3.0 Phosphorus Behaviour in the Soil

Key Messages:

- Plants take up P as orthophosphate ions ($H_2PO_4^-$ or HPO_4^{-2}) from the soil solution at the root surface.
- Phosphorus is present in the soils as a variety of dynamic "pools" of organic and inorganic forms that range in availability and interact with each other through chemical reactions and biological transformations.
- Water-soluble P fertilizer undergoes a series of adsorption and precipitation reactions with calcium and magnesium in high pH (alkaline) soils and iron and aluminum in low pH (acid) soils that remove the P from the soil solution and transform it into adsorbed and less soluble forms.
- Plant uptake of orthophosphate from the soil solution shifts the equilibrium so that P moves from the less available pools towards plant-available solution P.
- Availability of P to the plant will depend on the concentration of P in the soil solution at the root surface and the ability of the soil to replenish the soil solution P from the less labile pools.
- Assessment of long-term P use efficiency must consider the accumulation of fertilizer P in soil pools that can be accessed by the plant over time.
- The short growing season and cold, frequently high pH, carbonated soils of the Northern Great Plains will affect P behaviour.

Summary

The native plant-available P in soils comes originally from the weathering of P-rich minerals such as apatite. Phosphorus can be added to the soil system through manures, crop residues, fertilizers, municipal wastes and by-products and can be lost from the soil system through crop removal, erosion and runoff and, under some conditions, through leaching and/or subsurface drainage.

Organic P in the form of growing plants and plant residues, animal waste, soil biota, soil organic matter, and soluble organic P present in the soil solution can make up as much as 25 to 60% of the total P content of surface soils. These forms vary in their lability or the ease with which they can be converted into plant-available orthophosphate. Organic phosphate can be mineralized into plant-available orthophosphates when soil microorganisms use the organic matter as an energy source and, conversely, mineral P can be immobilized when soil microorganisms incorporate it into their biomass. Immobilization and mineralization operate in a cyclical process with P being tied-up as the microorganisms grow and P being released as they die and decompose. Organic phosphorus can also be converted to orthophosphate by soil phosphatase operating outside of living organisms.

The inorganic forms of P in the soil include the phosphate ions in the soil solution, P that is adsorbed on the surface of soil particles, P that is precipitated as secondary P minerals such as Ca, Mg, Fe and Al phosphates, and the P that is present as primary P minerals such as apatite.

These P pools vary in availability and P will move back and forth between the pools in a series of equilibrium reactions. The reactions of the labile pools are relatively rapid while reactions of the non-labile pools may take months to years.

Plants take up P as orthophosphate ions ($H_2PO_4^-$ or HPO_4^{2-}) from the soil solution at the root surface. The soil solution normally contains very low P concentrations, typically much less than 0.1% of the total quantity of P in the soils. Even with a moderate P concentration, the soil solution will contain substantially less than 1 lb/acre of plant-available P to the 6-inch depth at any time, far less than the crop requires for growth. Roots will intercept P as they grow into new soil that has not been depleted, but they contact only a small part of the soil and P that is directly intercepted by the root is only a small fraction of the P requirements. Most plant P is supplied by replenishment of the very low concentration of P in the rhizosphere surrounding the plant root through diffusion along the concentration gradient created by active uptake of P by plant roots. Diffusion through the soil solution is very slow and the path of movement through the soil moisture films around the soil particles is long and winding. Therefore, the net movement of P though the soil is small, in the range of 0.13 mm per day.

Availability of P to the plant will depend on the concentration of P in the soil solution at the root surface and the ability of the soil to replace the P removed by the root. The concentration of P in the soil solution is called the intensity factor (I) and the ability of the soil to replenish the P in the soil solution is call the quantity factor (Q) or the P buffering capacity. Replenishment occurs from the pool of labile P that will rapidly equilibrate with the soil solution and become available in the short-term. Non-labile forms will equilibrate more slowly and are a longer-term source of replenishment for the labile reserves and the soil solution. The labile forms include easily mineralizable organic P, the relatively soluble forms of precipitated P and the adsorbed P that is readily exchangeable. The non-labile P forms include the more strongly adsorbed forms and more sparingly soluble forms. Soil P will move among solution, labile and non-labile forms in response to changes in the relative concentration of P in the various pools driven by plant uptake and phosphorus applications.

