^{-1}$ for 6 years and P depletion for 3 years. Means groupings indicated by lowercase letters are used to compare between different sites within each year. Means followed by the same letter are not significantly different.**

**Table 2.2 Effect of sites and years on soil P fractions**

| SITE (S) | $H_2O - P_t$ (mg kg$^{-1}$) | $NaHCO_3$-$P_t$ (mg kg$^{-1}$) | $NaOH$ -$P_t$ (mg kg$^{-1}$) | $HCl$ -$P_t$ (mg kg$^{-1}$) | $Res\_P_t$ (mg kg$^{-1}$) | Total P (mg kg$^{-1}$) | Labile $P_t$ (mg kg$^{-1}$) | Non-labile $P_t$ (mg kg$^{-1}$) | Labile $P_t$ (%) | Non-labile $P_t$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| CARMAN | 76 | 68 | 26 | 146 | 120 | 437 | 144 | 293 | 32 | 68 |
| FT SASK. | 103 | 156 | 32 | 270 | 286 | 846 | 259 | 587 | 30 | 70 |
| ELLERSLIE | 68 | 110 | 42 | 146 | 200 | 566 | 178 | 388 | 30 | 70 |
| EAST OF SPRUCE | 61 | 72 | 13 | 191 | 220 | 556 | 133 | 423 | 23 | 77 |
| FORREST | 45 | 60 | 10 | 151 | 262 | 526 | 105 | 421 | 19 | 81 |
| **YEAR (Y)** | | | | | | | | | | |
| 2003 | 42 | 45 | 15 | 161 | 215 | 478 | 87 | 391 | 18 | 82 |
| 2009 | 107 | 128 | 35 | 190 | 220 | 680 | 235 | 445 | 34 | 66 |
| 2012 | 63 | 106 | 24 | 191 | 218 | 601 | 169 | 432 | 28 | 72 |

**ANALYSIS OF VARIANCE**

**P > F value**

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Y** | <0.0001 | <0.0001 | <0.0001 | 0.012 | 0.88 | <0.0001 | <0.0001 | 0.0023 | <0.0001 | <0.0001 |
| **S** | 0.0006 | <0.0001 | 0.0013 | 0.0016 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 | <0.0001 |
| **Y*S** | 0.0004 | 0.0008 | 0.16 | 0.50 | 0.98 | 0.0015 | 0.0002 | 0.60 | 0.17 | 0.17 |

The NaOH-$P_t$ fraction was not significantly affected by the two-way year × site interaction (Table 2.2) but generally rose during the accumulation phase and declined during the depletion phase (Appendix 2.D). The NaOH-$P_t$ fraction was also greater at sites with slightly acidic soils (i.e. pH < 7 such as at Ellerslie) than at sites with alkaline soils (pH > 7 such as East of Spruce) (Appendix 2.D). According to the modified Hedley fractionation technique, NaOH-$P_t$ represents the P fraction that is adsorbed on amorphous Fe and Al minerals (Hedley et al. 1982). Results from the Mehlich-3 Fe (M3-Fe) analysis confirmed that the slightly acidic soils have the highest content of easily extractable Fe (Table 2.1). Richards et al. (1995) reported that precipitation of secondary minerals likely occurs in these types of soils (crystalline variscite (Al phosphate) and strengite (Fe phosphate) compounds); likewise, NaOH-$P_t$ may contribute to the labile fractions when diminished since it is moderately labile.

Calcium-bound phosphates extractable with 1$M$ HCl (HC1-$P_t$) were not significantly affected by the two-way year × site interactions; however, HC1-$P_t$ generally rose during the accumulation phase and did not decline during the depletion phase (Appendix 2.E). It was also observed that the HCl-$P_t$ fraction significantly increased across the sites, most especially, in the Fort Saskatchewan site.

The HCl-$P_t$ fraction was significantly affected by the year effect, which recorded an increase from 2003 to 2009 (Table 2.2). However, Zhang et al. (2004) reported that addition and depletion of P fertilizer has no significant effect on HCl-$P_i$, moderately stable fraction. It has been assumed that HCl-$P_i$ represents the primary mineral P (apatite or other calcium phosphate minerals) and is not readily available to plants (Johnson et al. 2003; Dieter et al. 2010; Yang and Post 2011).

The residual P fraction was significantly affected only by the main effect of site (Figure 2.6).

Across all sites, Table 2.2 showed that Fort Saskatchewan soil had the greatest amount of residual P (285 mg kg$^{-1}$) whereas the Carman soil had the smallest amount (120 mg P kg$^{-1}$). The East of Spruce soil, on the other hand, was intermediate between these two soils (220 mg P kg$^{-1}$). The lack of a year effect contrasts with the results of Vu et al. (2008), who reported an increase in residual P with increasing P fertilizer rates.

### 2.4.2. Effect of long-term P application on labile and non-labile P fractions

In this study, the H$_2$O- and NaHCO$_3$-P$_t$ constitute the labile P$_t$ and NaOH-, HCl- and residual-P$_t$ make up the non-labile P fractions. Labile-P fraction was significantly affected by the main effects (year, site) and by their interaction (Table 2.2). Although, there was a significant effect of year and site on non-labile P, there was no significant two-way year x site interaction for this fraction (Table 2.2).

Long-term application of P fertilizer across all soil types significantly increased the labile and non-labile P fractions (Figure 2.7 & 2.8, Table 2.2). However, for labile-P, there was a significant year x site interaction. In the treated soils, there was a significant increase in the labile P fractions that ranged from 92 to 262 mg kg$^{-1}$ across the sites with an average increase of 148 mg kg$^{-1}$ after 6 yr of P application (Figure 2.7).

During the depletion phase in treated soils, there was a significant decrease in labile fractions ranging from 30 to 146 mg kg$^{-1}$, across all sites except East of Spruce and Ellerslie (Figure 2.7). In contrast, there was no significant decrease in non-labile P fractions (Figure 2.9).
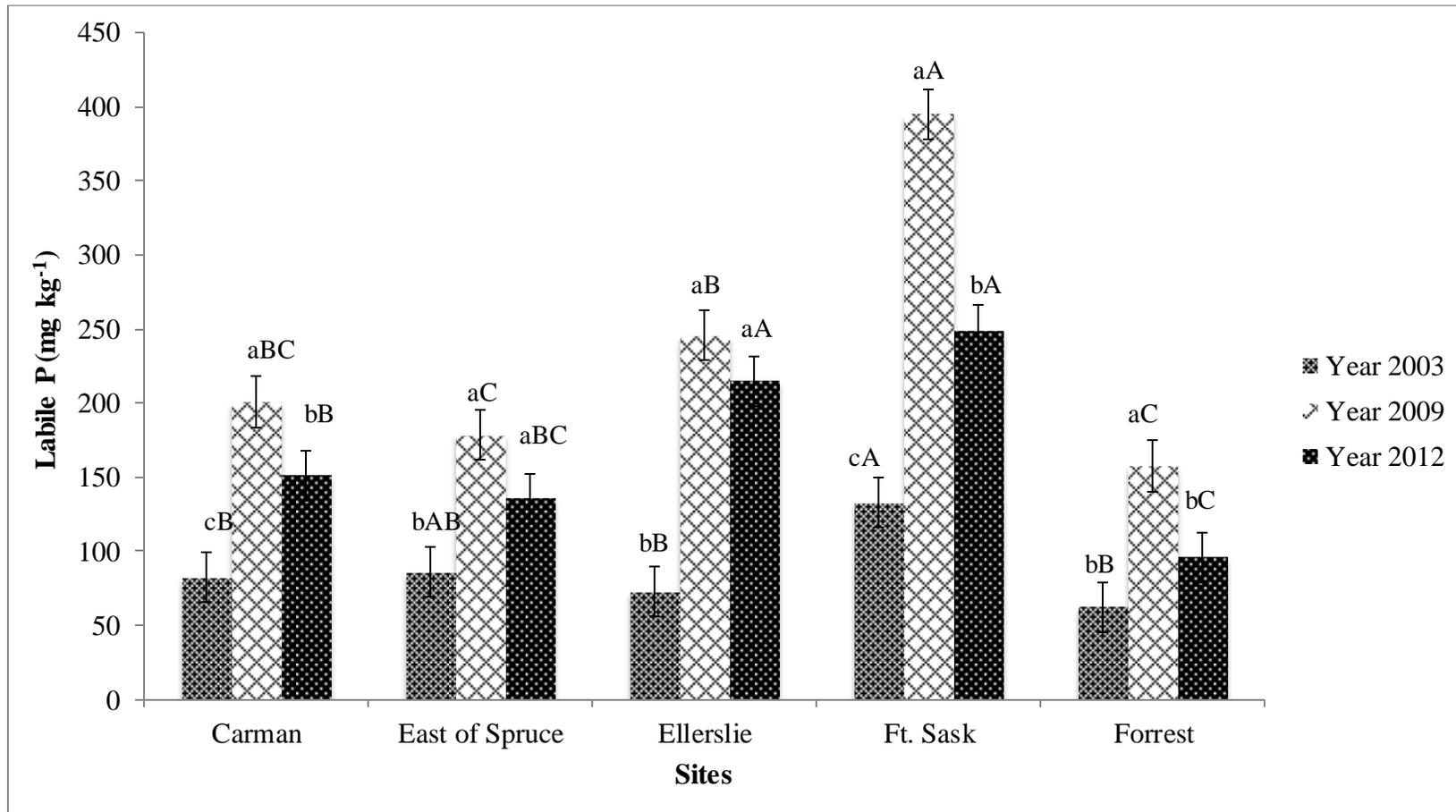
**Figure 2.7 Absolute amounts of labile $P_t$ at 80 kg P ha$^{-1}$ at all years across the sites. Means groupings indicated by lowercase letters are used to compare different years within each site. Means groupings indicated by uppercase letters are used to compare each year across all sites. Means followed by the same letter are not significantly different.**
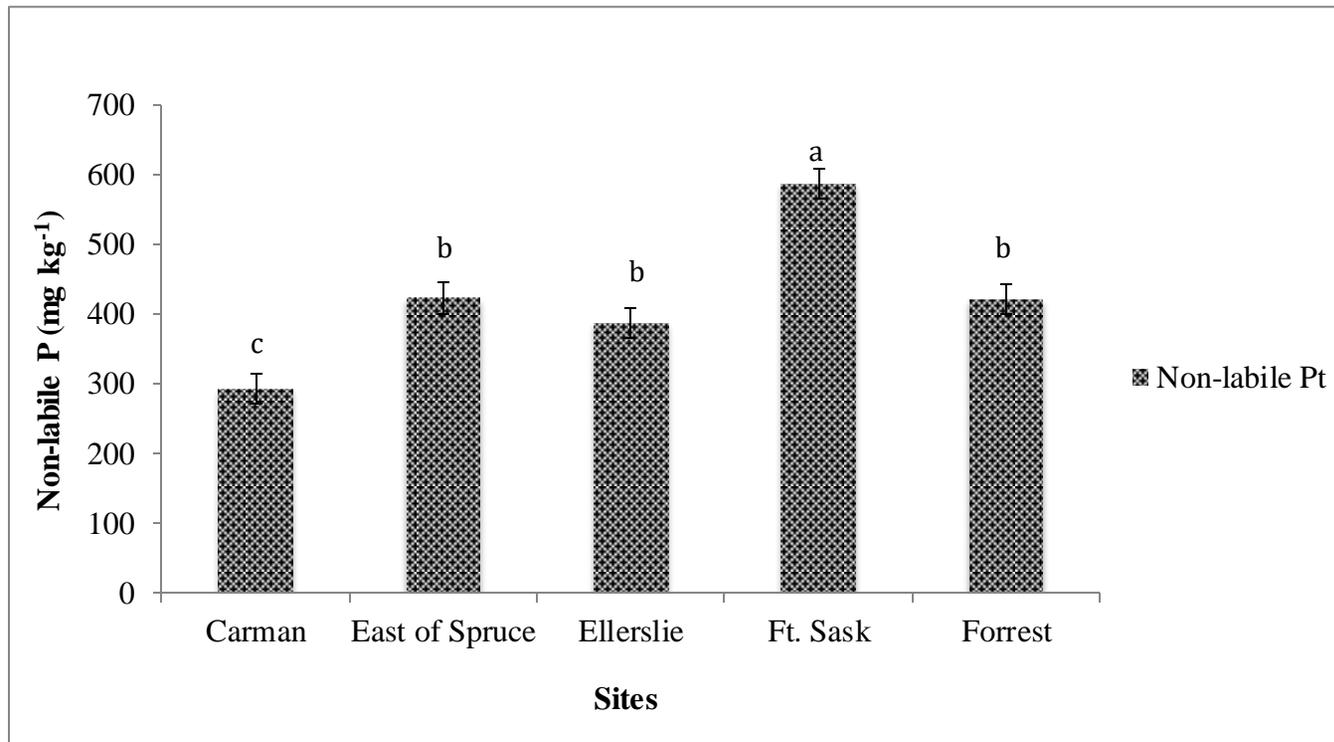
**Figure 2.8 Absolute amounts of non-labile $P_t$ at 80 kg P ha$^{-1}$ across the sites. Means groupings indicated by lowercase letters are used to compare different sites averaged for all years. Means followed by the same letter are not significantly different.**
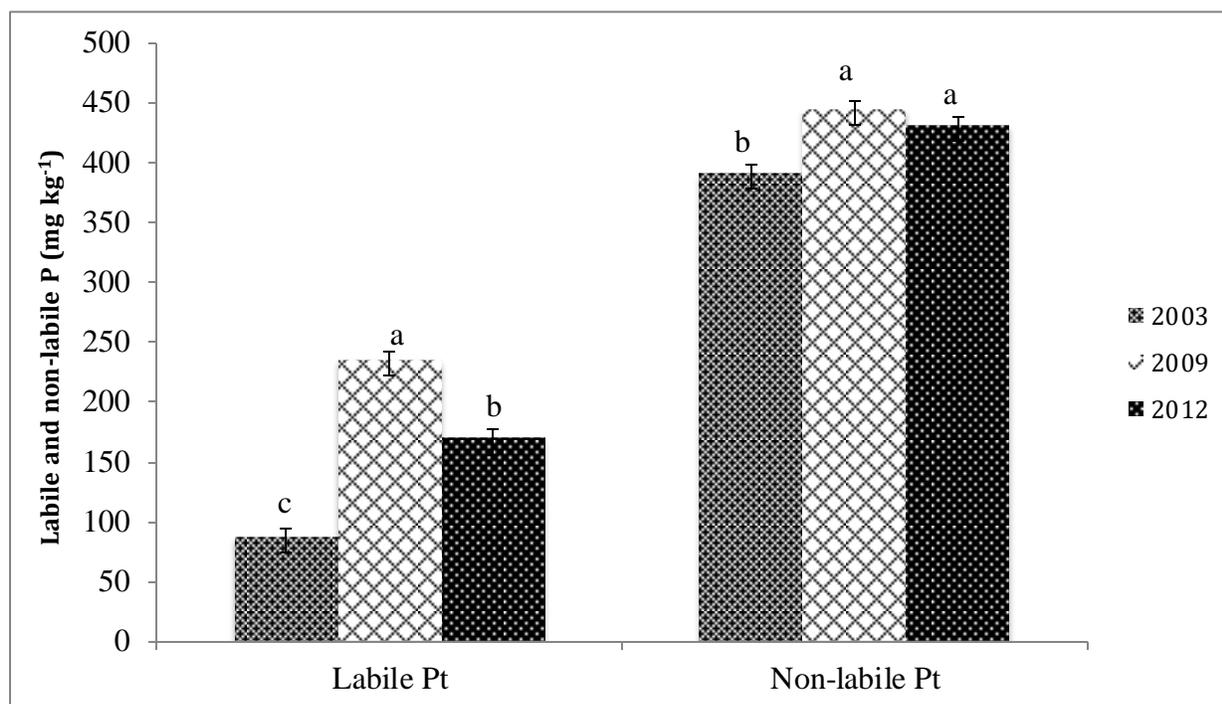
**Figure 2.9 Effect of application years on labile and non-labile P fractions. Mean groupings indicated by lower letters are used to compare application years in each fraction. Means followed by the same letter are not significantly different.**

### 2.4.3. Proportion of soil P fractions in the different prairie soils

The response of the phosphorus fractions to fertilizer application differed across sites. In general, the proportions of $H_2O$-$P_t$ and $NaHCO_3$-$P_t$ fractions showed the largest response to fertilization (Figure 2.10, Table 2.3). These results were similar to those reported by Kashem et al. (2004) in an incubation experiment using inorganic mono-ammonium phosphate fertilizer on a Gleyed Rego Black Chernozem. The authors reported that $H_2O$ and $NaHCO_3$ fractions increased with the rate of P application with the different amendments. In our study, the proportion of soil P fractions was similar in the slightly acidic soils (Carman and Ellerslie). At the end of the application years, there was an increase in the proportion of labile $P_t$ ($H_2O$- and $NaHCO_3$-$P_t$) and $NaOH$-$P_t$ but a decrease in the $HCl$-$P_t$ and residual P fractions (Figure 2.10, Table 2.3).

The $H_2O$-, $NaHCO_3$- and $NaOH$- $P_t$ showed a corresponding increase during the accumulation phase at all the sites (Table 2.3). $H_2O$- $P_t$ significantly declined in the depletion phase but no significant decline was observed in $NaHCO_3$-$P_t$ (Table 2.3). The $NaOH$- $P_t$ was the smallest when compared to other fractions after 7 years of P application, ranging from 2.4 to 8.7 % of total P across all sites. There was further reduction of $NaOH$- $P_t$ fraction from 0.8 to 7.6 % of total P after 3 years of P depletion (Figure 2.10). However, there was a significant decline on $NaOH$- $P_t$ in depletion phase (Table 2.3). A decrease in the proportion of $HCl$-$P_t$ and Residual-P fraction from year 2003 to 2009 was observed (Figure 2.10, Table 2.3). This result was consistent with the study by Kashem et al. (2004), who reported a corresponding decrease in the proportion of the recalcitrant fractions ($HCl$-P and Residual P) with the application of high rates of fertilizer P. In the depletion plots that had previously received the high fertilizer rate, there was a corresponding increase in the proportions of $HCl$-$P_t$ and Residual-P fraction (Figure 2.10, Table 2.3).

| | $H_2O - P_t$ (mg kg$^{-1}$) | $NaHCO_3 - P_t$ (mg kg$^{-1}$) | $NaOH - P_t$ (mg kg$^{-1}$) | $HCl - P_t$ (mg kg$^{-1}$) | $Res\_P_t$ (mg kg$^{-1}$) |
|---|---|---|---|---|---|
| **Table 2.3 Effects of sites and years on proportion of soil P fractions** | | | | | |
| SITE (S) | | | | | |
| CARMAN | 17a | 15b | 6ab | 34 | 28d |
| FT SASK. | 12b | 18a | 4bc | 32 | 35c |
| ELLERSLIE | 11bc | 18a | 7a | 26 | 37bc |
| EAST OF SPRUCE | 11bc | 13bc | 2cd | 34 | 40b |
| FORREST | 8c | 11c | 2d | 29 | 51a |
| | | | | | |
| YEAR (Y) | | | | | |
| 2003 | 9c | 9b | 3b | 34a | 45a |
| 2009 | 16a | 18a | 5a | 28b | 33c |
| 2012 | 11b | 17a | 4b | 32a | 37b |
| **ANALYSIS OF VARIANCE** | | | | | |
| **P > F value** | | | | | |
| Y | <0.0001 | <0.0001 | 0.0004 | <0.0001 | <0.0001 |
| S | 0.0006 | <0.0001 | 0.0002 | 0.069 | <0.0001 |
| Y*S | 0.23 | 0.42 | 0.21 | 0.06 | 0.64 |