When water-soluble P fertilizer is applied to the soil, the P in solution undergoes a series of adsorption and precipitation reactions that remove it from the soil solution and move it into the labile and non-labile pools. On low pH (acid) soils, P retention is dominated by reactions with Fe and Al, while on high pH (alkaline) soils, Ca and Mg reactions dominate. These retention reactions reduce the availability of P fertilizers over time, but the process is reversible and the retained P forms can become available in response to P removal from the soil solution. Phosphate precipitation increases with increasing concentration of the reacting ions, so high concentrations of Ca, Mg or phosphate will increase precipitation on high pH soils while increasing concentrations of Fe, Al or phosphate will increase precipitation on low pH soils.

When a droplet or granule of water-soluble fertilizer is applied to the soil, it will attract liquid water and water vapour from the soil, dissolving the granule within a few days. As the water moves toward the fertilizer, highly concentrated P solution will diffuse away from the granule or droplet, along the osmotic concentration gradient towards areas of lower concentration outside of

the fertilizer reaction zone. The highly concentrated solution may dissolve soil minerals and release cations such as Al, Fe, Ca and Mg that precipitate the P in solution. The residual granule or droplet and the immediate area around contain insoluble P compounds from the original fertilizer and the compounds that have precipitated from the fertilizer P and the reacting cations. Beyond this is a zone of soil next to the granule where the capacity of the soil to adsorb P has been saturated, and precipitates have formed from the reaction of the fertilizer solution with the metal ions and organic matter released from the soil. As distance from the granule increases, the solution becomes more dilute and the soil will be able to adsorb the P without being saturated.

Mass flow of reacting cations in the soil water moving towards the granule may increase the precipitation of phosphate, particularly on calcareous soils, reducing the movement of phosphate away from the granule and reducing the volume of the fertilizer reaction zone. Blending ammonium-based fertilizers with phosphate can reduce the retention of P fertilizer and increase its availability. In some soils, when P fertilizer is applied as a solution rather than as a granule there is less movement of water carrying reacting ions towards the fertilizer, so precipitation is reduced, and P will move further away from the site of application. Use of solution P has provided large increases in P use efficiency on dry, highly calcareous soils in Australia, but the same benefits have not been demonstrated on the Northern Great Plains.

Although retention reactions will reduce P fertilizer's immediate availability, a large proportion of the P that is not used by the crop in the year of application will remain in the soil as residual P that can be used by the crop in subsequent years. Residual P can be increased in the soil by large, one-time applications of P fertilizer or built up gradually over time if P applied in fertilizers or manures is greater than that removed through crop uptake. If P removal is greater than P addition, the residual P will often remain in labile P forms for several years and serve as a long-term source for plant uptake. However, the residual P compounds in soil tend to slowly decrease in availability over time (e.g., several years), due to changes in chemical form that reduces their solubility. Changes in soil P over time will be a function of the balance between P input and removal. Where P input exceeds P removal, soil P fractions can increase and where removal is greater than input, P reserves will decline. Consideration of fertilizer P use efficiency should consider both the immediate and the long-term, residual benefits of the fertilizer applied. Many long-term studies have shown that recovery of applied P can be very high if P balance is considered over the long-term.

Detailed Information

3.1 The phosphorus cycle

The phosphorus cycle is the biogeochemical cycle in which P moves through soil, water and organisms. Unlike several other biogeochemical cycles, the atmosphere is not involved substantially in the P cycle, because P and P compounds rarely move through a gaseous phase under normal conditions, especially in terrestrial environments. However, there can be small amounts of atmospheric movement of P in air-borne dust particles moving through wind erosion. In natural systems, soils contain phosphate that originated from the weathering of P-rich minerals such as apatite ($Ca_{10}(X)(PO_4)_6$, where X represents F^-, Cl^-, OH^-, or CO_3^{2-} (Pierzynski and McDowell 2005). As soils weather and develop over time, soil pH decreases and the Ca phosphates will change to amorphous and crystalline Al phosphate and then to Fe phosphate (Sample et al. 1980). Phosphorus can be added to the system through manures, crop residues, fertilizers, municipal wastes and by-products and will be lost from the systems through crop removal, erosion and runoff, and under some conditions through leaching or drainage (Figure 1).

The organic forms of P can comprise as much as 25 to 60% or more of the total P content of soils and include growing plants and plant residues, animal waste, soil biota, soil organic matter, and soluble organic P present in the soil solution (Doyle and Cowell 1993; Liu et al. 2015). The amount of organic P in the soil may vary seasonally, reflecting the dynamic nature of mineralization-immobilization reactions that affect both P_o and P_i (Dormaar 1972). Factors that decrease the total amount of organic matter in the soil, such as excess cultivation and summer fallowing will lead to a reduction in total organic P. Most naturally occurring organic P is in the form of esters of orthophosphoric acid . The organic phosphate forms in the soil include inositol phosphates, nucleic acids, nucleotides, phospholipids and sugar phosphates (Stewart et al. 1980; Stewart and Tiessen 1987). In Chernozemic soils, about 10-30% of the organic P is in the form of inositol phosphate; phospholipids make up 1-2%; less than 1% are nucleic acids and about 70% are unidentified (Stewart et al. 1980). Studies using ^{31}P NMR spectroscopy to characterize soils from a long-term P study in Swift Current found P_o species in the phosphonate, orthophosphate monoester and orthophosphate diester compound classes (Liu et al. 2015) Identified monoesters included various stereoisomers of inositol hexakisphosphate, choline phosphate, glucose 6-phosphate diester degradation products including glycerophosphates and mononucleotides. Orthophosphate diesters occurred as DNA and two types of unknown diesters. There was also a range of unidentified monoesters. However, only a small portion of the soil organic phosphorus is biologically active and much of the organic P in the soil has accumulated as chemically resistant and aggregate-protected forms (Stewart and Tiessen 1987). Procedures that fractionate P_o using sequential extractants of increasing strength that remove P fractions of varying availability can be used to characterize the bioavailable P pools in the soil (Bowman and Cole 1978; Hedley and Stewart 1982; Hedley et al. 1982).
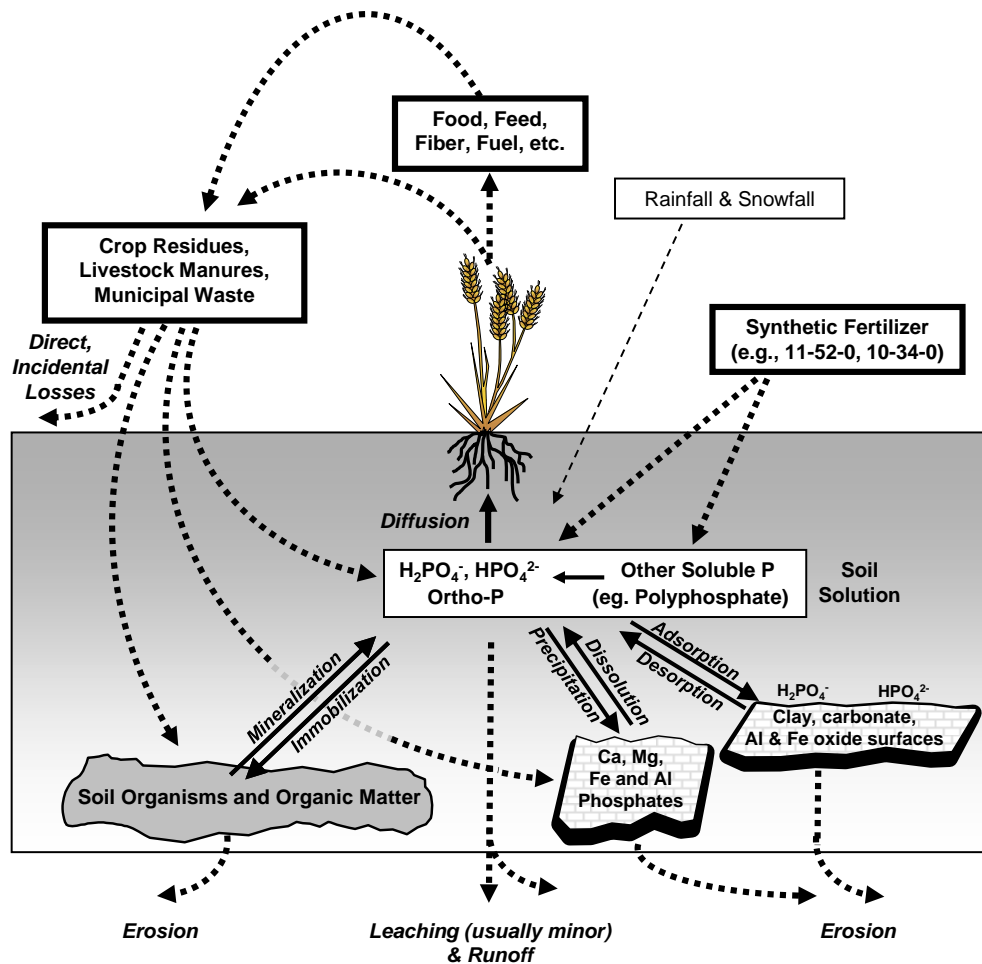
Figure 1. Simplified phosphorus cycle. Dashed lines represent phosphorus gains or losses in the soil system; solid lines represent internal transformations within the soil system (https://www.gov.mb.ca/agriculture/environment/nutrient-management/pubs/effects-of-manure%20-fertilizer-on%20soil%20fertility-quality.pdf, accessed April 30, 2019).