Mean groupings indicated by lower case letters are used to compare sites or sampling years within each fraction. Means followed by the same letter are not significantly different.
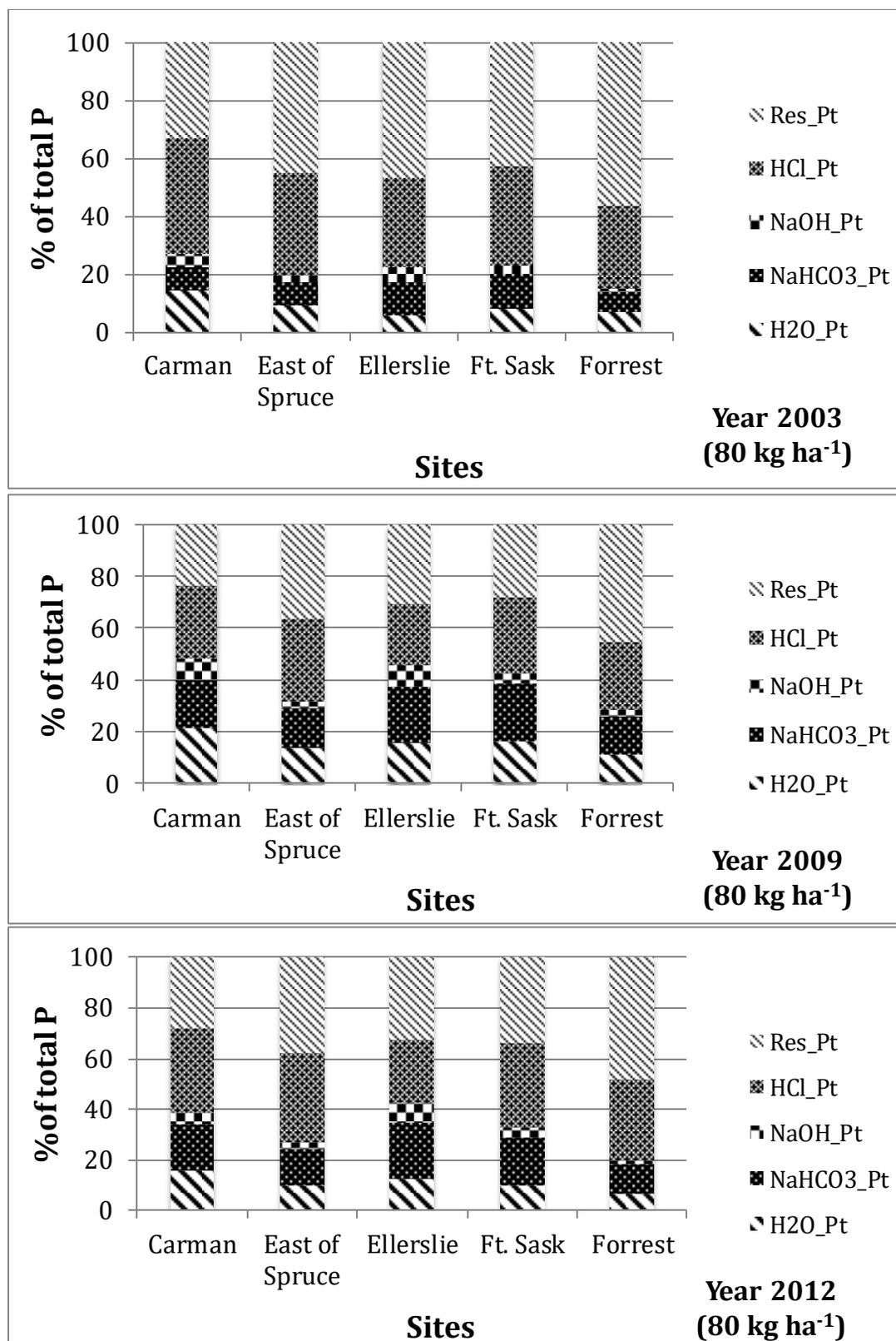
**Figure 2.10** Phosphorus fractions in treated sites across the years

### 2.4.4. Changes in P fractions during fertilizer accumulation and depletion phases

The $H_2O$- and $NaHCO_3$-P fractions significantly increased with P fertilizer application at all sites during the accumulation phase (Figure 2.11, Table 2.4). Results showed a greater concentration of $H_2O$- and $NaHCO_3$-P fractions could be found in the Fort Saskatchewan site, which has highest amounts of silt and M3-Ca content (Table 2.1). It is also important to note that $NaHCO_3$-P fraction was significantly correlated to silt content and M3-Ca (Table 2.5). However, there was no significant increase in the NaOH-, HCl- and residual-P fraction across all the sites following the addition of fertilizer (Table 2.4). The HCl-P fraction has been reported to be the occluded, stable calcium bound phosphate under neutral or alkaline conditions (Cross and Schlesinger 1995; Jalali and Ranjbar 2010; Yang and Post 2011). Zhang et al. (2004) reported a linear increase in residual P at a rate of 6.2 mg P $kg^{-1}$ $yr^{-1}$ with high rate of fertilizer addition. The author also stated that residual P might be the product of precipitated inorganic P and humified organic P compounds.

The results that were obtained during the depletion phase supports our earlier stated hypothesis as the P fractions that increased during the accumulation phase (i.e. the $H_2O$- and $NaHCO_3$-P) was the fraction that was significantly decreased to the greatest extent during the depletion phase (Table 2.4). This was not surprising as these fraction constituted a portion of the labile P, and probably taken up by the plants in the absence of further P additions and hence the decline of P in these fractions (Figure 2.11).

Unlike the NaOH- and HCl- P fraction, there was a significant change across all the sites in the residual P fraction at the depletion phase (Figure 2.11). Residual P fraction slightly increased in Carman, Fort Saskatchewan and Ellerslie sites but significantly decreased in East of Spruce and Forrest sites. Also of interest was the fact that the residual P that increased during the P addition

phase at the Forrest site also declined during the depletion phase, calling into question the recalcitrant (non-labile) nature of this fraction in this particular soil.

### 2.4.5. Relationships between the soil P fractions and soil properties

There was no significant correlation between soil properties and $H_2O$-$P_t$. The silt content and M3-Ca was strongly and positively correlated ($P < 0.05$) with $NaHCO_3$-$P_t$ (Table 2.5). This indicates that soils with high M3-Ca and high silt content (Fort Saskatchewan and Ellerslie) have high concentrations of $NaHCO_3$-P, which is in readily available form for plants (Table 2.1). There was no significant correlation between soil properties and non-labile fractions ($NaOH$-$P_t$, $HCl$-$P_t$ and Res-$P_t$). Total P was positively and strongly correlated ($P < 0.001$) with M3-Ca and silt content, similar to the trend for $NaHCO_3$-$P_t$. It was observed that soils with high M3-Ca and high silt (Fort Saskatchewan and Ellerslie) had high concentrations of total P (Table 2.1).

| SITE (S) | $H_2O$-Pa (mg kg$^{-1}$) | $H_2O$-Pd (mg kg$^{-1}$) | $NaHCO_3$-Pa (mg kg$^{-1}$) | $NaHCO_3$-Pd (mg kg$^{-1}$) | NaOH-Pa (mg kg$^{-1}$) | NaOH-Pd (mg kg$^{-1}$) | HCl-Pa (mg kg$^{-1}$) | HCl-Pd (mg kg$^{-1}$) | Res-Pa (mg kg$^{-1}$) | Res-Pd (mg kg$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| CARMAN | 56bc | -39a | 64b | -11a | 26 | -21 | -5 | 6 | -3 | 8a |
| FT SASK. | 115a | -83b | 147a | -63b | 24 | -12 | 78 | -11 | 2 | 11a |
| ELLERSLIE | 78b | -29a | 95b | -2a | 37 | -10 | 21 | 1 | 5 | 4a |
| EAST OF SPRUCE | 41c | -33a | 52b | -10a | 6 | -10 | 19 | 1 | -2 | -9b |
| FORREST | 38c | -36a | 58b | -26a | 9 | -11 | 31 | 7 | 22 | -21b |

**Table 2.4 Effects of sites on accumulation and depletion of soil P fractions**

### ANALYSIS OF VARIANCE

### P > F value

| S | 0.0012 | 0.0102 | 0.0033 | <0.0001 | 0.1569 | 0.7477 | 0.3673 | 0.8424 | 0.9740 | <0.0001 |
|---|---|---|---|---|---|---|---|---|---|---|

Pa: change in P fractions in accumulation phase (concentration of fractions in year 2009 minus year 2003)

Pd: change in P fractions in depletion phase (concentration of fractions in year 2012 minus year 2009)

Mean groupings indicated by lower letters are used to compare sites in each fraction. Means followed by the same letter are not significantly different.
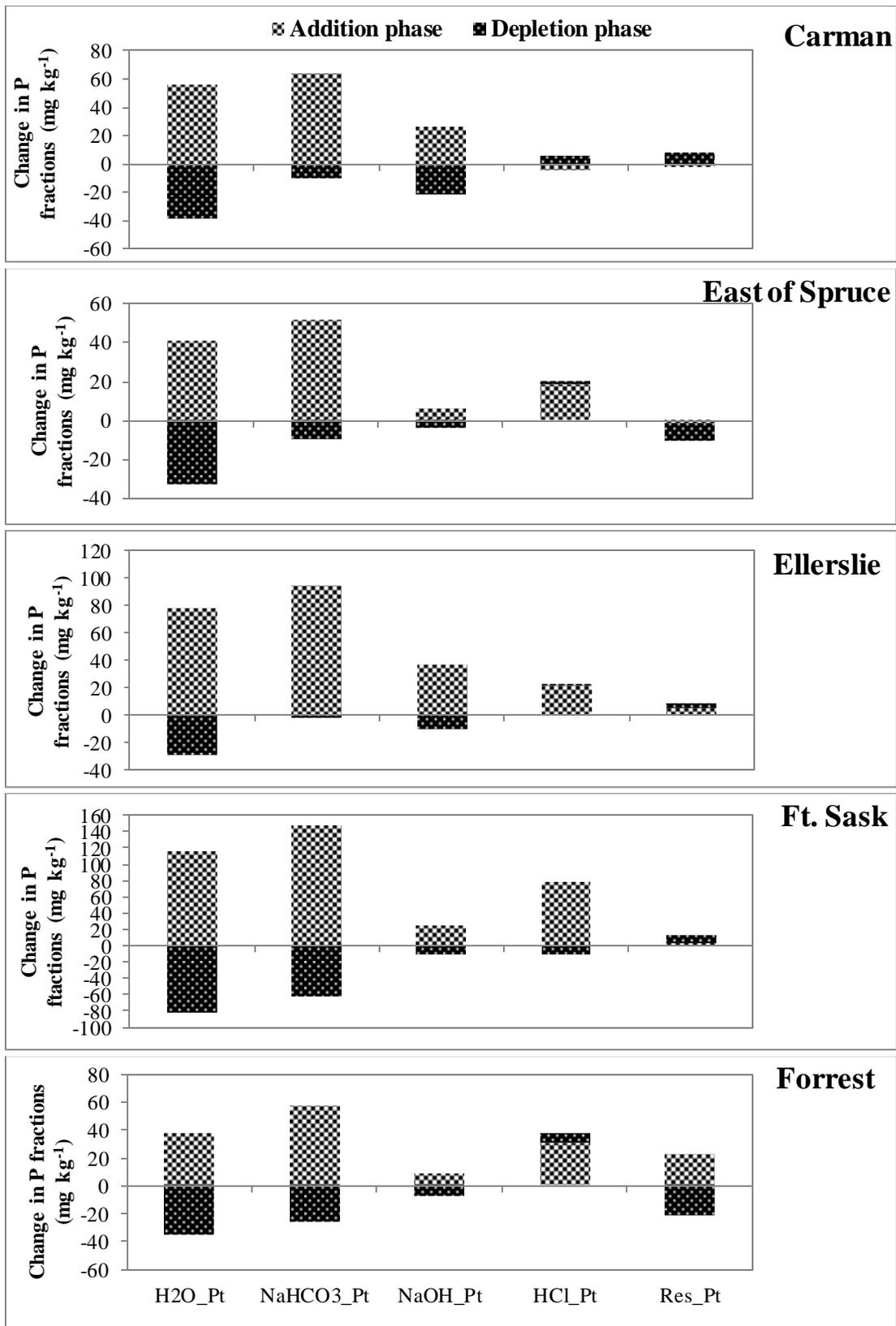
**Figure 2.11** Addition and depletion of phosphorus fractions in all treated sites across the years

51

**Table 2.5 Correlation coefficients between soil properties and soil P fractions at all years across sites (using linear equation, n=5)**

|  | pH | Clay | Silt | Sand | CEC | Organic_C | M-3 Fe | M-3 Ca | M-3 Mg | M-3 P |
|---|---|---|---|---|---|---|---|---|---|---|
| **$H_2O\_P_t$** | -0.7 | -0.1 | 0.4 | -0.2 | 0.2 | 0.5 | 0.5 | 0.4 | -0.2 | 0.8 |
| **$NaHCO_3\_P_t$** | -0.2 | 0.6 | **0.9*** | -0.8 | 0.7 | 0.6 | 0.3 | **0.9*** | 0.3 | 0.3 |
| **$NaOH\_P_t$** | -0.7 | 0.5 | 0.6 | -0.7 | 0.6 | 0.6 | 0.8 | 0.6 | -0.3 | 0.3 |
| **$HCl\_P_t$** | 0.6 | -0.1 | 0.4 | 0.0 | 0.1 | 0.1 | -0.7 | 0.4 | 0.8 | 0.2 |
| **$Res\_P_t$** | 0.7 | 0.1 | 0.6 | -0.3 | 0.6 | 0.5 | -0.5 | 0.6 | 0.7 | -0.3 |
| **Total_P** | 0.2 | 0.7 | **1*** | -0.9 | 0.9 | 0.7 | 0.1 | **1*** | 0.5 | -0.1 |

## 2.5. Conclusions

Repeated application of phosphorus affected the distributions of P fractions in the soil. There were significant increases in the labile ($H_2O$-$P_t$ and $NaHCO_3$-$P_t$) and moderately labile P forms ($NaOH$-$P_t$) in treated plots across all sites. The main effects of year and site significantly increased and decreased the labile P fractions during the addition and depletion phases, respectively. Varying soil types also act as a contributing factor to the different proportion of P fractions obtained in the study.

Continuous application of P fertilizer in excess of crop removal significantly increased the proportion of total P in labile forms and significantly decreased the non-labile P fractions except $NaOH$-$P_t$. In the depletion phase, the proportion of total P in $H_2O$-$P_t$ fractions decreased significantly which may be as a result of crop removal, dilution with tillage and stabilization of P into less labile forms. However, the non-labile P fractions (HCl- and Res- $P_t$) significantly increased during the depletion phase. Although, this study only considered the $0 - 7.5cm$ depth, further studies need to be done below the current depth.

These findings showed the effect of continuous P fertilizer addition on the labile P fractions, which represents the most readily plant-available P in the short term. Results also showed that some of these labile P fractions are still in the available form and there is the possibility for P loss to surface waters, thereby leading to eutrophication. However, since these findings were limited to only the high rate of P application, there is need to study the distribution of soil P fraction with the addition of low or moderate P application rates on varying soils for valuable fertilizer recommendations.

## 2.6. References

Akinremi, O. O., Armisen, N., Kashem, A. and H.H. Janzen. 2003. Evaluation of analytical methods for total P in organic amendments. Commun. Soil Sci. Plant Anal. 34: 2987-2997.

Beck, M.A., and P.A. Sanchez. 1994. Soil P fraction dynamics during 18 years of cultivation on a Typic Paleudult. Soil Sci. Soc. Am. J. 58:1424–1431.

Carter, M.R., and E.G. Gregorich. 2008. Soil sampling and methods of analysis. Canadian Society of Soil Science ; CRC Press, [Pinawa, Manitoba]; Boca Raton, FL.

Cross, A.F., and W.H. Schlesinger. 1995. A literature review and evaluation of the Hedley fractionation- Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma (64): 197–214.

Dieter, D., H. Elsenbeer, and B.L. Turner. 2010. Phosphorus fractionation in lowland tropical rainforest soils in central Panama. CATENA 82(2): 118–125.

Grant, C., D. Flaten, M. Tenuta, S. Malhi, and W. Akinremi. 2013. The effect of rate and Cd concentration of repeated phosphate fertilizer applications on seed Cd concentration varies with crop type and environment. Plant Soil 372(1–2): 221–233.

Jalali, M., and F. Ranjbar. 2010. Aging effects on phosphorus transformation rate and fractionation in some calcareous soils. Geoderma 155(1–2): 101–106.

Johnson, A.H., J. Frizano, and D.R. Vann. 2003. Biogeochemical implications of labile phosphorus in forest soils determined by the Hedley fractionation procedure. Oecologia 135(4): 487–499.

Kashem, M.A., O.O. Akinremi, and G.J. Racz. 2004a. Extractable phosphorus in alkaline soils amended with high rates of organic and inorganic phosphorus. Can. J. Soil Sci. 84(4): 459–467.

Kashem, M.A., O.O. Akinremi, and G.J. Racz. 2004b. Phosphorus fractions in soil amended with organic and inorganic phosphorus sources. Can. J. Soil Sci. 84(1): 83–90.

Lambert, R., C. Grant, and S. Sauve. 2007. Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. Sci. Total Environ. 378(3): 293–305.

McDowell, R., A. Sharpley, P. Brookes, and P. Poulton. 2001. Relationship between soil test phosphorus and phosphorus release to solution. Soil Sci. 166(2): 137–149.

Richards, J.E., T.E. Bates, and S.C. Sheppard. 1995. Changes in the forms and distribution of soil phosphorus due to long-term corn production. Can. J. Soil Sci. 75(3): 311–318.

Samadi, A. 2003. A study on distribution of forms of phosphorus in calcareous soils of Western Australia. J. Agric. Sci. Technol. JAST 5(1–2): 39–49.

Soinne, H. 2009. Extraction methods in soil phosphorus characterisation - Limitations and applications. Available at https://helda.helsinki.fi/bitstream/handle/10138/20847/extracti.pdf?sequence=1 (verified 27 September 2014).

Tiessen, H., J.W.B. Stewart, and J.O. Moir. 1983. Changes in organic and inorganic phosphorus composition of two grassland soils and their particle size fractions during 60–90 years of cultivation. J. Soil Sci. 34:815–823.

Wagar, B.I., J.W.B. Stewart, and J.O. Moir. 1986. Changes with time in the form and availability of residual fertilizer phosphorus on Chernozemic soils. Can. J. Soil Sci. 66(1): 105–119.

Walker, T.W., and J.K. Syers. 1976. The fate of phosphorus during pedogenesis. Geoderma 15(1): 1–19.

Yang, X., and W.M. Post. 2011. Phosphorus transformations as a function of pedogenesis: A synthesis of soil phosphorus data using Hedley fractionation method. Biogeosciences 8(10): 2907–2916.

Zhang, T.Q., A.F. MacKenzie, B.C. Liang, and C.F. Drury. 2004. Soil test phosphorus and phosphorus fractions with long-term phosphorus addition and depletion. Soil Sci. Soc. Am. J. 68(2): 519–528.

# 3. CUMULATIVE EFFECTS OF P APPLICATION RATES AND P BALANCE ON SOIL TEST P CHANGE IN DIFFERENT PRAIRIE SOILS

## 3.1. Abstract

An improved understanding of the impact of application of P fertilizer on soil test P (STP) changes with time is important for sustainable P management guidelines. This study was carried out to investigate changes in soil test P during continuous P application and depletion phases in different soil types. It shows how STP methods relate to P balance and how STP method correlates with soil properties. Mono-ammonium phosphate (MAP) fertilizer was added at rates of 0, 20, 40 and 80 kg P ha$^{-1}$ to five soils across the prairies under a durum wheat-flax cropping sequence for 8 years followed by a 3 year P depletion and stabilization phase when no P fertilizer was added. Soil P concentration at two depths were measured using the agronomic soil test P methods (Olsen- P and Mehlich-3 P), and an environmental soil test P method (water-extractable P). Results showed that Mehlich-3 extracted the greatest amount of P from the two depths and Olsen-extractable P was intermediate while the smallest amount was extracted with water. The amount of surplus P (fertilizer in excess of crop removal) required to raise water-extractable P by 1 mg P kg$^{-1}$ would be 23, 20, 27, 19 and 20 kg P ha$^{-1}$ at the $0 - 7.5$ cm depth raised for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites respectively, after 8 years of P addition. A surplus of 13, 12 and 11 kg P ha$^{-1}$ at the $0 - 7.5$ cm depth raised Olsen soil test P by 1 mg P kg$^{-1}$ for Carman, Forrest and Fort Saskatchewan sites except East of Spruce and Ellerslie sites which had non-significant regression. A surplus of 7, 3 and 4 kg P ha$^{-1}$ at the $0 - 7.5$ cm depth raised Mehlich-3 soil test P by 1 mg P kg$^{-1}$ for East of Spruce, Carman and Forrest sites; but Ellerslie and Fort Saskatchewan sites were non-significant. The rate of change in water-extractable P at $0 - 7.5$ cm depth was positively correlated with Mehlich-3 extractable iron, (M3-

Fe, r = 0.87). The rate of change in Olsen-extractable P at the 0 – 7.5 cm depth was negatively correlated with the sand content (r= -0.90, $P < 0.05$) and positively correlated with CEC (r= 0.97, $P < 0.01$). At the 7.5 – 15 cm depth, Olsen-extractable P was positively correlated with Mehlich-3 extractable iron, (M3-Fe, r = 0.60). Mehlich-3 extractable P was negatively correlated with the silt content (r = -0.90, $P < 0.05$) and M3-Ca (r = -0.90, $P < 0.05$). These results appear to suggest that the rate of change of extractable P, particularly Olsen P, with P application was site independent.

### 3.2. Introduction

Farmers have an interest in maintaining the economic and environmental sustainability of their farms. The low plant recovery of fertilizer P in the year of application, coupled with annual application of P by farmers to ensure economic yield, can lead to the build-up of phosphorus on some farmer's fields if P is applied in excess of crop removal. This build-up of soil P can increase the potential for P loss by surface runoff with negative environmental impact. In order to reduce the potential for P loss, there is the need to carry out regular soil testing as a mean of managing fertilizer P application (Kumaragamage et al. 2007). The main purpose of soil testing is to determine the level of available P in the soil that is required to prevent P-deficiency of crops (Fixen and Grove 1990). Availability of P is dependent on weather, type of crop grown, soil properties and time (McKenzie and Bremer 2003).