The organic forms of P in the soil can be converted to inorganic orthophosphates by mineralization, when microbes in the soil release orthophosphates as they metabolize organic matter as an energy source (Stewart and Tiessen 1987). Phosphatase enzymes in living cells cleave a phosphate group from a substrate to convert organic matter P into plant-available phosphate (Margalef et al. 2017). Mineralization of soil organic P can also be catalysed by phosphatase enzymes that are produced by bacteria, fungi and plants roots and released into the soil through excretion or cell lysis (Gould and Bole 1980; Margalef et al. 2017; Stewart and Tiessen 1987). Phosphatase activity is usually greater in the rhizosphere than in the surrounding soil because of the high biological activity in the vicinity of the root (Stewart and Tiessen 1987). Some organic phosphate esters are quickly broken down while others are more stable and may accumulate in the soil over time, depending on the balance between production and decomposition. Mineralization of organic P is important for providing plant-available inorganic P especially on highly weathered soils where available mineral forms have been depleted. Labile forms of organic P may move more readily through the soil than do labile inorganic P ions

(Stewart and Tiessen 1987). The high mobility of labile organic P can therefore potentially affect both movement of P to plant roots and environmental risk of P movement to water.

Inorganic phosphate can be immobilized by soil microorganisms that require it for their metabolism and incorporate it into their biomass (Figure 1). Immobilization and mineralization operate in a cyclical process with P being tied-up as the microorganism grow and released as they die and decompose.

The inorganic forms of P in the soil include the phosphate ions in the soil solution, P that is adsorbed on the soil particles, P that is precipitated as secondary P minerals such as Ca, Mg, Fe and Al phosphates, and the P that is present as primary P minerals, such as the various forms of apatite. Apatite can slowly weather over time and release orthophosphate into the soil solution. The secondary P minerals are also involved in equilibrium reactions where they dissolve to release orthophosphate or are precipitated by retention of solution orthophosphate with Ca, Mg, Fe and Al (Figure 1). Phosphate ions can be adsorbed onto the soil particles in a chemical binding process that is reversed through desorption, where the ions are released into the soil solution.

The soil solution will contain some soluble organic phosphates, pyrophosphate and polyphosphate; however, because plants take up P as orthophosphate, this is the main form of solution P that is of interest for crop production. The concentration of plant available orthophosphate in the soil solution is referred to as the intensity factor (I). The dominant form of orthophosphate in the soil solution depends on the soil pH (Figure 2). Within the normal range of soil pH, HPO_4^{-2} dominates if pH is greater than 7.2 and $H_2PO_4^-$ dominates at pH levels below 7.2 (Pierzynski and McDowell 2005). Uptake rates of orthophosphate by plants tend to be greatest between pH of 5 and 6, indicating that orthophosphate is primarily taken up by the plant in the monovalent form (Schachtman et al. 1998).
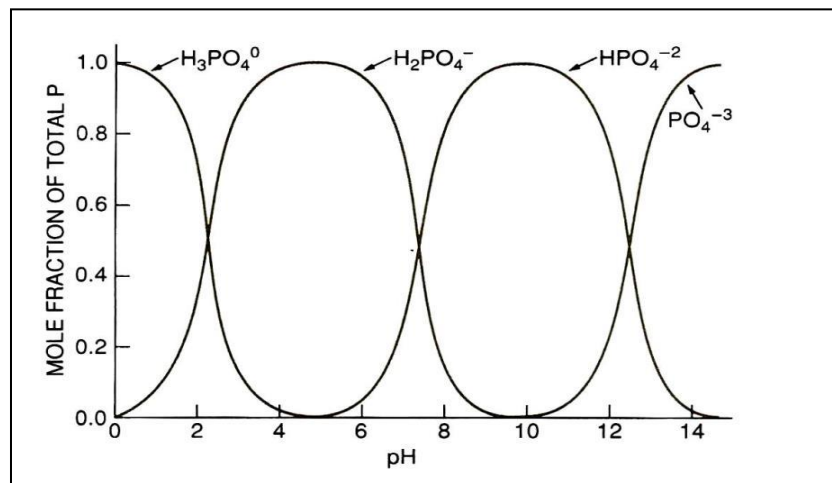