Soil test methods can be divided into agronomic and environmental soil tests. Agronomic soil testing methods vary in the amount of nutrient that is extracted by a wide range of extracting solutions. These extracting solution ranges from dilute to strong acid and to buffered alkaline solutions (Ige et al. 2006). The commonly used agronomic soil test P methods include Olsen-P, Mehlich-3P, and Kelowna methods (Olsen et al. 1954; Mehlich 1984; Van Leirop 1988). Olsen-

P is a buffered alkaline extractant (weak) primarily used for pH neutral to calcareous soils (Olsen et al. 1954) and to a lesser extent in acidic soils. It is the traditional soil testing method for Manitoba soils due to the calcareous origin of many Manitoba soils. Mehlich-3 and Kelowna extraction methods were developed for use in a wide variety of soils (Ige et al. 2006). However, Mehlich-3 is more effective on acid soils than on alkaline soils (Mehlich 1984). On the other hand, environmental soil test P methods focus on the portion of the extracted P that can be easily lost to runoff and the extractants used are mild in nature. Examples include water-extractable P (Van der Paauw 1971), $CaCl_2$ -P (Self-Davis et al. 2000) and $NH_4Cl$-P (Racz 1979).

Application of P fertilizer in excess of crop removal leads to P surplus in the soil, hence an increase in soil test P. Different studies have been carried out to determine factors that influence changes in STP including source of P applied (Griffin et al. 2003; Haden et al. 2007; Kumaragamage et al. 2011), initial P level in soil (Pote et al. 2003), rate of P application and soil test P method employed (Kashem et al. 2004b; Kumaragamage et al. 2007), intrinsic soil properties (Allen and Mallarino 2006; Ige et al. 2006), and effect of time (Kashem et al. 2004b; Haden et al. 2007). Kumaragamage et al. (2011) reported that the amounts of P required to raise Olsen-P by 1 mg P $kg^{-1}$ after 6 weeks of applying mono-ammonium P fertilizer were 1.5 and 1.9 mg P $kg^{-1}$ for Newdale clay loam and Lone sand sites respectively. Saha et al. (2013) reported that the application of 60 and 120 kg $P_2O_5$ $ha^{-1}$increased Olsen-P in calcareous, sandy-loam soil by 7.8 and 9.4 mg $kg^{-1}$, respectively, over the unfertilized control after 40 years of using different phosphatic fertilizers. A study carried out by Bailey et al. (1977) on two calcareous chernozemic soils in southwestern Manitoba, showed that continuous cropping of wheat-flax rotation for 8 years after a single broadcast application of superphosphate fertilizer of 0, 100, 200 and 400 kg P $ha^{-1}$ reduced the $NaHCO_3$- extractable P in the 0 -15 cm depth to 4, 8, 20 and 52 kg P $ha^{-1}$ for

Carroll soil and 4, 7, 26 and 54 kg P ha$^{-1}$ for Waskada soil. respectively. A study conducted by Zhang et al. (2004) on clay soil in Eastern Canada showed that the net addition of 6.3 kg P ha$^{-1}$ of P fertilizer would increase soil M-3P by 1.0 mg P kg$^{-1}$ after 10 yr of fertilizer application at rates ranging from 44 to 132 P ha$^{-1}$ yr$^{-1}$ to corn fields. However, soil M-3P decreased after 4 yrs of depletion in plots that previously received a high annual rate of P fertilizer (132 kg P ha$^{-1}$ yr$^{-1}$) for 6 years. During 4 yrs of P depletion, net removal of 4.2 kg P ha$^{-1}$ yr$^{-1}$ by crops led to a decrease of M-3P by 1.0 mg P kg$^{-1}$.

Since there has been little research work carried out on this topic on Western Canadian prairie soils, knowledge of how soil test P changes over time in a long-term durum wheat-flax rotation will be valuable for P recommendations in this region. In Manitoba, the Olsen-P values of 0-5, 5-10, 10-15, 15-20, 20 and above 20 ppm have been rated agronomically as very low, low, medium, high, very high and extremely high, respectively (MAFRI 2007). These soil test values determine the recommended fertilizer placement rates either as seed-placed, side banded, banded or broadcasted for each crop type. The Olsen-P value of 15 ppm is regarded as agronomically optimum in Manitoba (Manitoba Phosphorus Expert Committee, 2006). Therefore, for long-term agronomic productivity, farmers should aim to raise soil test P concentrations to this level. However, it is also important that farmers stay within the P regulatory thresholds to reduce the risk of potential environmental impact on surface waters.

This long-term research was carried out in three provinces during 8 yr of continuous application of mono-ammonium P fertilizer followed by 3 yr of P depletion. The objectives of our study were to (i) determine how soil test P changes over time across soil type during application and depletion phases and (ii) evaluate soil test P changes using yearly P removal across soil types.

## 3.3. Materials and Methods

The soil test phosphorus experiment was conducted on seven field sites across Alberta (Ellerslie, Fort Saskatchewan and Carstairs), Saskatchewan (Sylvania) and Manitoba (Carman, East of Spruce, and Forrest) with varying soil types. However, due to poor weather conditions, Carstairs and Sylvania sites had incomplete data sets and were eliminated from this analysis. The five experimental sites that we worked on consisted of Carman (Orthic Black Chernozem), Forrest (Orthic Black Chernozem), East of Spruce (Orthic Black Chernozem), Ellerslie (Eluviated Black Chernozem), and Fort Saskatchewan (Eluviated Black Chernozem). Information on the physicochemical properties of the soils (Table 3.1), experimental design and soil sampling were discussed in detail in chapter 2. As such only the information that is pertinent to the current study will be provided in this chapter.

In this study, P was applied at the rates of 0, 20, 40 and 80 kg P ha$^{-1}$ each year during the P accumulation stage (2002 – 2009), using three sources of granular commercial mono-ammonium phosphate (MAP) fertilizers containing low (4 ppm), moderate (70 ppm) or high (230 ppm) concentrations of Cd, making a total of 10 treatments with four replications at each site. Phosphorus balance was calculated as the cumulative amount of P added in 8 years less the grain P removal for all soil types. Cumulative effects of the different P rates were observed after eight years of application (2002 – 2009) and three years of P depletion (2010 -2012) at two depths of soil (0 -7.5 cm and 7.5 – 15 cm).

## 3.3.1. Extraction Experiment

A total of four representative soil samples collected from the field sites at the two depths were air-dried and sieved using a 2-mm sieve. Extractable phosphorus was determined using three methods, namely Olsen P, Mehlich-3 P and water-extractable P. Soil samples were analysed for

Olsen extractable P (Olsen-P) by shaking 1.0 g of soil with 20 mL of 0.5 N sodium bicarbonate solution (pH of 8.5) in the presence of 0.25 g of charcoal, for 30 min (Olsen and Sommers 1982). Mehlich-3 extractable P (M3-P) was determined by shaking 2.5 g of air dried soil samples with 25 mL of Mehlich-3 extracting reagent (1.5 M NH4F + 0.1 M EDTA + $NH_4NO_3$ + $CH_3COOH$ + $HNO_3$) for 5 min and filtering the suspension through Whatman No. 40 filter paper (Mehlich 1984). A portion of the Mehlich-3 extracting agent was also analyzed for Mehlich-3 extractable iron, calcium and magnesium using the inductively coupled plasma (ICP) emission spectroscopy. Water-extractable P (Water-P) was determined by extracting 2 g of soil with 20 mL of de-ionized water, shaking the suspension for 1 h on a reciprocating shaker (Self-Davis et al. 2000). The suspension was centrifuged, filtered using No. 42 Whatman filter paper and stored in a refrigerator at 4°C for P determination.

The P in the various extracts was determined colorimetrically using the acid molybdate blue method as described by Murphy and Riley (1962). The absorbance at wavelength of 882 nm was measured using a scanning spectrophotometer (Ultrospec 3100 pro). The net surplus of P applications was calculated after correcting for the grain P removal for all soil types. Including in-house laboratory reference soil material and blank for the soil extraction assessed reliability of the analytical procedures. Values of soil test P were within the confidence intervals given in the standard and reference material.

### 3.3.2. Statistical analysis

The PROC UNIVARIATE carried out on Water- P, Olsen- P and M3- P showed that the residuals were normally distributed (i.e. the Shapiro-Wilk statistic was greater than 0.9). Analysis of variance was performed using the PROC Mixed procedure of SAS Version 9.4 (SAS Institute 2011) on all extracts with four factors, experimental sites, rates, depths and time being

represented as fixed effects and blocks as random effect. The Kenward-Roger method was used to determine degrees of freedom. The mean comparison method used was Least Significant Difference (LSD) means. Mean comparison was carried out on the amount of P extracted by the different extracting agents. The various extraction methods were related to the P balance using regression analysis. Spearman correlation analysis was used to determine the influence of the different extraction methods (generated using the 2009 data set) and pH, soil texture, cation exchange capacity, organic carbon, and Mehlich-3 calcium, magnesium, iron and phosphorus. A probability level $\leq 0.05$ was considered significant.

**Table 3.1 Physical and chemical properties of research sites**

| Site | pH[a] | Clay[c] % | Silt[c] % | Sand[c] % | CEC[a] cmol kg$^{-1}$ | Organic C[a] mg kg$^{-1}$ | M3-Fe[b] mg kg$^{-1}$ | M3-Ca[b] mg kg$^{-1}$ | M3-Mg[b] mg kg$^{-1}$ | M3-P[b] mg kg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 0 - 7.5 cm | | | | | |
| East of Spruce | 7.4 | 36 | 38 | 26 | 34 | 28 | 8 | 499 | 26 | 4 |
| Carman | 5 | 19 | 14 | 67 | 16 | 37 | 29 | 204 | 11 | 7 |
| Forrest | 7.4 | 22 | 32 | 46 | 35 | 38 | 10 | 478 | 20 | 3 |
| Ellerslie | 6.2 | 43 | 42 | 15 | 42 | 40 | 29 | 538 | 19 | 4 |
| Ft. Sask. | 7.3 | 35 | 43 | 22 | 42 | 51 | 17 | 620 | 22 | 6 |
| | | | | | 7.5 - 15 cm | | | | | |
| East of Spruce | 7.4 | 35 | 39 | 26 | 34 | 28 | 5 | 1442 | 30 | 1 |
| Carman | 5.1 | 24 | 14 | 62 | 16 | 37 | 29 | 228 | 12 | 6 |
| Forrest | 7.5 | 26 | 39 | 35 | 35 | 38 | 8 | 726 | 21 | 1 |
| Ellerslie | 6.4 | 45 | 40 | 15 | 42 | 40 | 35 | 588 | 21 | 3 |
| Ft. Sask. | 7.6 | 36 | 41 | 23 | 42 | 51 | 18 | 691 | 23 | 3 |

[a] pH, CEC, Organic C: sampled at 0 -15 cm depth in year 2003, adapted from Grant et al. (2013)
[b] M3-Fe, Mehlich-3 extractable Fe; M3-Ca, Mehlich-3 extractable Ca; M3-Mg, Mehlich-3 extractable Mg; M3-P, Mehlich-3 extractable P (values obtained at 0 - 7.5cm depth interval from samples taken in 2012)
[c] Clay, Silt, Sand (values obtained at 0 – 7.5 and 7.5 – 15 cm depth interval from samples taken in 2012)

## 3.4. Results and Discussion

The soil types used in this study varied in pH, cation exchange capacity (CEC), organic carbon, texture, M3-Ca, M3-Mg, M3-Fe and M3-P. The soils varied from alkaline to acidic pH (pH 7.4 for the soil from East of Spruce and Forrest to pH 5.0 for the soil from Carman) and the soil type varied from orthic black chernozem to eluviated black chernozem (Table 3.1). The soil texture varied from silty clay soil (43% clay content in Ellerslie) to sandy loam soil (19% clay content in Carman). The CEC was greatest in the eluviated black chernozem soils at Ellerslie and Fort Saskatchewan (42 cmol kg$^{-1}$) and smallest in the orthic black chernozem soil at Carman (16 cmol kg$^{-1}$). Organic carbon concentration varied from 51 g kg$^{-1}$ in Fort Saskatchewan soil to 28 g kg$^{-1}$ in East of Spruce soil. In the 0 – 7.5 cm depth, M3-Fe was greatest in both Ellerslie and Carman soils (29 mg kg$^{-1}$) and smallest in East of Spruce soils (8 mg kg$^{-1}$). At the 7.5 -15 cm depth, M3-Fe was greatest in Ellerslie (35 mg kg$^{-1}$) and smallest in East of Spruce (5 mg kg$^{-1}$). The soil from Fort Saskatchewan had the most M3-Ca (620 mg kg$^{-1}$) and the soil from Carman had the least (204 mg kg$^{-1}$) in the 0 -7.5 cm depth. However, in the 7.5-15 cm depth, East of Spruce has the highest concentration of M3-Ca (1442 mg kg$^{-1}$) and Ca was consistently lowest in Carman soil (228 mg kg$^{-1}$). The M3-Mg had a different pattern from that of M3-Ca as the East of Spruce soil has the highest concentration of M3-Mg (26 and 30 mg kg$^{-1}$ for 0 - 7.5 cm and 7.5-15 cm depth) and the smallest was in the Carman soil (11 and 12 mg kg$^{-1}$ for 0-7.5 cm and 7.5-15 cm depth) respectively (Table 3.1). The M3-P was greatest at Carman at 7 and 6 mg kg$^{-1}$ and smallest in the Forrest soil at 3 and 1 mg kg$^{-1}$ for the 0 – 7.5 cm and 7.5 – 15 cm depths respectively.

### 3.4.1. Effect of fertilizer accumulation and depletion on soil extractable P

The soil test P values obtained with the different chemical extractants varied widely due to the differences in the extracting ability of the reagent. The agronomic soil test P methods (Olsen and Mehlich-3 extraction methods) extracted more P than the environmental method (water extraction method). The water-P ranged from $0.9 - 39.7$ mg P kg$^{-1}$ and $0.4 - 28.9$ mg P kg$^{-1}$ at the end of the addition period (2009) and the depletion period (2012) respectively (Appendix 3.A1 and A2). The M3-P ranged from $0.9 - 234.3$ mg P kg$^{-1}$ and $3.6 - 155.9$ mg P kg$^{-1}$ for the end of the addition period (2009) and the depletion period (2012) respectively (Figure 3.1a and b). The Olsen-P values for the two depths ranged between $1.0 - 90.4$ mg P kg$^{-1}$ and $0.7 - 53.9$ mg P kg$^{-1}$ across the soil types at the end of the addition period (2009) and depletion period (2012) respectively (Appendix 3.B1 and B2). Ige et al. (2006) also reported the ability of Mehlich-3 extractant to extract greater amount of P than the other extracting methods. The amount of P that was extracted by these methods depended on the acidic nature of the reagents and their interaction with the soils. Mehlich-3 extracted more P because of its acidic nature and was not neutralized by carbonates, since the carbonate concentration of the soils was low, as indicated by the moderate soil pH values. On the other hand, the Water-P, an environmental soil test method, correlates poorly with runoff dissolved reactive P (DRP) and total dissolved P (TDP) making it less effective in predicting runoff concentration than the agronomic soil test methods (Kumaragamage et al. 2011).

Due to the calcareous origin of Manitoba soils, the agronomic soil test P method that is widely used in Manitoba is the Olsen method. Based on Manitoba Soil Fertility Guide (Manitoba Agriculture and Food 2001), soils are categorized agronomically as Very Low (Olsen-P of 0–5 mg kg$^{-1}$), Low (Olsen-P of 5–10 mg kg$^{-1}$), Medium (Olsen-P of 10–15 mg kg$^{-1}$), High (Olsen-P

of 15–20 mg kg$^{-1}$) and Very High (20+ mg kg$^{-1}$).
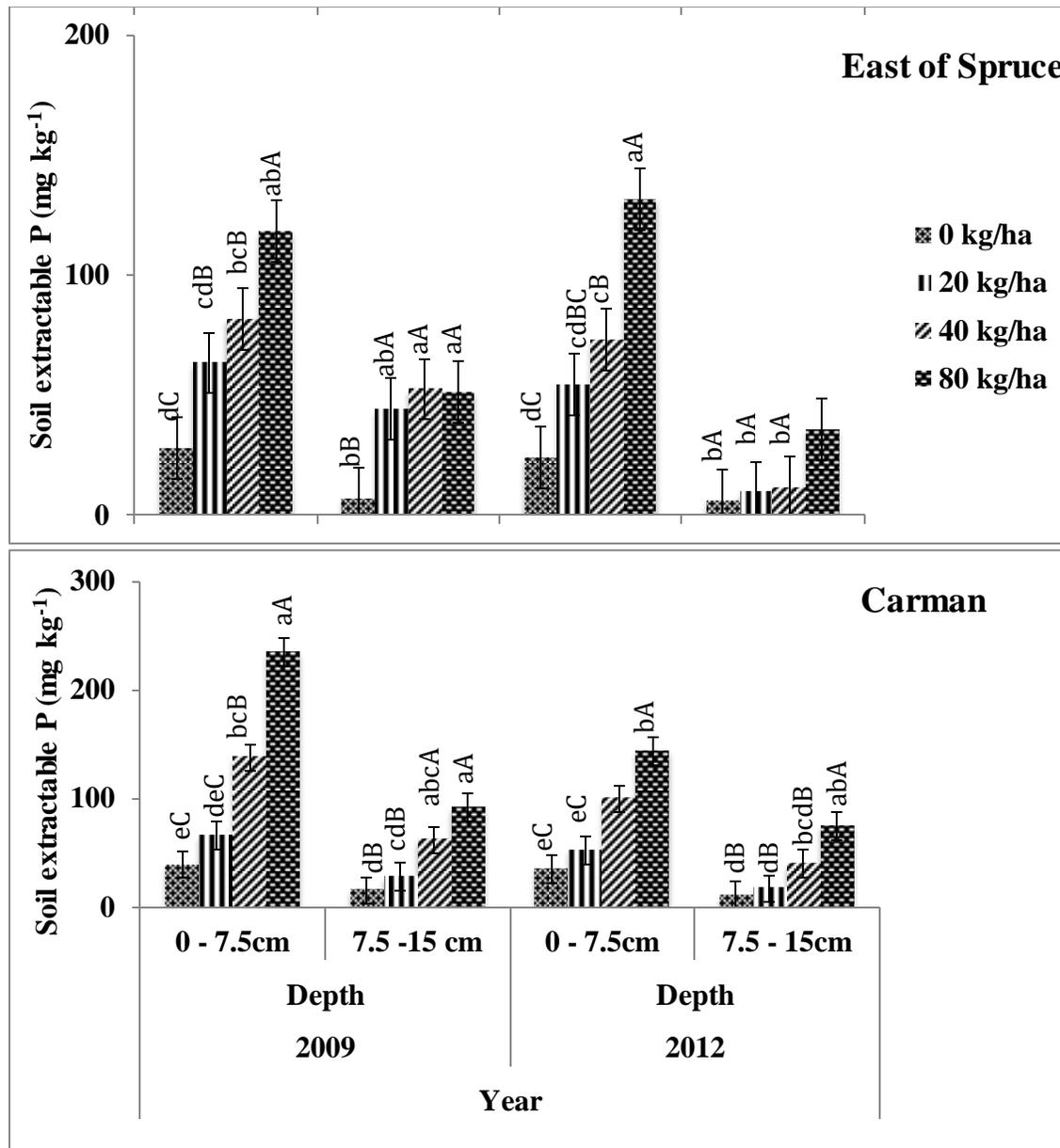


**Figure 3.1a Effect of P rate on Mehlich-3 extractable P in 2009 and 2012 for 0 - 7.5 and 7.5 - 15 cm soil depths at East of Spruce and Carman sites. Means groupings indicated by the lowercase letters are used to compare between depths within a given rate and year. Means groupings indicated by uppercase letters are used to compare rates within a given depth and year. Means followed by the same letter are not significantly different.**
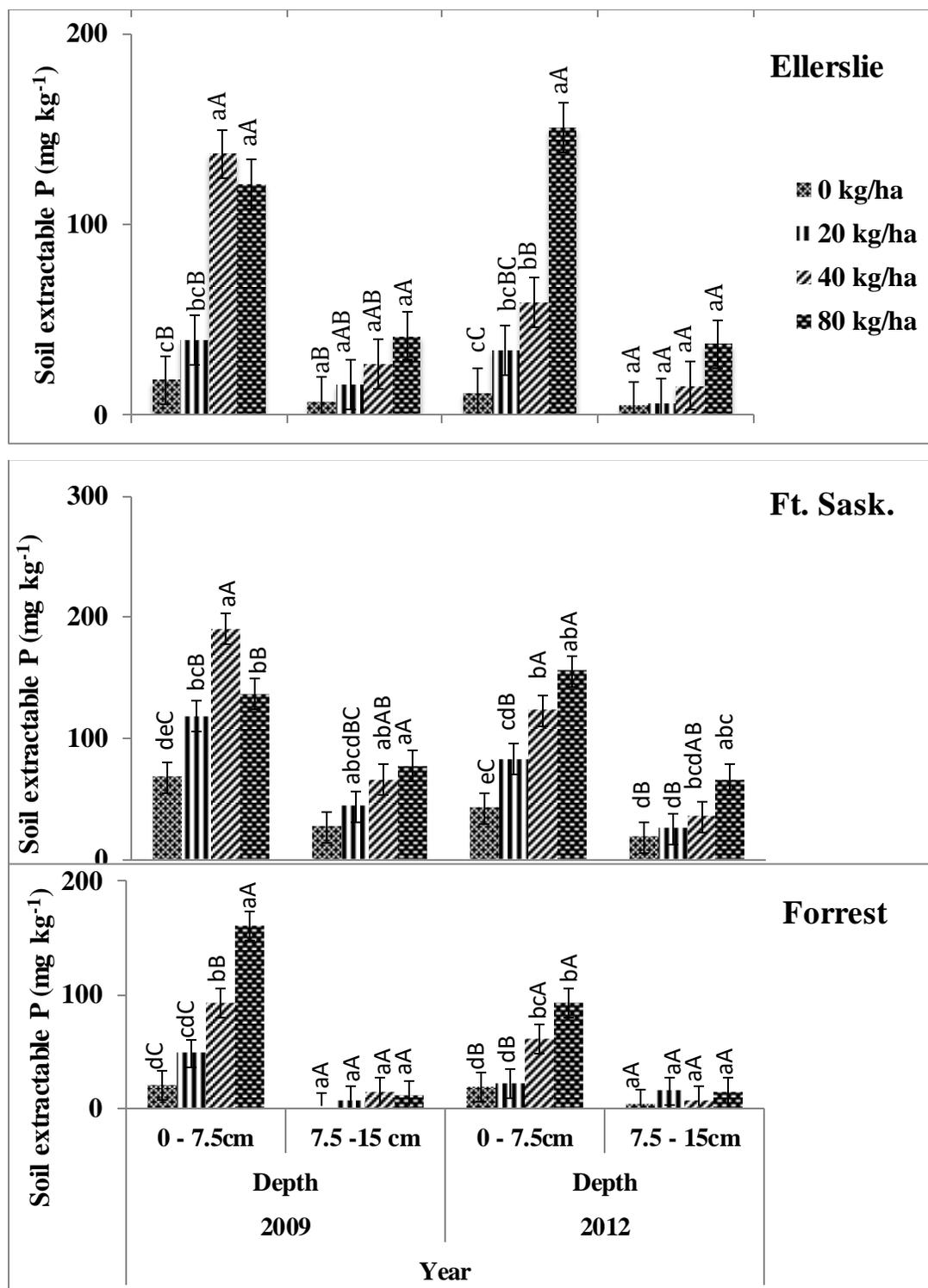
**Figure 3.1b Effect of P rate on Mehlich-3 extractable P in 2009 and 2012 for 0 - 7.5 and 7.5 - 15 cm soil depths at Ellerslie, Fort Saskatchewan and Forrest sites. Means groupings indicated by the lowercase letters are used to compare between depths within a given rate and year. Means groupings indicated by uppercase letters are used to compare rates within a given depth and year. Means followed by the same letter are not significantly different.**

In our study, the majority of the Olsen-P values at all rates of P application are in the very high category for all the sites (using the 0-7.5 cm depth data set). However, after 3 years of P depletion, the Olsen-P in the soil with smallest rate of P application (20 kg P ha$^{-1}$) fell into the medium category at all the sites except Fort Saskatchewan. At the 7.5-15 cm depth, most of the Olsen-P values at all rates of P application, except the 80 kg P ha$^{-1}$, fell into the medium to high categories. Excluding Carman and Fort Saskatchewan, Olsen-P values at all other sites also belong to the medium to high categories. Following three years of depletion, the Olsen-P within the 7.5-15 cm depth, at all rates of P application were found in or below the medium category at all sites except Carman and Fort Saskatchewan. At these two sites (Carman and Fort Saskatchewan), Olsen-P within the 7.5-15 cm depth at the 80 kg P ha$^{-1}$ was in the high to very high category. Therefore, at annual rates of application greater than 20 kg P ha$^{-1}$, there was a surplus of P, increasing P fertility in the soil as well as the risk of P loss to surface waters.

### 3.4.2. Effect of time, depths, sites and rates of P fertilizer application on soil test P

In this study, P levels increased with the rate of P fertilizer application for all soil test methods during the P accumulation phase, but decreased following 3 years of depletion (Table 3.2).

**Table 3.2 Group means of the effect of sites, rates, years and depth on soil extractable P**

| EFFECTS | Water Ex-P | Olsen Ex-P | Mehlich Ex-P |
|---|---|---|---|
| SITE | MEAN | MEAN | MEAN |
| East of Spruce | 8 | 22 | 50 |
| Carman | 13 | 25 | 72 |
| Ellerslie | 8 | 20 | 46 |
| Fort Saskatchewan | 13 | 34 | 80 |
| Forrest | 5 | 15 | 37 |
|  |  |  |  |
| RATE |  |  |  |
| 0 kg ha$^{-1}$ | 3 | 9 | 20 |
| 20 kg ha$^{-1}$ | 5 | 17 | 40 |
| 40 kg ha$^{-1}$ | 10 | 27 | 69 |
| 80 kg ha$^{-1}$ | 18 | 40 | 97 |
|  |  |  |  |
| YEAR |  |  |  |
| 2009 | 11 | 32 | 65 |
| 2012 | 7 | 14 | 48 |
|  |  |  |  |
| DEPTH |  |  |  |
| 7.5 CM | 14 | 34 | 85 |
| 15 CM | 4 | 13 | 29 |
|  |  |  |  |
|  | P-VALUE |  |  |
| SITE | 0.0018 | <0.0001 | <0.0001 |
| YEAR | <0.0001 | <0.0001 | <0.0001 |
| SITE*YEAR | 0.0014 | 0.0005 | 0.1738 |
| RATE | <0.0001 | <0.0001 | <0.0001 |
| SITE* RATE | 0.0014 | 0.0008 | <0.0001 |
| YEAR* RATE | <0.0001 | <0.0001 | <0.0001 |
| SITE*YEAR* RATE | 0.0752 | 0.6100 | <0.0001 |
| DEPTH | <0.0001 | <0.0001 | <0.0001 |
| SITE*DEPTH | 0.0002 | 0.0011 | 0.0814 |
| YEAR*DEPTH | <0.0001 | <0.0001 | 0.0153 |
| SITE*YEAR*DEPTH | 0.3248 | 0.0204 | 0.0046 |
| RATE *DEPTH | <0.0001 | <0.0001 | <0.0001 |
| SITE* RATE *DEPTH | 0.0212 | 0.0018 | 0.0004 |
| YEAR* RATE *DEPTH | 0.0013 | 0.0121 | 0.3961 |
| SITE*YEAR* RATE *DEPTH | 0.0891 | 0.0545 | 0.0001 |

### 3.4.2.1. Water-extractable P

Across all the sites, the Fort Saskatchewan site had the greatest water extractable P (6-34 mg kg$^{-1}$) whereas the Forrest site had the least concentration (2-19 mg kg$^{-1}$) at the 0 – 7.5 cm depth. The Ellerslie site was the intermediate between these soils with water extractable P (WEP) that ranged between 2-30 mg kg$^{-1}$ (Figure 3.2). Differences between sites, however, varied with P application rates and soil depth, as shown by a significant interaction of site $\times$ rate $\times$ depth (Table 3.2). There were no significant differences between the two depths at the 0 kg ha$^{-1}$ rate of the WEP at all sites except Fort Saskatchewan. There was an increase in the WEP in response to the application rates at all other sites and at both depths, except for the Forrest site where there was no significant difference among all the rates at the 7.5-15 cm depth. At the 0-7.5 cm depth, the WEP increased significantly at Fort Saskatchewan site in the 20 kg ha$^{-1}$ rate of P application. At the 40 kg ha$^{-1}$ rate of P application, WEP was greatest in Carman and Fort Saskatchewan sites compared to all sites for the 0-7.5 cm depth. There was no significant difference in Carman, Ellerslie and Fort Saskatchewan sites for the 80 kg ha$^{-1}$ rate of P application of the 0-7.5 cm depth. No significant differences were observed across all sites at the 0 and 20 kg ha$^{-1}$ rate of P application for the 7.5-15 cm depth.

The effect of rate of P application was also evident across the sites and also varied with the sampling depth and year resulting in a significant interaction of year $\times$ rate $\times$ depth (Table 3.2). There were significant differences at all rates of application for the 0-7.5 and 7.5-15 cm depths at the end of the accumulation (2009) and depletion phases (2012). At the 0-7.5 cm depth interval, WEP at the different rates of P application significantly declined between the accumulation and depletion phases. At the 7.5-15 cm depth, there were significant decreases in WEP between the accumulation and depletion phases for all rates of P except the 0 kg ha$^{-1}$. At the 7.5-15 cm depth,

no significant differences in WEP were observed for the 0 and 20 kg ha$^{-1}$ rates of P application during accumulation phase. At the 7.5-15 cm depth, no significant differences in WEP were observed at the 0, 20 and 40 kg ha$^{-1}$ rates of P application in depletion phase (Figure 3.3).

### 3.4.2.2. Mehlich-3 extractable P

The main effects and interactions of site, rate, depth and year were significant for M3-P. The effect of application rate on M3-P varied with site, year and soil depth, as shown by the significant Site $\times$ Year $\times$Rate $\times$ Depth interaction (Table 3.2). At the 0-7.5 cm depth, M3-P behaved exceptionally, as the high rate (80 kg P ha$^{-1}$) of application did not follow the trend of having the greatest amount of extractable P. The results showed that the medium rate (40 kg P ha$^{-1}$) has the greatest amount of extractable P for the Fort Saskatchewan site, which was inconsistent with the results from other sites (Figure 3.1a & 3.1b). Result from Table 3.1 showed that M3-Ca was greatest in Fort Saskatchewan site, thus, it was expected that M3-P should be higher at these sites but the opposite was the case and the reason is unknown.

### 3.4.2.3. Olsen-extractable P

The effect of rates of application varied with year and depth of soil, as shown by the three-way interaction Year $\times$ Rate $\times$ Depth (Table 3.2). As shown in Figure 3.4, Olsen-P for each depth declined at all sites during the depletion phase except for the 7.5-15 cm depth at Forrest leading to a significant 3 way interaction. After 3 years of cessation of P application, Olsen-P significantly decreased at the rate of 0, 20, 40, and 80 kg P ha$^{-1}$ at the 0-7.5 and 7.5-15 cm depth, respectively. Figure 3.4 showed that the proportional decline in Olsen-P for the high rate was less than the proportional decline in Olsen-P for the low rate. This indicates that the high rate retained a larger proportion of P in a plant available form. These results are similar to those of

71

Laboski and Lamb (2003) and Kashem et al. (2004b), who also observed that available-P was reduced with time in P amended soils.

The effect of P application rates also varied with depth and site as seen in Figure 3.5 leading to a significant interaction of Site $\times$ Rate $\times$ Depth on Olsen-P. There were significant differences at all rates of application for the two depths at all sites. The concentration of Olsen-P at the Fort Saskatchewan site significantly increased with the absolute values of 72 mg P $kg^{-1}$ and 35 mg P $kg^{-1}$ for 0-7.5 and 7.5-15 cm depths respectively. The 20, 40 and 80 kg $ha^{-1}$ rates of application for the 7.5-15 cm depth at the Forrest site were not significantly different. It was also observed that the Fort Saskatchewan site had a high amount of Olsen-P in the zero fertilizer plot (0 kg P $ha^{-1}$); perhaps, this is due to cumulative fertilizer history prior to the study (Figure 3.5).