Figure 2. Influence of pH on the distribution of orthophosphate species in solution (Havlin et al. 2014).

The soil solution normally contains very low concentrations of P, typically ranging from as low as 10^{-8} M in very low fertility tropical soil, 10^{-6} M in deficient soils and as high as 10^{-4} M in high P soils (Syers et al. 2008). The amount of P in the soil solution will normally be less than 1% of the total quantity of P in the soils. Even with a moderate P concentration, the soil solution will contain substantially less than 1 lb/acre of dissolved P to the 6-inch depth at any time, far less than the crop requires for growth.

Roots will intercept nutrients as they grow into new soil that has not been depleted, but roots contact only a small proportion of the soil surfaces in any particular growing season. While root volume and architecture will vary substantially among plants due to genetic and environmental conditions, the P accessed by direct root interception will make up only a very small percentage of the crop requirements (Barber 1995; Gahoonia and Nielsen 2004; Marschner and Rengel 2012). Barber (1995) calculated that corn grown on a silt loam soil would obtain only 1% of its P requirement through direct interception.

The majority of P is supplied by replenishment of the very low concentration of P in the rhizosphere surrounding the plant root. The movement of P to the root surface through the soil occurs by mass flow or diffusion. Mass flow refers to the movement of dissolved nutrients with water as it moves to the roots to meet the plant's transpirational water demand, while diffusion is the movement of nutrients through the soil solution from an area of high concentration to an area of low concentration, without any water movement. Because the concentration of P in the soil solution is very low, the total amount of P that will move to the plant root via mass flow will also be very low, in the order of 2-3% of the total amount required for optimum crop growth (Johnston et al. 2014). Most P movement to the rhizosphere occurs through diffusion, driven by the concentration gradient created by the active uptake of P by plant roots. However, the speed of diffusion of phosphate ions though the soil solution is very slow and the path of movement through the soil moisture films around the soil particles is long and crooked, or "tortuous". Therefore, the net movement of P though the soil is small, in the range of 0.13 mm per day. To support optimum crop growth, there must be a supply of P in the soil surrounding the root that can replenish the soil solution in contact with the root surface. During periods of peak P demand, the P in the soil solution at the root hair surface must be replenished at least 10 to 20 times per day (Syers et al. 2008). Therefore, the ability of the soil to replenish the soil solution P as it is extracted by crop roots is critical for ensuring an adequate P supply to the growing crop.

The ability of the soil's reserves of P to replenish the P in the soil solution is referred to as the quantity factor (Q) or the P buffering capacity. The P in the soil solution is replenished from the organic and inorganic reserves of P that are present as solids or on soil surfaces. These reserves are broadly divided into "labile" and "non-labile" forms. Labile P describe the forms of P in the soil that will rapidly equilibrate with the soil solution and become available in the short-term, while non-labile forms will equilibrate more slowly and are a longer-term source of replenishment for the labile reserves and the soil solution. The labile forms include easily mineralizable organic P, the relatively soluble forms of precipitated P and the adsorbed P that is readily exchangeable. Conversely, the non-labile P includes the more stable organic P, the strongly adsorbed forms and more sparingly soluble forms.