The effect of site varied with year and depth of soil, as shown by the interaction of Site $\times$ Year $\times$ Depth in Table 3.2. There are significant differences across all sites at the 0-7.5 and 7.5-15 cm depths at the end of addition (2009) and depletion phase (2012). The Fort Saskatchewan site had the greatest Olsen-P value at both the 0-7.5 and 7.5-15 cm depths (Figure 3.6). At the end of depletion phase (2012), Olsen-P significantly declined at all sites except for the 7.5-15 cm depths at Forrest site. The absolute values of decrease for Olsen-P ranged between 20-29 and 4-15 mg $kg^{-1}$ for the 0-7.5 and 7.5-15 cm depth intervals.
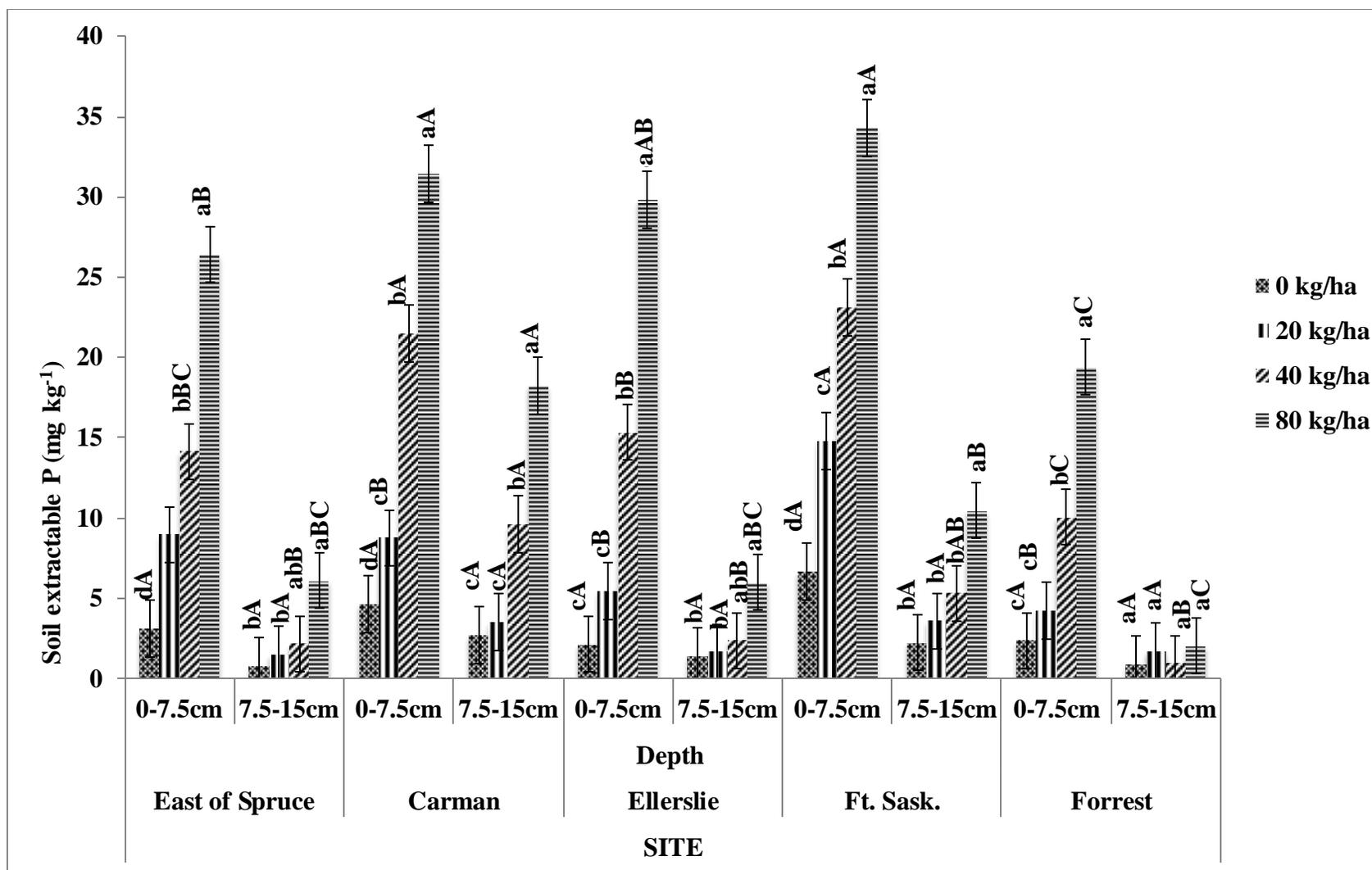
**Figure 3.2 Effect of application rates on water extractable P averaged for all years at two depths in different sites (site x rate x depth). Means groupings indicated by the lowercase letters are used to compare rates within a given depth and site. Means groupings indicated by the uppercase letters are used to compare across sites for a given rate and depth. Means followed by the same letter are not significantly different.**
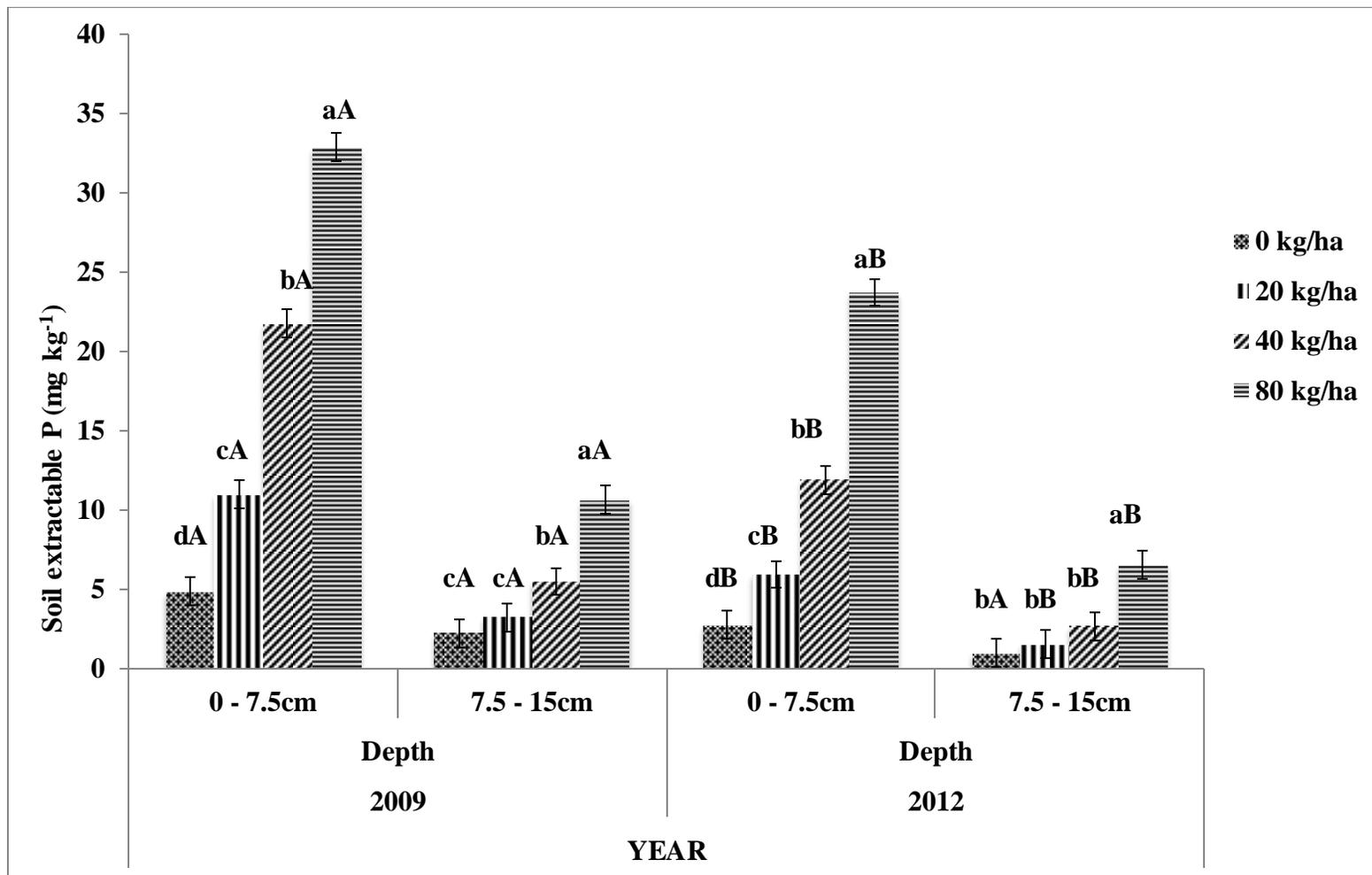
**Figure 3.3 Effect of application rates on water extractable P averaged across all sites at two depths in different years (year x rate x depth). Means groupings indicated by the lowercase letters are used to compare rates within a given depth and year. Means groupings indicated by the uppercase letters are used to compare rates of a given depth and year. Means followed by the same letter are not significantly different.**
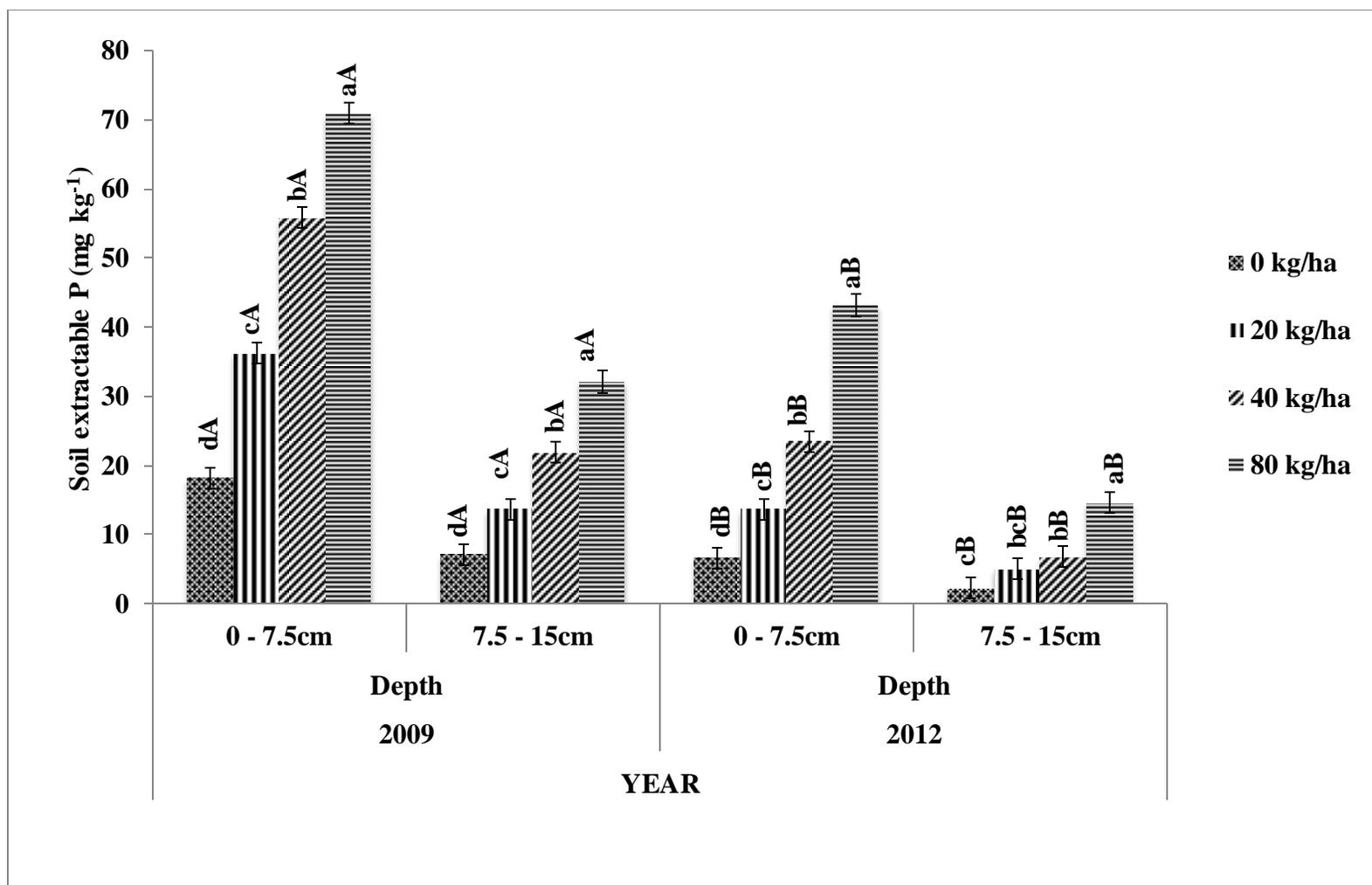
**Figure 3.4 Effect of application rates on Olsen extractable P averaged across all sites at two depths in different years (year x rate x depth). Means groupings indicated by the lowercase letters are used to compare rates within a given depth and year. Means groupings indicated by the uppercase letters are used to compare rates of a given depth and year. Means followed by the same letter are not significantly different.**
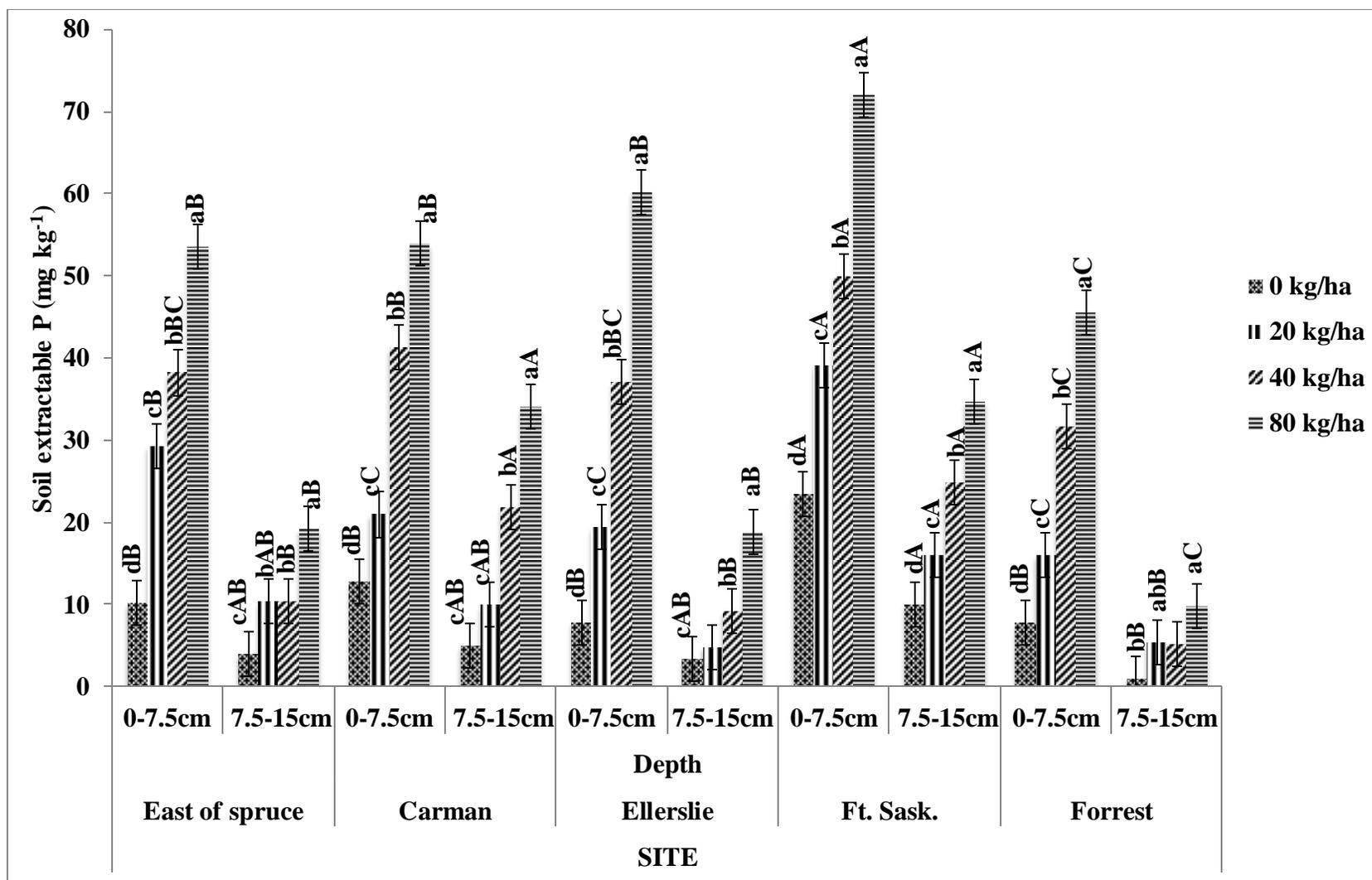
**Figure 3.5 Effect of application rates on Olsen extractable P averaged for all years at two depths at different sites (site x rate x depth). Means groupings indicated by the lowercase letters are used to compare rates within a given depth and year. Means groupings indicated by the uppercase letters are used to compare across sites for a given rate and depth. Means followed by the same letter are not significantly different.**
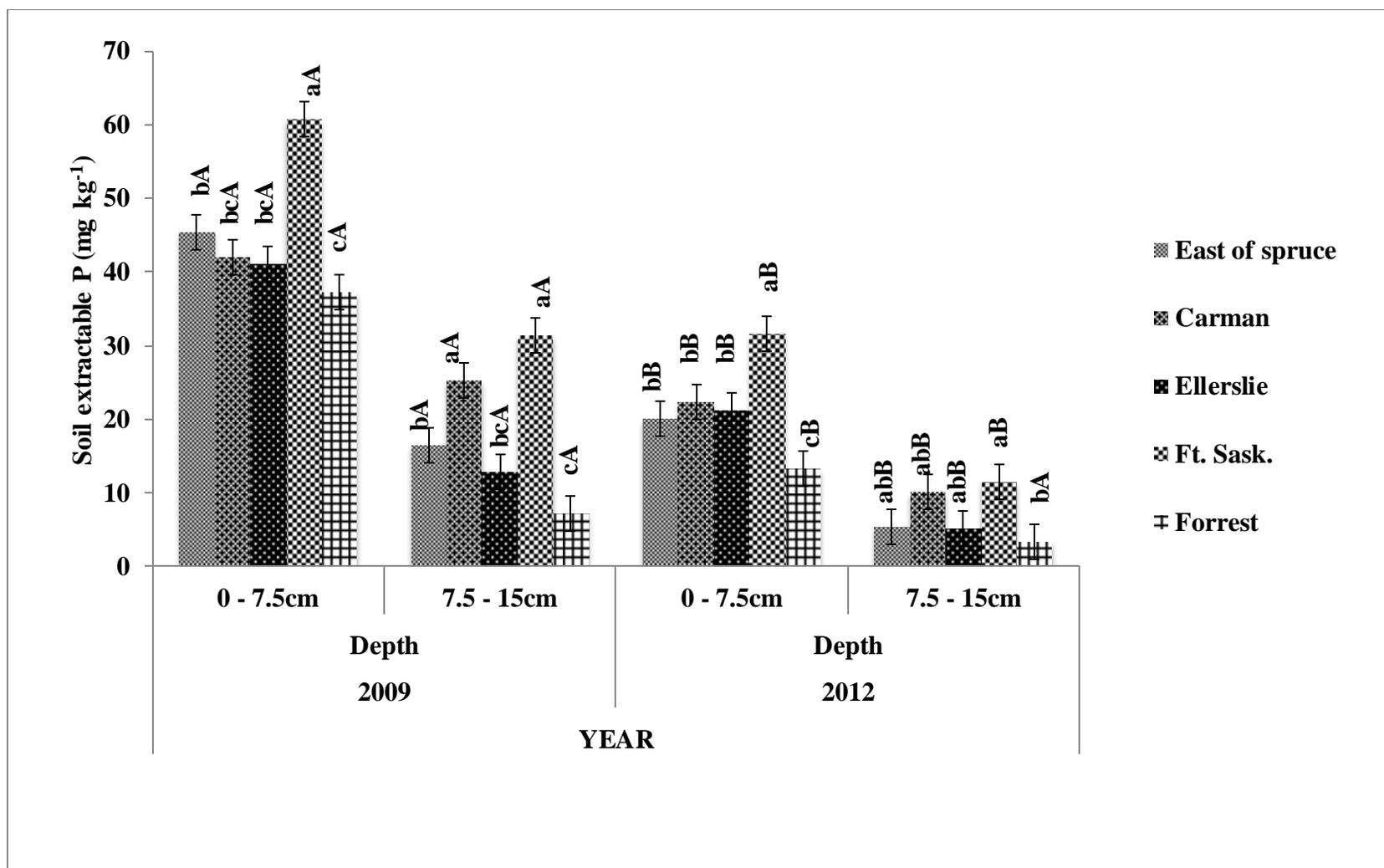
**Figure 3.6 Effect of year and depth on Olsen extractable P averaged for all rates at different sites (site x year x depth). Means groupings indicated by the lowercase letters are used to compare between different sites depths within each depth for a given year. Means groupings indicated by the uppercase letters are used to compare between years for a given site and depth. Means followed by the same letter are not significantly different.**

77

### 3.4.3. Rate of change in soil test P in the different soil types for the accumulation phase

The Water-, Olsen- and M3-P were regressed against the net surplus of P applications (after correcting for the grain P removal) for all soil types (Figure 3.7a – e). The regression coefficient (slope for the linear regression) shows the rate of change of soil test P during the P accumulation phase (2002 – 2009).

The slopes of Water-P for the surface layer (0 – 7.5 cm) were 0.043, 0.050, 0.036, 0.051 and 0.049 for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites (Figure 3.7a - e). The coefficients of determination for the linear relationship, $R^2$, of Water-P across all the sites were significant and ranged from 0.92 to 0.99 for the 0 – 7.5 cm depth. Based on these slopes, a net surplus of 23, 20, 27, 19 and 20 kg P ha$^{-1}$ for the 0 – 7.5 cm depth would raise Water-P by 1 mg P kg$^{-1}$ for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites respectively after 8 years of annual P addition (Table 3.3). The findings by Shepherd and Withers (1999) reported that the amount of P fertilizer applied in excess of crop removal (100 kg P ha$^{-1}$), to raise water-P by 1 mg kg$^{-1}$ is 5 mg kg$^{-1}$ (23 kg ha$^{-1}$ for 35 cm depth) after three years of amendments on a temperate acid soil.

The slopes of Water-P for the 7.5 – 15 cm depth were 0.010, 0.029, 0.010 and 0.017 for East of Spruce, Carman, Ellerslie and Fort Saskatchewan sites (Figure 3.7a - e). The coefficients of determination for the linear relationship, $R^2$, of Water-P are significant at all the sites except Forrest for the 7.5 – 15 cm depth. A net surplus of 100, 33, 105 and 57 kg P ha$^{-1}$ for the 7.5 – 15 cm depth would raise Water-P by 1 mg P kg$^{-1}$ for East of Spruce, Carman, Ellerslie and Fort Saskatchewan sites respectively after 8 years of annual P addition (Table 3.3).

For the Olsen-P, the slopes increases in extractable P, relative to P surplus for the surface layer (0 – 7.5 cm) were surprisingly similar at all sites except East of Spruce and Ellerslie which are

non-significant (Figure 3.7a - e). The coefficient of determination for the linear relationship, $R^2$, of Olsen-P across all the sites ranged from 0.90 to 0.99. Based on these slopes, a surplus of 13, 12 and 11 kg P ha$^{-1}$ would raise Olsen-P by 1 mg P kg$^{-1}$ for Carman, Forrest and Fort Saskatchewan sites (Table 3.3). Messiga et al. (2010), who reported that at an application of 100 kg ha$^{-1}$, it would take 3.3 mg kg$^{-1}$ (11.6 kg ha$^{-1}$) of fertilizer to raise Olsen-P by 1 mg kg$^{-1}$ on a slightly alkaline sandy loam soil of 0 – 25 cm depth. Richards et al. (1995) reported that 16.4 kg P ha$^{-1}$ would raise Olsen-P by 1 mg kg$^{-1}$ on southern Ontario soils of 0 – 15 cm depth.

The slopes of Olsen-P for the 7.5 – 15 cm depth varied from 0.019 – 0.061 across all sites (Figure 3.7a - e). The coefficients of determination for the linear relationship, $R^2$, of Olsen-P across all the sites were significant and ranged from 0.95 to 0.99 for the 7.5 – 15 cm depth. A net surplus of 32, 16, 51, 30 and 18 kg P ha$^{-1}$ for the 7.5 – 15 cm depth would raise Olsen-P by 1 mg P kg$^{-1}$ for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites respectively after 8 years of annual P addition (Table 3.3).

Unlike what we observed for water- and Olsen-P, the slope of M3-P in the surface layer (0 – 7.5 cm) varied substantially at all sites except Ellerslie and Fort Saskatchewan, which are non-significant (Figure 3.7a - e). This may be due to the fact that M3 solution is a much stronger reagent and it extracted acid-soluble P such as Ca-associated P and some Fe- and Al-phosphate (Kumaragamage et al., 2007). The coefficient of determination for the linear relationship, $R^2$, of M3-P at all sites except Ellerslie and Fort Saskatchewan was not as high as those for water- and Olsen-P. Annual applications of P fertilizer at different rates showed that a surplus of 7, 3 and 4 kg P ha$^{-1}$ would raise M3 soil test P by 1 mg P kg$^{-1}$ for East of Spruce, Carman and Forrest sites respectively (Table 3.3). These results are within the same order of magnitude to those observed by Zhang et al. (2004), who reported that the amount of additional P required to increase M3-P

by 1 mg kg$^{-1}$ for the 0 – 20 cm depth was 6.3 kg ha$^{-1}$ after 10 years of continuous application of triple super-phosphate (TSP).

The slopes of M3-P for the 7.5 – 15 cm depth ranged from 0.06 – 0.12 across all sites (Figure 3.7a - e). The coefficients of determination for the linear relationship, $R^2$, of M3-P across all the sites except East of Spruce and Forrest were significant and ranged from 0.92 to 0.99 for the 7.5 – 15 cm depth. A net surplus of 8,18 and 12 kg P ha$^{-1}$ for the 7.5 – 15 cm depth would raise M3-P by 1 mg P kg$^{-1}$ for Carman, Ellerslie and Fort Saskatchewan sites respectively after 8 years of annual P addition (Table 3.3).

**Depth 0 - 7.5 cm**

y = 0.3099x + 54.923
R² = 0.9857, P = 0.0072

y = 0.0759x + 26.247
R² = 0.9032, P = 0.0496

y = 0.0497x + 9.7513
R² = 0.9383, P = 0.0314

◆ Mehlich-P
■ Olsen-P
▲ Water-P

**Depth 7.5 - 15 cm**

y = 0.1216x + 23.909
R² = 0.9702, P = 0.0150

y = 0.0606x + 12.699
R² = 0.9671, P = 0.0166

y = 0.0297x + 4.8426
R² = 0.9609, P = 0.0198

◆ Mehlich-P
■ Olsen-P
▲ Water-P

Extractable P (mg/kg)

Annual net rate of P application (kg ha$^{-1}$)
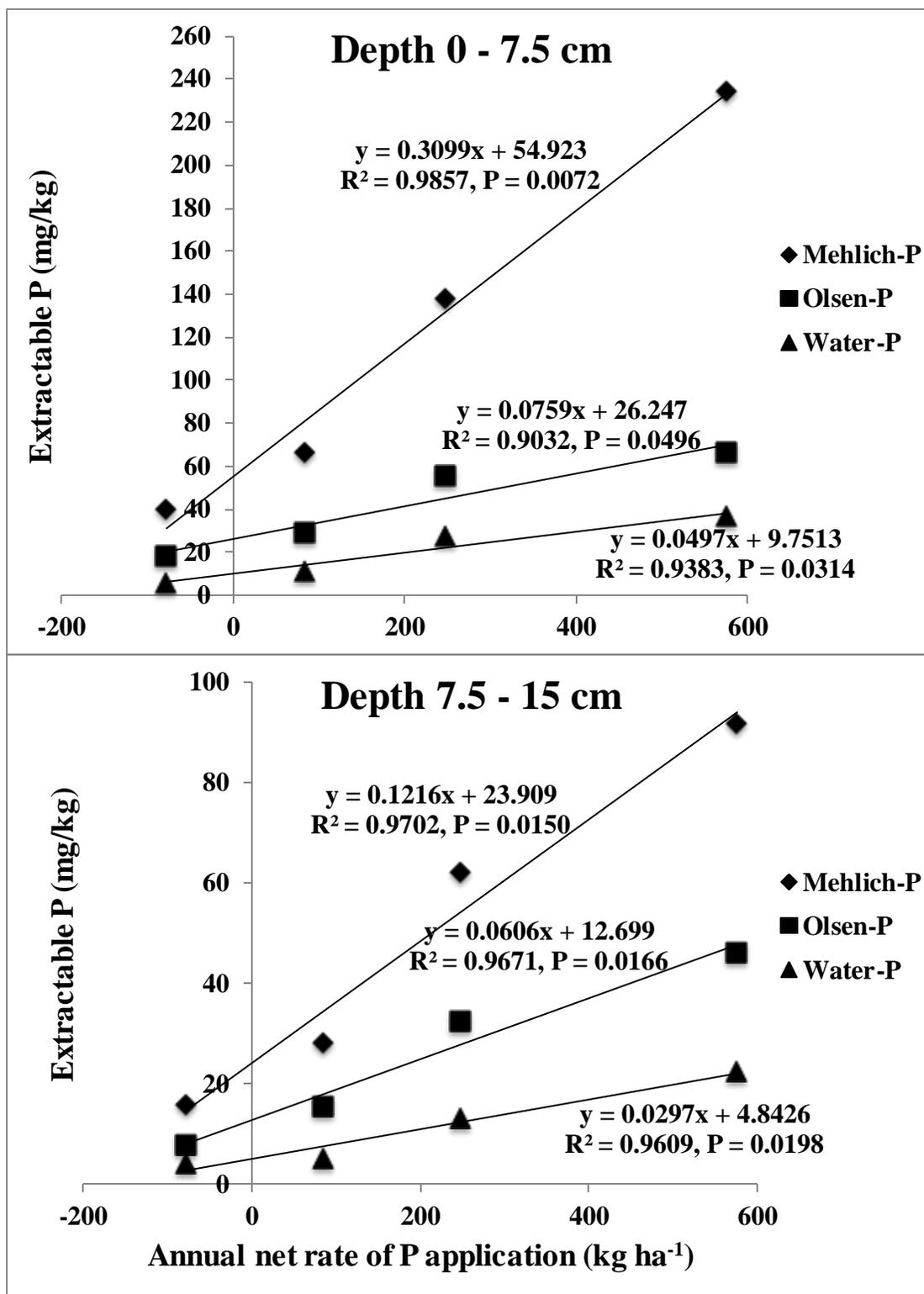
**Figure 3.7a Changes in soil test P with net P balance at 0-7.5 cm and 7.5-15 cm depth at Carman site after adjusting for yearly P removal (2002 - 2009).**
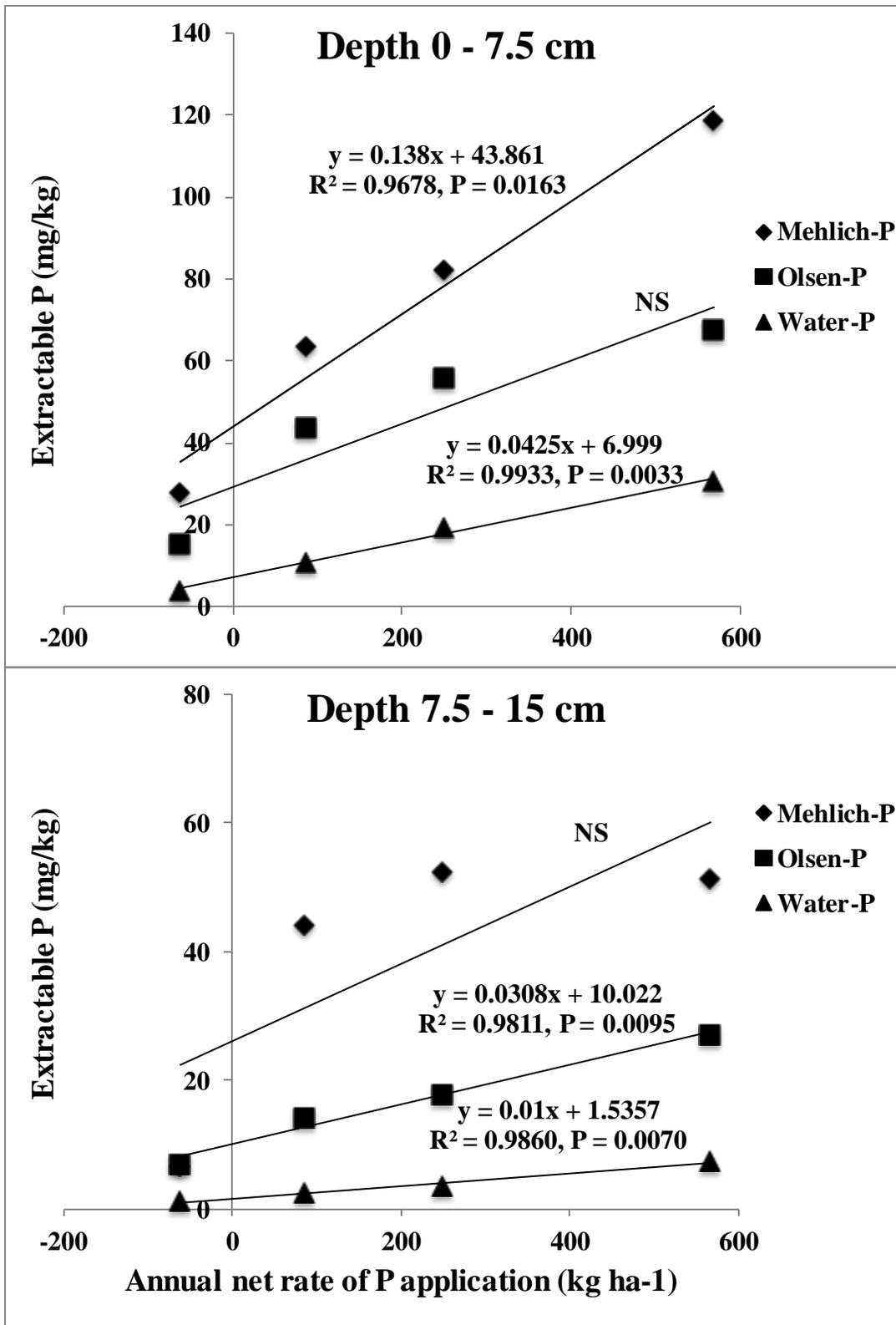
**Figure 3.7b Changes in soil test P with net P balance at 0-7.5 cm and 7.5-15 cm depth at East of Spruce site after adjusting for yearly P removal (2002 - 2009).**

**Depth 0 - 7.5 cm**

$y = 0.2303x + 33.764$
$R^2 = 0.9970, P = 0.0015$

$y = 0.0834x + 20.467$
$R^2 = 0.9467, P = 0.0270$

$y = 0.0364x + 4.6053$
$R^2 = 0.9940, P = 0.0030$

◆ Mehlich-P
■ Olsen-P
▲ Water-P

**Depth 7.5 - 15 cm**

NS

$y = 0.0195x + 3.3465$
$R^2 = 0.9571, P = 0.0217$

NS

◆ Mehlich-P
■ Olsen-P
▲ Water-P

Extractable P (mg/kg)

Annual net rate of P application (kg ha-1)
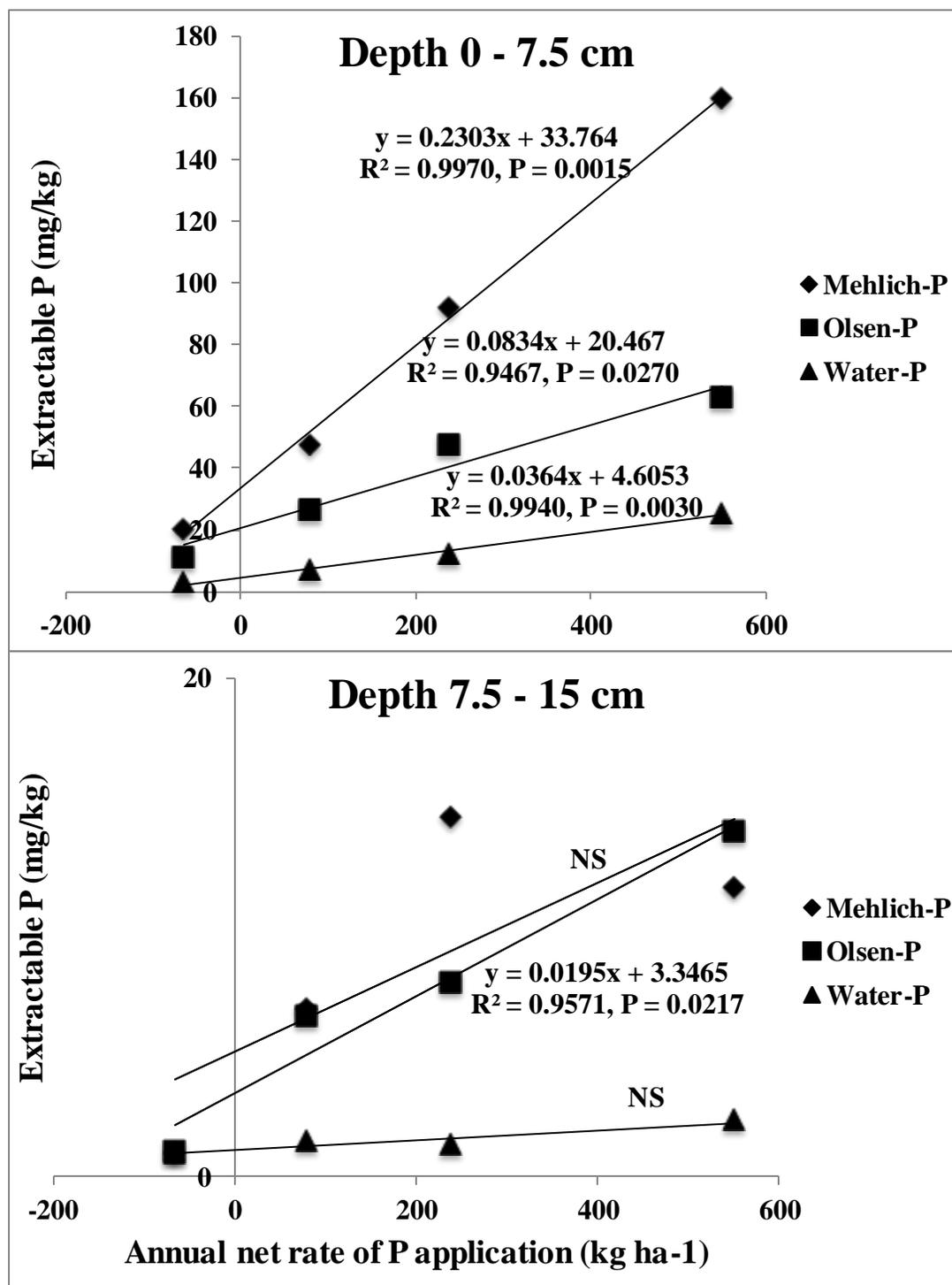
**Figure 3.7c Changes in soil test P with net P balance at 0-7.5 cm and 7.5-15 cm depth at Forrest site after adjusting for yearly P removal (2002 - 2009).**
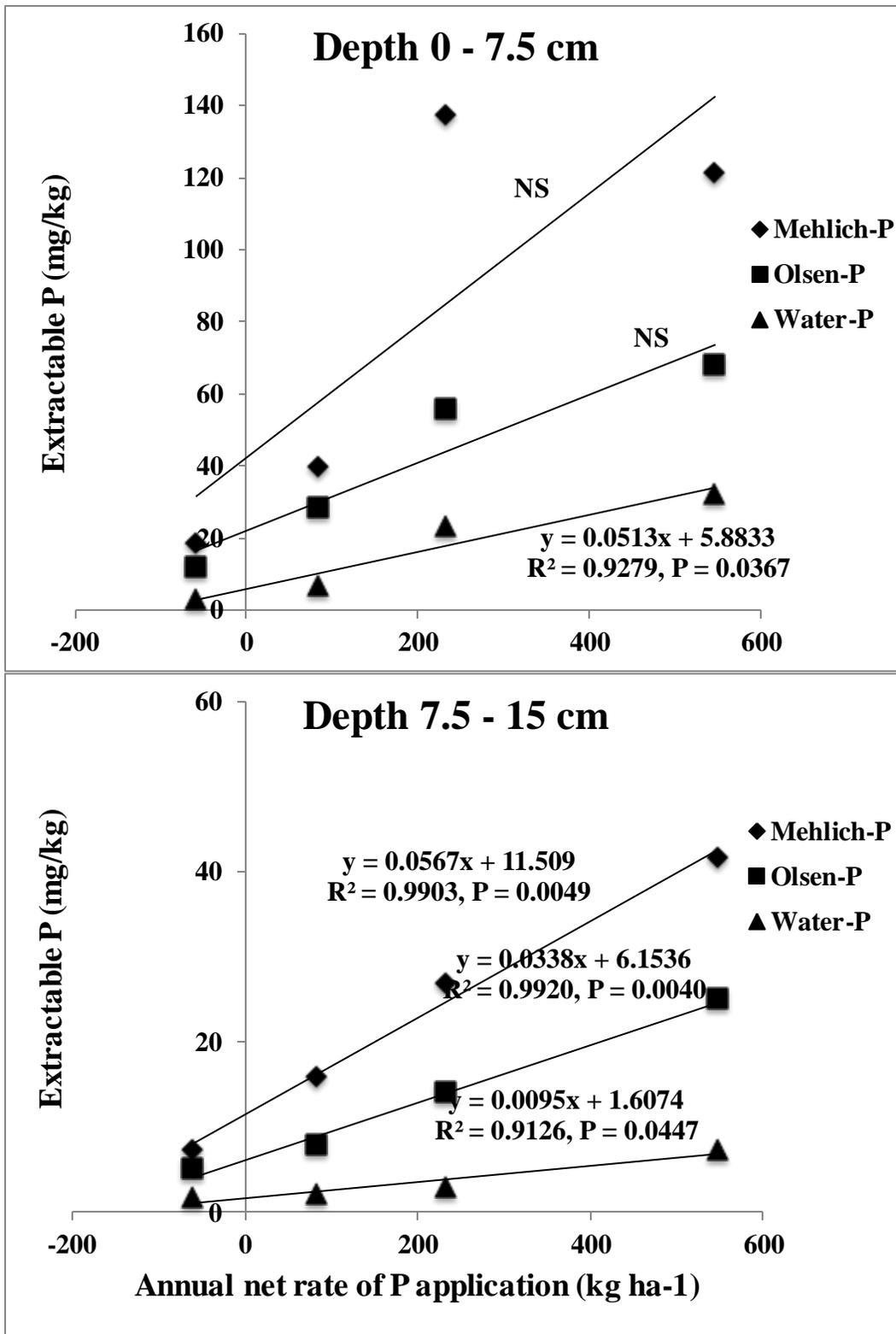
**Figure 3.7d Changes in soil test P with net P balance at 0-7.5 cm and 7.5-15 cm depth at Ellerslie site after adjusting for yearly P removal (2002 - 2009).**
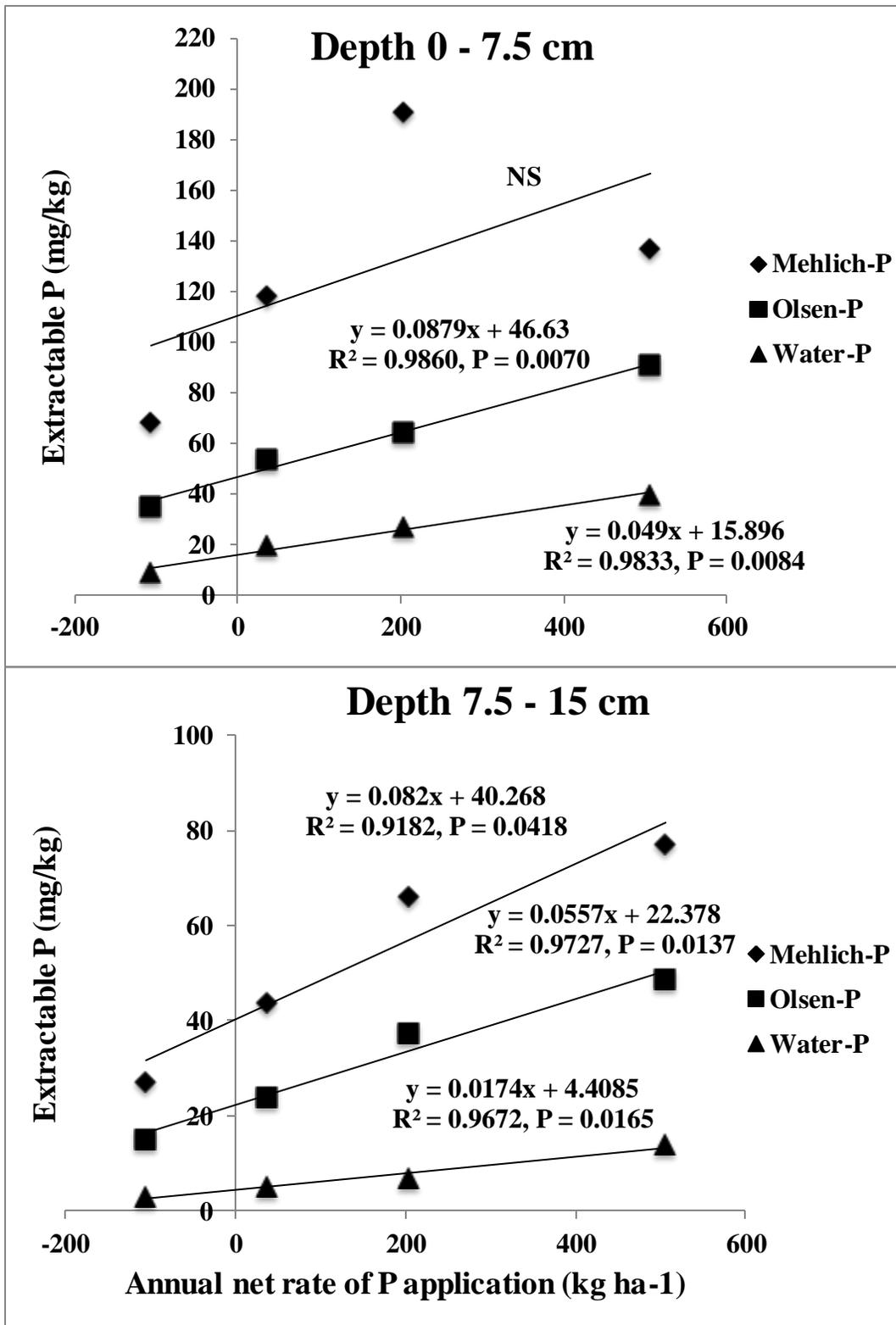
**Figure 3.7e Changes in soil test P with net P balance at 0-7.5 cm and 7.5-15 cm depth at Fort Saskatchewan site after adjusting for yearly P removal (2002- 2009).**

**Table 3.3 Effect of P surplus on soil test P at the end of 8 years of P application (0-7.5 and 7.5-15 cm depth)**

| Sites | Amount of surplus fertilizer P (kg P ha$^{-1}$) required to raise STP by 1 ppm | | | Depth (cm) |
| --- | --- | --- | --- | --- |
| | Water - P | Olsen - P | Mehlich - 3 P | |
| East of Spruce | 23.5 | NS | 7.2 | 0 – 7.5 |
| | 100.0 | 32.5 | NS | 7.5 – 15 |
| Carman | 20.1 | 13.2 | 3.2 | 0 – 7.5 |
| | 33.7 | 16.5 | 8.2 | 7.5 – 15 |
| Forrest | 27.5 | 12.0 | 4.3 | 0 – 7.5 |
| | NS | 51.3 | NS | 7.5 – 15 |
| Ellerslie | 19.5 | NS | NS | 0 – 7.5 |
| | 105.3 | 29.6 | 17.6 | 7.5 – 15 |
| Fort Sask. | 20.4 | 11.4 | NS | 0 – 7.5 |
| | 57.5 | 18.0 | 12.2 | 7.5 – 15 |

NS: Non-significant

### 3.4.4. Correlation between the rate of change of soil test P at the accumulation stage and the soil properties

Correlation analysis was carried out to explore the relationship between soil properties and rate of change in response to net annual P application rates (i.e. the slope of the soil test P response to net annual P application rate). Across all the sites, the slightly acidic soils (Carman and Ellerslie sites) with high M3-Fe content have higher slope value of water-P.

The rate of change in Olsen-P was inversely correlated with sand content ($r = -0.90$, $P < 0.05$) and positively correlated with cation exchange capacity, CEC ($r = 0.97$, $P < 0.01$) (Table 3.4). This implies that an increase in sand content results in a decrease in the rate of change in Olsen-extractable P. On the other hand, as cation exchange capacity increases, the rate of change in Olsen-extractable P in turn increases accordingly. Ellerslie and Fort Saskatchewan sites with high CEC had the highest rate of change of Olsen-extractable P in response to net P applied. On the other hand, Carman had the highest sand content and it is the site with the smallest slope value. These results are the opposite of what was expected; Olsen-P response to surplus P was expected to increase with sand content and decrease with CEC. Thus, further investigation needs to be carried out to determine what other factors, apart from the depth of cultivation, which might be contributing to this change.

The rate of change in M3-P in response to rate of surplus P applied was inversely correlated with silt content ($r = -0.90$, $P < 0.05$) and M3-Ca ($r = -0.90$, $P < 0.05$). These results indicate that as the silt content and M3-Ca increases, the rate of change of M3-P decreases. In this study, the Carman site, with the smallest concentrations of silt and M3-Ca had the greatest rate of change in M3-P at $0 - 7.5$cm depth. The Fort Saskatchewan site, on the other hand, with high content of silt and M3-Ca, had the smallest rate of change of M3-P.

The correlation analysis between the rates of change of soil test P with soil properties at the 7.5-15 cm depth produced weak correlation values that were not significant.

**Table 3.4 Correlation coefficients between soil properties and slopes for the regression relationships of extractable-P (using linear equation, n=5)**

| | pH | Clay | Silt | Sand | CEC | Organic_C | M-3 Fe | M-3 Ca | M-3 Mg |
|---|---|---|---|---|---|---|---|---|---|
| **Soil depth (0 – 7.5 cm)** | | | | | | | | | |
| **Slope_Water** | -0.87 | 0.30 | 0.20 | -0.40 | 0.21 | 0.30 | 0.87 | 0.20 | -0.60 |
| **Slope_Olsen** | 0.05 | 0.70 | 0.80 | **-0.9*** | **0.97*** | 0.80 | 0.21 | 0.80 | 0.10 |
| **Slope_M3** | -0.41 | -0.60 | **-0.9*** | 0.70 | -0.62 | -0.40 | 0.41 | **-0.9*** | -0.80 |
| **Soil depth (7.5 -15 cm)** | | | | | | | | | |
| **Slope_Water** | -0.30 | -0.30 | -0.21 | 0.30 | -0.41 | -0.10 | 0.20 | -0.50 | -0.15 |
| **Slope_Olsen** | -0.40 | -0.10 | -0.05 | 0.10 | -0.15 | 0.20 | 0.60 | -0.80 | -0.41 |
| **Slope_M3** | -0.30 | -0.30 | -0.21 | 0.30 | -0.41 | -0.10 | 0.20 | -0.50 | -0.15 |

* Bold values represent figures with significant values at $P < 0.05$

### 3.5. Conclusions

The magnitude of soil test P increases and decreases varied with the rate of P applied, the soil properties (pH, CEC, texture, organic matter etc.), time and cumulative fertilizer history of soil. Continuous application of P fertilizer in excess of removal led to an increase in soil test P. On the other hand, cessation of P application during the depletion phase also led to a reduction in the soil test P. Of the STP methods evaluated, M3-P extracted the most P at the two depth intervals and Olsen-extractable P was intermediate while water extracted the smallest amount of P. The majority of the applied P was found in the surface soil (0 – 7.5 cm depth). The addition of 23, 20, 27, 19, 20 kg P ha$^{-1}$ raised Water-extractable P by 1 mg P kg$^{-1}$ for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites respectively following after 8 years of P application. The addition of 13, 12 and 11 kg surplus P ha$^{-1}$ raised Olsen soil test P by 1 mg P kg$^{-1}$ for Carman, Forrest and Fort Saskatchewan sites. However, East of Spruce and Ellerslie sites have non-significant regression for Olsen soil test P. The addition of 7, 3 and 4 kg P ha$^{-1}$ raised Mehlich-3 soil test P by 1 mg P kg$^{-1}$ for East of Spruce, Carman and Forrest sites; but the slopes of regression are non-significant in Ellerslie and Fort Saskatchewan sites. Analysis showed that there is no significant relationship between the rate of change of water-P and soil properties. Other unknown factors might actually be contributing to this rate of change; thus, further studies needed to be carried out to examine the direct and indirect effects of soil properties on the rate of change of WEP. Soils having low sand content (Ellerslie and Fort Saskatchewan) and high CEC had greater rate of change of Olsen-P while soils with high silt content and M3-Ca (Fort Saskatchewan), had smaller rate of change of M3-P.