Conceptually, this gives a series of pools of various P forms that will shift with changes in relative concentration (Johnston et al. 2014; Syers et al. 2008) (Figure 3). The first of the soil reserves of inorganic P is the pool of soluble P in the soil solution that is immediately available for plant uptake. The second pool is P that adsorbed on the surface of the soil constituents. It can be readily desorbed to replenish the soil solution as it is depleted by plant uptake. The third pool is P that is adsorbed more strongly to surface constituents or possibly adsorbed on internal surfaces on the soil components but will become plant available over a slightly longer timescale of months to years. The fourth pool is strongly bonded to soil components or is precipitated as slightly soluble P compounds or may be poorly available due to its position deep in the soil matrix. It has a low availability but may be released for plant uptake over many years. Transfer of P from one pool to another is reversible with the time-frame for reaction reflecting the availability of the pools.

Immediately accessible	*High accessibility*	*Low accessibility*	*Very low accessibility*
In solution	Readily extractable	Low extractability	Very low extractability
Soil solution P	Surface-adsorbed P	Strongly bonded or absorbed P	Very strongly bonded or mineral or precipitated P
Pool 1	*Pool 2*	*Pool 3*	*Pool 4*
Immediately available	Readily available	Less readily available	Very low availability

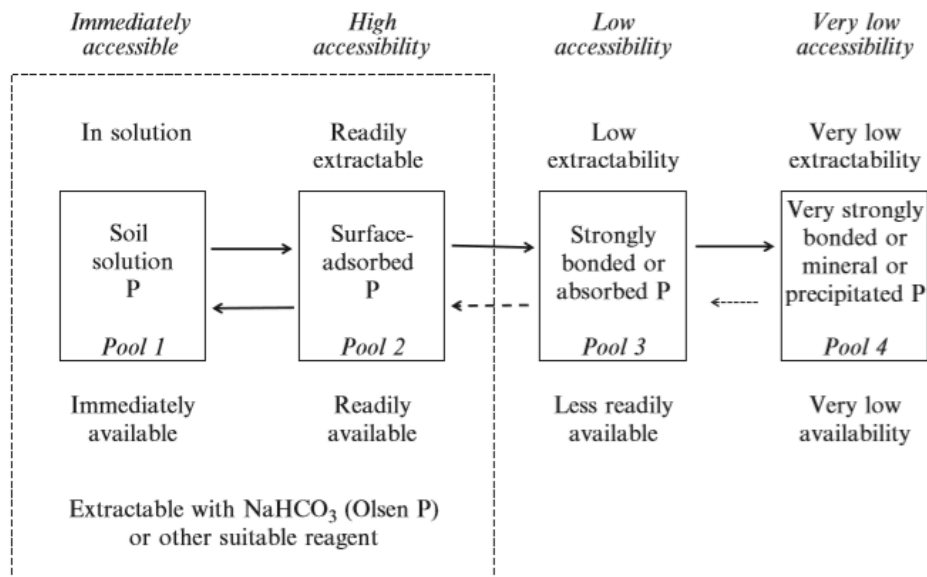Extractable with NaHCO$_3$ (Olsen P) or other suitable reagent

Figure 3. Conceptual diagram for the forms of inorganic P in soils categorized in terms of accessibility, extractability and plant availability (Johnston et al. 2014)

Adsorption/desorption and precipitation/dissolution reactions are concentration dependent, so addition or depletion of P in the soil solution will shift the direction of the equilibria and lead to movement of P along the availability gradient. In natural ecosystems, with limited external inputs of P, the P removed by plant uptake system will be ultimately replenished by the slow weathering of naturally occurring primary P minerals such as apatite. In managed ecosystems, such as cropland, external inputs of P and plant uptake from the soil solution will influence the direction of soil reactions.

3.2 What happens when P fertilizer is added to the soil?

When water-soluble P fertilizer is applied to the soil, only a small proportion of it remains in solution. The solution P undergoes a series of reactions that move the inorganic P from the solute phase and reduce its bioavailability (Hedley and McLaughlin 2005; McLaughlin et al. 2011; Sample et al. 1980). The reactions include adsorption on the surface of the soil particles, diffusion (absorption) where the P adsorbed on the soil particle moves to inner surfaces of the particles where it is less accessible, and precipitation of new sparingly soluble solid phase P with most of the P initially precipitating as high solubility reaction products. These are transient forms of P that are subsequently distributed between the readily and less readily available pools by adsorption and then absorption (Johnston et al. 2014). Phosphorus retention is by both precipitation and adsorption that often occur simultaneously (Ajiboye et al. 2007; Ajiboye et al. 2008).