## 3.6. References

Allen, B.L., and A.P. Mallarino. 2006. Relationships between Extractable Soil Phosphorus and Phosphorus Saturation after Long-Term Fertilizer or Manure Application. Soil Sci. Soc. Am. J. 70(2): 454.

Bailey, L.D., E.D. Spratt, D.W.L. Read, F.G. Warder, and W.S. Ferguson. 1977. Residual effects of phosphorus fertilizer. II. For wheat and flax grown on chernozemic soils in Manitoba. Can. J. Soil Sci. 57(3): 263–270.

Cross, A.F., and W.H. Schlesinger. 1995. A literature review and evaluation of the Hedley fractionation- Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. Geoderma (64): 197–214.

Dieter, D., H. Elsenbeer, and B.L. Turner. 2010. Phosphorus fractionation in lowland tropical rainforest soils in central Panama. CATENA 82(2): 118–125.

Fixen, P.E., and J.H. Grove. 1990. Testing soils for phosphorus, pp. 141-180. In: R.L. Westerman (ed.), Soil Testing and Plant Analysis. 3rd ed. SSSA Book Series 3. Soil Science Society of America, Madison, WI.

Grant, C., D. Flaten, M. Tenuta, S. Malhi, and W. Akinremi. 2013. The effect of rate and Cd concentration of repeated phosphate fertilizer applications on seed Cd concentration varies with crop type and environment. Plant Soil 372(1–2): 221–233.

Griffin, T.S., C.W. Honeycutt, and Z. He. 2003. Changes in soil phosphorus from manure application. Soil Sci. Soc. Am. J. 67(2): 645–653.

Haden, V.R., Q.M. Ketterings, and J.E. Kahabka. 2007. Factors Affecting Change in Soil Test Phosphorus Following Manure and Fertilizer Application. Soil Sci. Soc. Am. J. 71(4): 1225.

Ige, D.V., O.O. Akinremi, D. Flaten, and M.A. Kashem. 2006. Comparison of soil test phosphorus methods in neutral to calcareous Manitoba soils. Can. J. Soil Sci. 86(4): 691–699.

Jalali, M., and F. Ranjbar. 2010. Aging effects on phosphorus transformation rate and fractionation in some calcareous soils. Geoderma 155(1–2): 101–106.

Johnson, A.H., J. Frizano, and D.R. Vann. 2003. Biogeochemical implications of labile phosphorus in forest soils determined by the Hedley fractionation procedure. Oecologia 135(4): 487–499.

Kashem, M.A., O.O. Akinremi, and G.J. Racz. 2004a. Extractable phosphorus in alkaline soils amended with high rates of organic and inorganic phosphorus. Can. J. Soil Sci. 84(4): 459–467.

Kashem, M.A., O.O. Akinremi, and G.J. Racz. 2004b. Phosphorus fractions in soil amended with organic and inorganic phosphorus sources. Can. J. Soil Sci. 84(1): 83–90.

Kumaragamage, D., O.O. Akinremi, D. Flaten, and J. Heard. 2007. Agronomic and environmental soil test phosphorus in manured and non-manured Manitoba soils. Can. J. Soil Sci. 87(1): 73–83.

Kumaragamage, D., D. Flaten, O.O. Akinremi, C. Sawka, and F. Zvomuya. 2011. Soil test phosphorus changes and phosphorus runoff losses in incubated soils treated with livestock manures and synthetic fertilizer. Can. J. Soil Sci. 91(3): 375–384.

Laboski, C.A., and J.A. Lamb. 2003. Changes in soil test phosphorus concentration after application of manure or fertilizer. Soil Sci. Soc. Am. J. 67(2): 544–554.

Lambert, R., C. Grant, and S. Sauve. 2007. Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. Sci. Total Environ. 378(3): 293–305.

McDowell, R., A. Sharpley, P. Brookes, and P. Poulton. 2001. Relationship between soil test phosphorus and phosphorus release to solution. Soil Sci. 166(2): 137–149.

McKenzie, R.H., and E. Bremer. 2003. Relationship of soil phosphorus fractions to phosphorus soil tests and fertilizer response. Can. J. Soil Sci. 83(4): 443–449.

Mehlich, A. 1984. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15: 1409–1416.

Messiga, A.J., N. Ziadi, D. Plénet, L.E. Parent, and C. Morel. 2010. Long-term changes in soil phosphorus status related to P budgets under maize monoculture and mineral P fertilization: Sensitivity of relationships between soil phosphorus and P budget. Soil Use Manag. 26(3): 354–364.

Olsen, S. R., C.V. Cole, F.S. Watanabe, and F.S. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA circular 939. U.S. Government Printing Office, Washington, DC.

Pote, D.H., J.A. Lory, and H. Zhang. 2003. Does initial soil P level affect water-extractable soil P response to applied P? Adv. Environ. Res. 7(2): 503–509.

Racz, G. J. 1979. Release of P in organic soils under aerobic and anaerobic conditions. Can. J. Soil Sci. 59: 337–339.

Richards, J.E., T.E. Bates, and S.C. Sheppard. 1995. Changes in the forms and distribution of soil phosphorus due to long-term corn production. Can. J. Soil Sci. 75(3): 311–318.

Saha, B.N., S. Saha, P. Poddar, and T. Chand. 2013. Phosphate Fractions as Influenced by Long-Term Phosphorus Fertilization. Indian J. Agric. Res. 47(1): 59–65.

Samadi, A. 2003. A study on distribution of forms of phosphorus in calcareous soils of Western Australia. J. Agric. Sci. Technol. JAST 5(1–2): 39–49.

Self-Davis, M. L., P.A. Moore Jr. and B. C. Joern. 2000. Determination of water or dilute salt extractable phosphorus in soils. Pages 24–26 in G. M. Pierzynski, ed. Methods of phosphorus analysis for soils, sediments, residuals and waters. Southern Cooperative Series Bull. No 396. Kansas State University, Manhattan, KS.

Shepherd, M.A., and P.J. Withers. 1999. Applications of poultry litter and triple superphosphate fertilizer to a sandy soil: effects on soil phosphorus status and profile distribution. Nutr. Cycl. Agroecosystems (54): 233–242.

Soinne, H. 2009. Extraction methods in soil phosphorus characterisation - Limitations and applications. Available at https://helda.helsinki.fi/bitstream/handle/10138/20847/extracti.pdf?sequence=1 (verified 27 September 2014).

Van der Paauw, F. 1971. An effective water extraction method for the determination of plant-available soil phosphorus. Plant Soil. 34: 467–481.

Van Leirop, W. 1988. Determination of available phosphorus in acid and calcareous soils with Kelowna multiple-element extractant. Soil Sci. 146: 284–291.

Wagar, B.I., J.W.B. Stewart, and J.O. Moir. 1986. Changes with time in the form and availability of residual fertilizer phosphorus on Chernozemic soils. Can. J. Soil Sci. 66(1): 105–119.

Walker, T.W., and J.K. Syers. 1976. The fate of phosphorus during pedogenesis. Geoderma 15(1): 1–19.

Yang, X., and W.M. Post. 2011. Phosphorus transformations as a function of pedogenesis: A synthesis of soil phosphorus data using Hedley fractionation method. Biogeosciences 8(10): 2907–2916.

Zhang, T.Q., A.F. MacKenzie, B.C. Liang, and C.F. Drury. 2004. Soil test phosphorus and phosphorus fractions with long-term phosphorus addition and depletion. Soil Sci. Soc. Am. J. 68(2): 519–528.

# 4. OVERALL SYNTHESIS

Broad knowledge of how soil P fractions changes over time when P fertilizer are applied to the soil is crucial in determining P utilization by crops over the long-term. This study was undertaken to examine the effect of continuous application of phosphorus fertilizers on soil test phosphorus in prairie soils and how the soil P fractions and the soil test P change with time. A sequential fractionation experiment was conducted to determine the effect of continuous P addition in excess of crop removal on the labile and non-labile P fractions of the soils and to determine what happens to these P fractions during the P depletion years. An extraction experiment was also carried out to determine how soil test P changes over time across soil type during application and depletion phases and evaluate soil test P changes using yearly P removal across soil types.

In the sequential fractionation experiment, we observed that the application of 80 kg ha$^{-1}$ of MAP for 6 years significantly increased the absolute value of soil P in the labile ($H_2O$-$P_t$ and $NaHCO_3$-$P_t$) and moderately labile $P_i$ ($NaOH$-$P_t$) fractions across all sites. These increases in the labile P fractions could be due to the increased saturation of the sorption sites with continuous P application. The labile fraction that increased during the accumulation phase was the P fractions that decreased significantly across all sites during the depletion phase. This was not surprising, as by definition, the lability of these fractions implied that they would supply the crop's requirements in the absence of further P additions.

Continuous addition of P fertilizer in excess of crop removal across all sites significantly increased labile P fractions but no significant change in the two-way year x site interaction in non-labile P ($NaOH$-P, $HCl$-P and Residual-P) fractions. However, there were significant increases in the non-labile P fractions during the accumulation years. The labile fractions also

significantly decreased during the depletion phase after continuous cropping with no P addition. In contrast, there was no significant change in the non-labile P fractions across all sites during the depletion phase.

At the treated plots, there was a corresponding increase in the proportion of total P extracted in the $H_2O$-, $NaHCO_3$- and NaOH- $P_t$ fractions and a decrease in the proportion of HCl-$P_t$ and Residual-P fraction during the accumulation phase across all sites. In the depletion phase at the treated sites, results showed that as the proportion of $H_2O$-, $NaHCO_3$- and NaOH- $P_t$ fractions decreased gradually with a concomitant increase in HCl-$P_t$ and Residual-P fractions.

During the accumulation phase, there was an increase in $H_2O$-, $NaHCO_3$-, NaOH- $P_t$ and HCl-$P_t$ fractions in absolute terms across all sites. HCl-$P_t$ fractions significantly increased in the Fort Saskatchewan site among all other sites, which showed no increase during the P accumulation years.

In the extraction experiment, the amount of soil test P extracted depended on the acidic nature of the reagents. Mehlich-3 extracted more P than other extracting methods (Olsen-P and Water-P). The result also showed that the application of rates above 20 kg P ha$^{-1}$ could result in surplus of P in soil, thereby increasing the risk of P loss to runoff. It is important to note that the soil test P varied with the soil type and the majority was found at the 0-7.5 cm depth. Soil test P also increased with an increase in the application rates. Olsen-P and Water-P increased linearly with the application rates except for Mehlich-3 P that behaved differently and the reason for Mehlich's unusual behavior is unknown. The Fort Saskatchewan site had the greatest Olsen-P and Water-P values and the Forrest site had the least amount at the end of the accumulation phase. After the depletion phase, there was a reduction in the amount of extracted P but results showed that some of the P applied at high rate was still available in the soil.

Rate of change of soil test P varied with the soil types. The addition of 23, 20, 27, 19 and 20 kg P ha$^{-1}$ raised Water-P by 1 mg P kg$^{-1}$ at the 0-7.5 cm depth for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites respectively during the accumulation phase. The addition of 13, 13, 12, 11 and 11 kg P ha$^{-1}$ raised Olsen soil test P by 1 mg P kg$^{-1}$ at the 0-7.5 cm depth for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites. The addition of 7, 3, 4, 5 and 9 kg P ha$^{-1}$ raised M3 soil test P by 1 mg P kg$^{-1}$ at the $0 - 7.5$ cm depth for East of Spruce, Carman, Forrest, Ellerslie and Fort Saskatchewan sites respectively.

Correlation results showed that an increase in sand content resulted in a decrease in the rate of change in Olsen-P, and as cation exchange capacity increased, the rate of increase in Olsen-P at the $0 - 7.5$ cm depth also increased. It was anticipated that the rate of change in Olsen-P should increase with sand content and decrease with CEC. Thus, further investigation needs to be carried out for clarity.

Comparison of both studies using the highest rate of MAP application (80 kg ha$^{-1}$) at the 0-7.5 cm depth, the result of the studies showed that the total P in the water extractable fraction for the modified Hedley fractionation method ($H_2O$-$P_t$) was three times more than the Water-extractable P (Water-P) extracted by the Self-Davis method at the end of the accumulation phase (Year 2009) across all sites except Fort Saskatchewan which was four times more. This difference may be due to differences in the magnitude of extraction period used in both experimental methods: water extractable P in the modified Hedley fractionation was determined by weighing 0.5 g soil in a centrifuge tube, sequentially extracting with 30 mL deionized water and shaking it for 16 hr. On the other hand, Water-extractable P using the Self-Davis method was determined by extracting 2 g of soil with 20 mL deionized water and with I hour of extraction time. The longer extraction period for water P in the Hedley fractionation technique therefore resulted in greater

expectable P compared to the Self-Davies method.

Similar to the water-P fraction, the labile P fraction (addition of $H_2O$ and $NaHCO_3$ –P) was also three times more than the Olsen-extractable P across all sites except Ellerslie and Fort Saskatchewan sites, which was four times more. The number of hours used in shaking soil sample for Olsen P was 30 minutes and the ratio of soil to $NaHCO_3$ solution is 1:20 whereas, 16 hr is required in shaking the labile P fraction at a ratio of 1:60 soil to solution. This study therefore showed that methodological differences could result in vast differences in the magnitude of P that is extracted from the soil even by the same extractant.

In summary, these studies showed that the continuous addition of MAP fertilizer increased the available P for plants uptake, but the available P at the high rate was still yet to be depleted even after 3 years of continuous cropping with no P added.

**Appendix 2.A Concentrations of labile and non-labile soil total P fractions across the years**

| SITE | YEAR | $H_2O\_P_t$ | $NaHCO_3\_P_t$ | $NaOH\_P_t$ | $HCl\_P_t$ | $Res\_P_t$ | $Total\_P_t$ |
|------|------|------|------|------|------|------|------|
| | | | | mg kg$^{-1}$ | | | |
| **Carman** | 2003 | 52 | 30 | 16 | 148 | 119 | 365 |
| | 2009 | 108 | 93 | 42 | 143 | 117 | 502 |
| | 2012 | 69 | 82 | 21 | 149 | 125 | 446 |
| **East of Spruce** | 2003 | 45 | 41 | 11 | 178 | 225 | 499 |
| | 2009 | 86 | 92 | 17 | 197 | 223 | 615 |
| | 2012 | 53 | 82 | 14 | 198 | 214 | 561 |
| **Ellerslie** | 2003 | 26 | 47 | 20 | 132 | 195 | 420 |
| | 2009 | 104 | 142 | 57 | 153 | 201 | 656 |
| | 2012 | 75 | 140 | 47 | 154 | 204 | 621 |
| **Fort Saskatchewan** | 2003 | 54 | 79 | 19 | 222 | 280 | 654 |
| | 2009 | 169 | 226 | 44 | 300 | 283 | 1021 |
| | 2012 | 86 | 163 | 32 | 289 | 294 | 863 |
| **Forrest** | 2003 | 32 | 30 | 8 | 129 | 254 | 452 |
| | 2009 | 70 | 88 | 15 | 159 | 276 | 608 |
| | 2012 | 34 | 62 | 8 | 166 | 254 | 525 |

**Appendix 2.B Effect of accumulation and depletion years on the different soil types in the $H_2O-P_t$ fraction**

| Year | Site | | | | |
|---|---|---|---|---|---|
| | **Carman** | **East of Spruce** | **Ellerslie** | **Fort Saskatchewan** | **Forrest** |
| **2003** | 52.14abB | 45.02abB | 25.77bC | 54.06aC | 31.97abB |
| **2009** | 107.99bA | 86.15bcA | 103.49bA | 169.21aA | 69.60cA |
| **2012** | 68.88abB | 53.22bcB | 74.58abB | 86.13aB | 33.87cB |
| **Site** | | | | | |
| **Carman** | | | 76.33 | | |
| **East of Spruce** | | | 61.46 | | |
| **Ellerslie** | | | 67.95 | | |
| **Fort Saskatchewan** | | | 103.14 | | |
| **Forrest** | | | 45.15 | | |
| **Year** | | | | | |
| **2003** | | | 41.79 | | |
| **2009** | | | 107.29 | | |
| **2012** | | | 63.34 | | |
| **ANOVA** | **df** | | | **Pr > F** | |
| **Year** | 2 | | | <.0001 | |
| **Site** | 4 | | | 0.0006 | |
| **Year * Site** | 8 | | | 0.0004 | |

[†] Mean values followed by the same lowercase letter within each year across the sites are not significantly different

[‡] Mean values followed by the same uppercase letter within each site across the years are not significantly different

**Appendix 2.C Effect of accumulation and depletion years on the different soil types in the NaHCO$_3$-P$_t$ fraction**

| Year | Site | | | | |
|---|---|---|---|---|---|
| | Carman | East of Spruce | Ellerslie | Fort Saskatchewan | Forrest |
| 2003 | 29.10bB | 40.80bB | 47.10bB | 78.90aC | 30.30bB |
| 2009 | 92.85cA | 92.40cA | 142.05bA | 225.75aA | 87.90cA |
| 2012 | 82.20bA | 82.20bA | 140.40aA | 162.60aB | 62.25bA |

| Site | |
|---|---|
| Carman | 68.05 |
| East of Spruce | 71.80 |
| Ellerslie | 109.85 |
| Fort Saskatchewan | 155.75 |
| Forrest | 60.15 |

| Year | |
|---|---|
| 2003 | 45.24 |
| 2009 | 128.19 |
| 2012 | 105.93 |

| ANOVA | df | Pr > F |
|---|---|---|
| Year | 2 | <.0001 |
| Site | 4 | <.0001 |
| Year * Site | 8 | 0.0008 |

[†] Mean values followed by the same lowercase letter within each year across the sites are not significantly different

[‡] Mean values followed by the same uppercase letter within each site across the years are not significantly different

**Appendix 2.D Effect of accumulation and depletion years on the different soil types in the NaOH-P$_t$ fraction**

| Year | Site | | | | |
|---|---|---|---|---|---|
| | Carman | East of Spruce | Ellerslie | Fort Saskatchewan | Forrest |
| **2003** | 16.20 | 11.10 | 20.40 | 19.20 | 7.48 |
| **2009** | 42.00 | 16.95 | 57.15 | 43.50 | 14.85 |
| **2012** | 20.70 | 20.70 | 46.95 | 31.95 | 8.11 |
| **Site** | | | | | |
| **Carman** | | | 26.30bc | | |
| **East of Spruce** | | | 13.49cd | | |
| **Ellerslie** | | | 41.50a | | |
| **Fort Saskatchewan** | | | 31.55ab | | |
| **Forrest** | | | 10.15d | | |
| **Year** | | | | | |
| **2003** | | | 14.88c | | |
| **2009** | | | 34.89a | | |
| **2012** | | | 24.03b | | |
| **ANOVA** | **df** | | **Pr > F** | | |
| **Year** | 2 | | <.0001 | | |
| **Site** | 4 | | 0.0013 | | |
| **Year * Site** | 8 | | 0.1576 | | |

[†] Mean values followed by the same lowercase letter are not significantly different

**Appendix 2.E Effect of accumulation and depletion years on the different soil types in the HCl-P$_t$ fraction**

| Year | Site | | | | |
|---|---|---|---|---|---|
| | Carman | East of Spruce | Ellerslie | Fort Saskatchewan | Forrest |
| **2003** | 147.53 | 177.83 | 131.69 | 221.67 | 128.57 |
| **2009** | 142.80 | 196.61 | 152.72 | 299.54 | 159.36 |
| **2012** | 149.00 | 197.93 | 154.20 | 288.95 | 165.96 |

| Site | |
|---|---|
| **Carman** | 146.44b |
| **East of Spruce** | 190.79b |
| **Ellerslie** | 146.20b |
| **Fort Saskatchewan** | 270.05a |
| **Forrest** | 151.30b |

| Year | |
|---|---|
| **2003** | 161.45b |
| **2009** | 190.20a |
| **2012** | 191.21a |

| ANOVA | df | Pr > F |
|---|---|---|
| **Year** | 2 | 0.0124 |
| **Site** | 4 | 0.0016 |
| **Year * Site** | 8 | 0.5012 |

[†] Mean values followed by the same lowercase letter are not significantly different

**Appendix 2.F Effect of accumulation and depletion years on the different soil types in the Res-P$_t$ fraction**

| Year | Site | | | | |
|---|---|---|---|---|---|
| | **Carman** | **East of Spruce** | **Ellerslie** | **Fort Saskatchewan** | **Forrest** |
| **2003** | 119.20 | 224.53 | 195.40 | 280.40 | 253.95 |
| **2009** | 116.58 | 222.75 | 200.88 | 282.58 | 275.85 |
| **2012** | 125.05 | 214.05 | 204.38 | 293.78 | 254.88 |
| **Site** | | | | | |
| **Carman** | | | 120.28c | | |
| **East of Spruce** | | | 220.44b | | |
| **Ellerslie** | | | 200.22b | | |
| **Fort Saskatchewan** | | | 285.58a | | |
| **Forrest** | | | 261.56a | | |
| **Year** | | | | | |
| **2003** | | | 214.70 | | |
| **2009** | | | 219.73 | | |
| **2012** | | | 218.43 | | |
| **ANOVA** | **df** | | | **Pr > F** | |
| **Year** | 2 | | | 0.8770 | |
| **Site** | 4 | | | <.0001 | |
| **Year * Site** | 8 | | | 0.9826 | |

[†] Mean values followed by the same lowercase letter are not significantly different

**Appendix 3.A1 Effect of P rate on water extractable P in 2009 and 2012 for 0 - 7.5 and 7.5 - 15 cm soil depths at East of Spruce and Carman sites.**
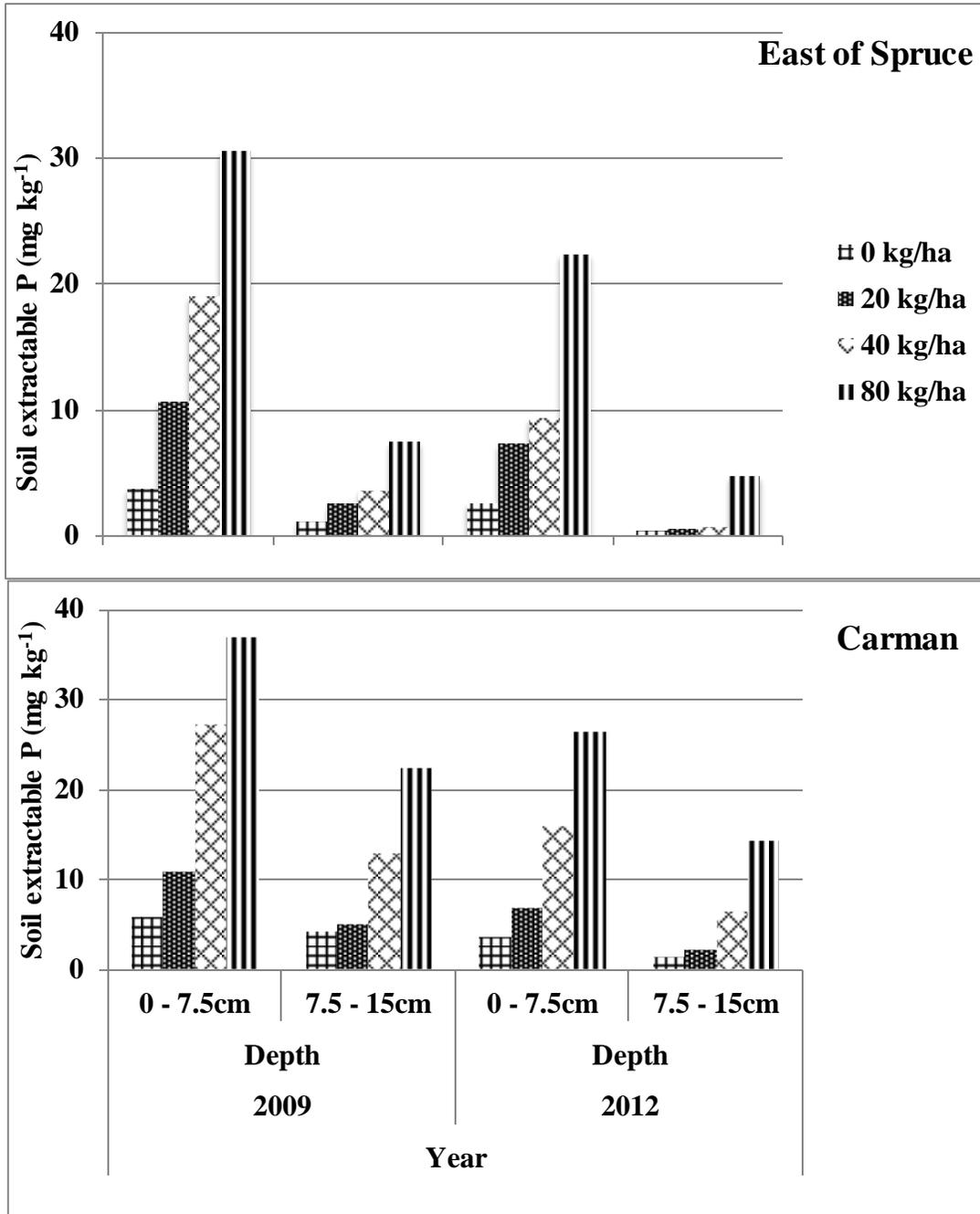
**Appendix 3.A2 Effect of P rate on water extractable P in 2009 and 2012 for 0 - 7.5 and 7.5 - 15 cm soil depths at Ellerslie, Fort Saskatchewan and Forrest sites.**
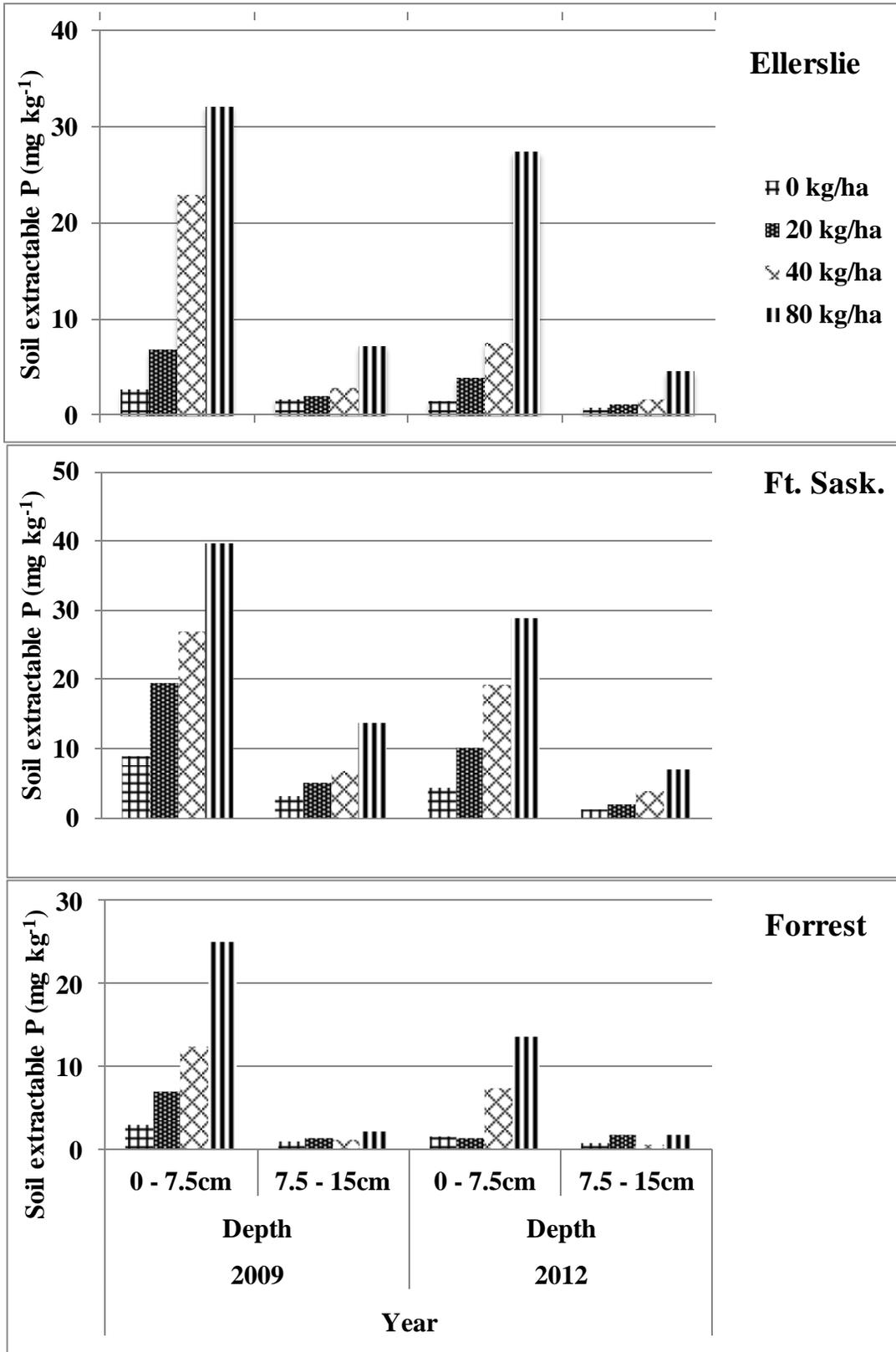
**Appendix 3.B1 Effect of P rate on Olsen extractable P in 2009 and 2012 for 0 - 7.5 and 7.5 - 15 cm soil depths at East of Spruce and Carman sites.**
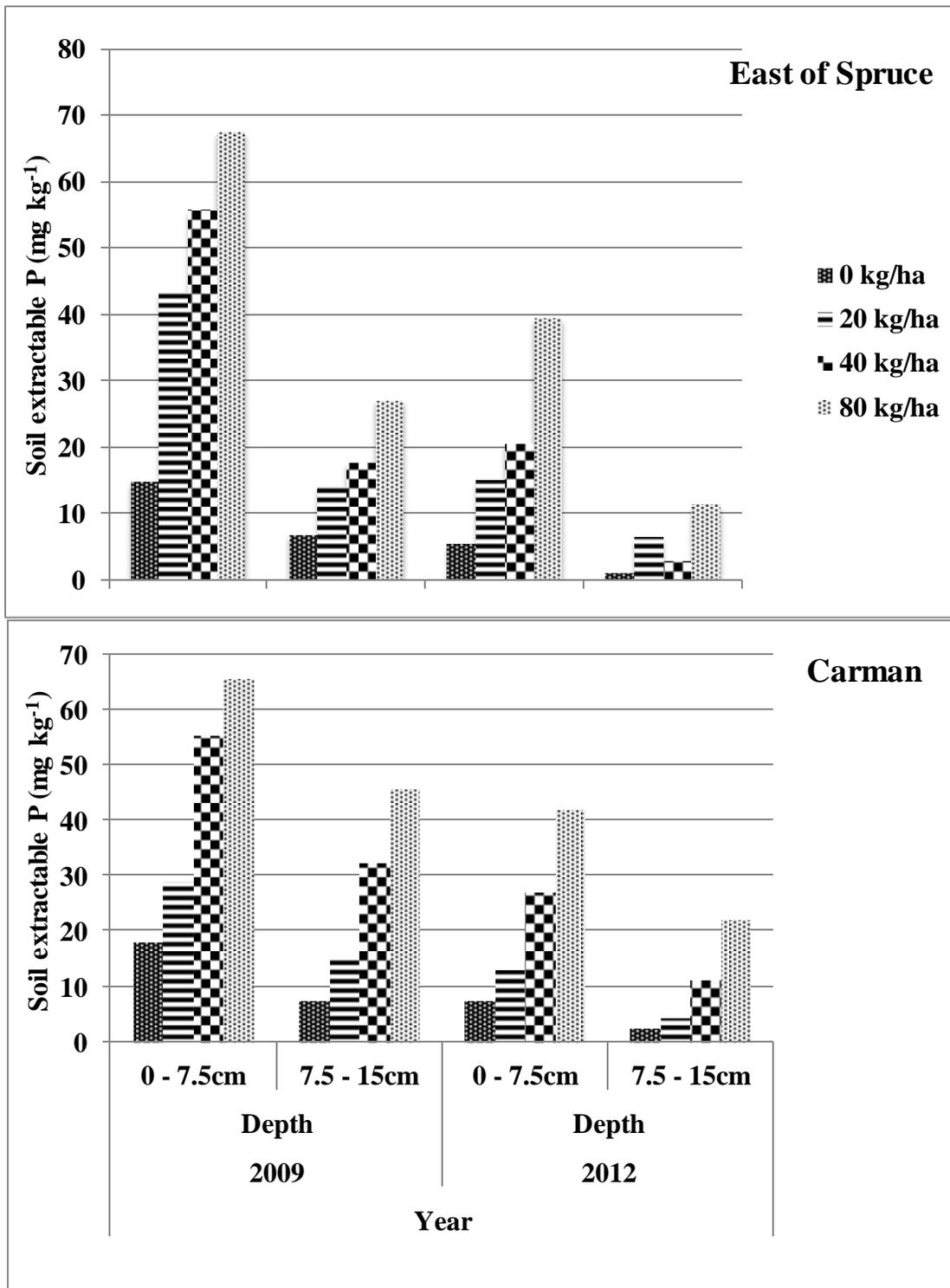
**Appendix 3.B2 Effect of P rate on Olsen extractable P in 2009 and 2012 for 0 - 7.5 and 7.5 - 15 cm soil depths at Ellerslie, Fort Saskatchewan and Forrest sites.**
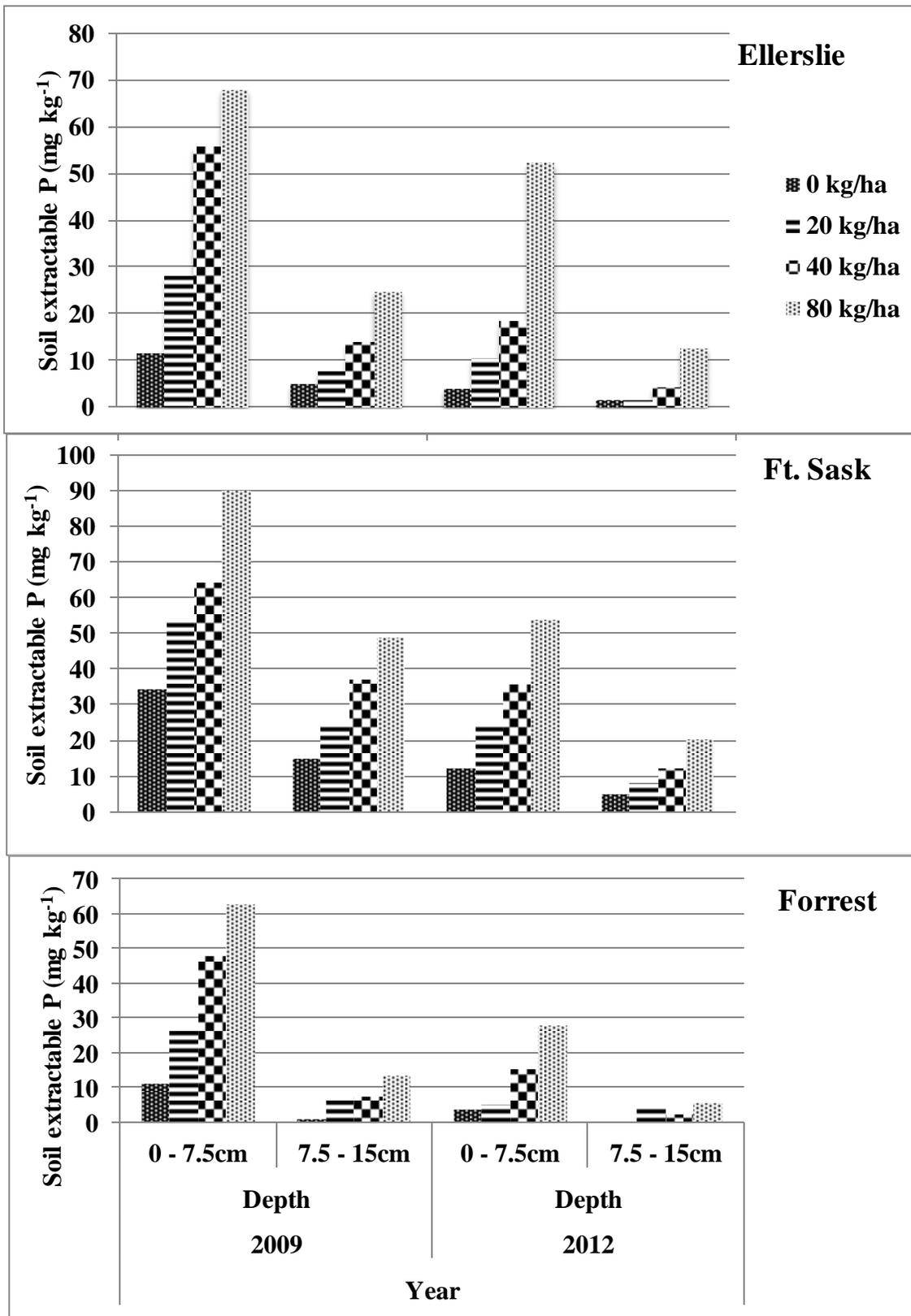
**Appendix 3.C Summary of regression coefficients for various soil test P methods at two soil depths during the P accumulation phase (R² value in parentheses)**

| | **East of Spruce** | **Carman** | **Ellerslie** | **Ft. Sask** | **Forrest** |
|---|---|---|---|---|---|
| | | | **Sites** | | |
| | | | **Topsoil (0-7.5 cm)** | | |
| **Water Ex-P** | 0.0425 (R² = 0.9933, P = 0.0033) | 0.0497 (R² = 0.9383, P= 0.0314) | 0.0513 (R² = 0.9279, P = 0.0367) | 0.0490 (R² = 0.9833, P = 0.0084) | 0.0364 (R² = 0.994, P = 0.0030) |
| **Olsen Ex-P** | NS | 0.0759 (R² = 0.9032, P = 0.0496) | NS | 0.0879 (R² = 0.986, P = 0.0070) | 0.0834 (R² = 0.9467, P = 0.0270) |
| **Mehlich Ex-P** | 0.1380 (R² = 0.9678, P = 0.0163) | 0.3099 (R² = 0.9857, P = 0.0072) | NS | NS | 0.2303 (R² = 0.997, P = 0.0015) |
| | | | **Topsoil (7.5-15 cm)** | | |
| **Water Ex-P** | 0.0100 (R² = 0.9860, P = 0.0070) | 0.0297 (R² = 0.9609, P = 0.0198) | 0.0095 (R² = 0.9126, P = 0.0447) | 0.0174 (R² = 0.9672, P = 0.0165) | NS |
| **Olsen Ex-P** | 0.0308 (R² = 0.9811, P = 0.0095) | 0.0606 (R² = 0.9671, P = 0.0166) | 0.0338 (R² = 0.9920, P = 0.0040) | 0.0557 (R² = 0.9727, P = 0.0137) | 0.0195 (R² = 0.9571, P = 0.0217) |
| **Mehlich Ex-P** | NS | 0.1216 (R² = 0.9702, P = 0.0150) | 0.0567 (R² = 0.9903, P = 0.0049) | 0.0820 (R² = 0.9182, P = 0.0418) | NS |

**Appendix 3.D Values of soil properties and rate of change in STP across all sites at two depths**

| Site | pH | Clay | Silt | Sand | CEC | Organic_C | M3_Fe | M3_Ca | M3_Mg | M3_P | Slope_Water | Slope_Olsen | Slope_M3 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **0 - 7.5 cm** | | | | | | | |
| East of Spruce | 7.4 | 36 | 38 | 26 | 34 | 28 | 8 | 499 | 26 | 4 | 0.043 | 0.077 | 0.14 |
| Carman | 5 | 19 | 14 | 67 | 16 | 37 | 29 | 204 | 11 | 7 | 0.050 | 0.076 | 0.31 |
| Forrest | 7.4 | 22 | 32 | 46 | 35 | 38 | 10 | 478 | 20 | 3 | 0.036 | 0.083 | 0.23 |
| Ellerslie | 6.2 | 43 | 42 | 15 | 42 | 40 | 29 | 538 | 19 | 4 | 0.051 | 0.094 | 0.18 |
| Ft. Sask. | 7.3 | 35 | 43 | 22 | 42 | 51 | 17 | 620 | 22 | 6 | 0.049 | 0.088 | 0.11 |
| | | | | | | **7.5 - 15 cm** | | | | | | | |
| East of Spruce | 7.4 | 35 | 39 | 26 | 34 | 28 | 5 | 1442 | 30 | 1 | 0.010 | 0.031 | 0.060 |
| Carman | 5.1 | 24 | 14 | 62 | 16 | 37 | 29 | 228 | 12 | 6 | 0.029 | 0.061 | 0.12 |
| Forrest | 7.5 | 26 | 39 | 35 | 35 | 38 | 8 | 726 | 21 | 1 | 0.002 | 0.019 | 0.016 |
| Ellerslie | 6.4 | 45 | 40 | 15 | 42 | 40 | 35 | 588 | 21 | 3 | 0.0095 | 0.034 | 0.057 |
| Ft. Sask. | 7.6 | 36 | 41 | 23 | 42 | 51 | 18 | 691 | 23 | 3 | 0.017 | 0.057 | 0.082 |