Adsorption reactions include quickly reversible adsorption reactions at the surface of soil particles and slower reactions that occur when the P moves onto adsorbing surfaces in the interior of soil particles (McLaughlin et al. 2011; Sample et al. 1980). On alkaline soils, calcium carbonate or mixtures of calcium carbonate and Fe oxides are important while in acidic and neutral soils, Al and Fe oxides dominate. Adsorption reactions are important where the concentration of P is less than the P adsorption maximum of the soil and the concentration of reacting ions such as Al, Fe, Ca, Mg, Si or other trace elements in the soil solution are too low to cause precipitation of their phosphate mineral products (Hedley and McLaughlin 2005; McLaughlin et al. 2011; Pierzynski and McDowell 2005). The amount and form of Al and Fe minerals in the soil will determine the extent of adsorption reactions, especially in acidic and neutral pH soils, although Ca may play a role even in acid soils (Beauchemin et al. 2003; Holford and Mattingly 1975; Khatiwada et al. 2014; Luo et al. 2017). Aluminum and Fe hydrous oxides in soil can occur as discrete compounds, as coatings on other soil particles, or as amorphous Al hydroxy compounds in the interlayers of Al silicates (Sample et al. 1980). Because of their abundance in soils and their large specific surface area, amorphous hydrous oxides of Fe and Al adsorb more P than crystalline forms of Al and Fe. The H^+ present in orthophosphate allows a 2-step ligand exchange process in negatively charged soils, leading to inner sphere surface complexes, with P bonded to one metal atom being labile and P bonded to 2 metal atoms being non-labile (Figure 4).
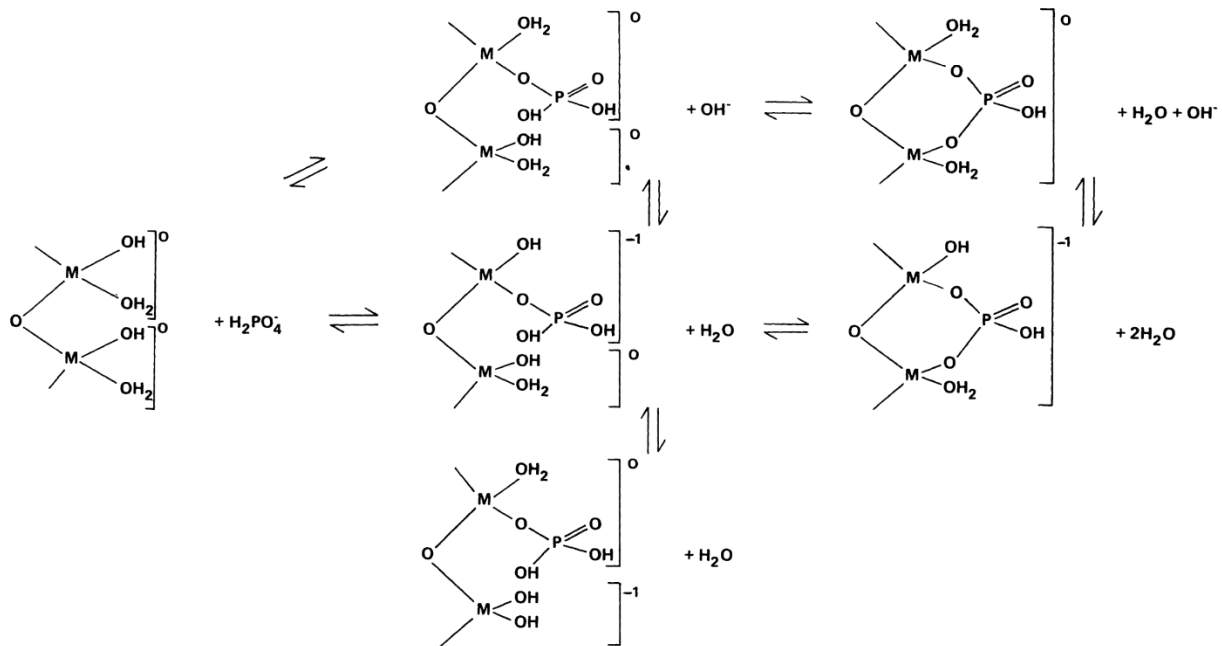
Figure 4. Phosphorus adsorption reactions on metal oxide surfaces (Barrow 1980). Mononuclear ligands with 1 P bonded to 1 metal atom are labile while binuclear or bridging ligands with 1 P bonded to 2 metal atoms are non-labile.

In calcareous soils, $CaCO_3$ will dominate the soil chemistry, although Al and Fe oxides may also be important (Holford and Mattingly 1975; McLaughlin et al. 2011; Sample et al. 1980; Weir and Soper 1962; Zhang et al. 2014). Phosphate can be adsorbed on free $CaCO_3$ at relatively low concentrations and held in a form that is less strongly bound and hence more plant-available than that adsorbed to hydrous oxides. During adsorption by $CaCO_3$, the phosphate ion replaces adsorbed water molecules, bicarbonate ions and hydroxy ions (McLaughlin et al. 2011; Sample et al. 1980). The adsorbing strength depends on the solubility of the compound formed with the surface Ca ions while the amount of adsorption is controlled by the area of adsorbing surface.

Soluble phosphorus can also be removed from solution through precipitation of new solid phases from the ions present in the soil solution when the concentration is high enough to exceed the solubility product of the precipitating substance. If the pH is 7 or lower, hydrous oxides of aluminum and iron will react with phosphate to form various Al- or Fe-P minerals, likely including amorphous analogs of variscite, as well as crystalline variscite ($AlPO_4 \bullet 2H_2O$) or strengite ($FePO_4 \bullet 2H_2O$) (Hedley and McLaughlin 2005; McLaughlin et al. 2011; Pierzynski et al. 1990a; Pierzynski et al. 1990b; Pierzynski and McDowell 2005; Sample et al. 1980). If the soil pH is above 7, phosphate will precipitate with Ca and Mg to produce minerals with lower solubility and decreasing proportions of P.

In calcareous soils, the dominant initial reaction product is dicalcium phosphate dihydrate (DCPD or $CaHPO_4 \bullet 2H_2O$) (Kar et al. 2017; Racz and Soper 1967; Sample et al. 1980). On soils containing high concentrations of Mg, dimagnesium phosphate trihydrate may also form.

Over time, reactions with Ca and/or Mg will continue, leading to formation of compounds with increasing ratios of Ca and/or Mg to P and decreasing solubility (Beauchemin et al. 2003; Doyle and Cowell 1993; Lombi et al. 2006; Sample et al. 1980; Zhang et al. 2014). The retention process reduces the availability of P over time; however, the process is reversible, and the retained or "fixed" P minerals can slowly become available as the crop removes P from the soil solution.

Table 1. Reaction products of P fertilizers in calcareous soils

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Compound & Sequence	Ca/P ratio	pK_{sp}[1]
Orthophosphate P ($H_2PO_4^-$ or HPO_4^{2-} eg. MAP) ↓	0/1	-- (v. soluble)
Dicalcium phosphate dihydrate (DCPD, $CaHPO_4 \bullet 2H_2O$) ↓	1/1	6.56 (sl. soluble)
Octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_6 \bullet 5H_2O$) ↓	8/6	93.81 (low solubility)
Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$)	10/6	111.82
or Fluorapatite (FA, $Ca_{10}(PO_4)_6F_2$)	10/6	120.86 (v. insoluble)

[1]The pKsp is the negative log of the solubility product constant (K_{sp}) which describes the equilibrium relationship between a solid and its respective ions in a saturated solution. Generically, K_{sp} = (Cation activity) x (Anion activity) in a saturated solution (that is, the product of the activity of each ion in solution). The higher the value of K_{sp}, the more soluble the compound while the higher the pKsp is, the less soluble the compound.

The soil's pH affects the solubility of the various phosphate compounds. In a high pH soil, H^+ is an ingredient in the dissolution reactions for calcium and magnesium phosphates, so low pH <u>increases</u> dissolution, e.g., for dissolution of dicalcium phosphate dihydrate (DCPD):

$$CaHPO_4 \cdot 2H_2O + \mathbf{H^+} \leftrightarrow H_2PO_4^- + Ca^{2+} + 2H_2O$$
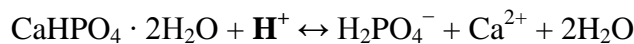
In acid soils, H^+ is a product of the dissolution reactions for iron phosphates, so low pH <u>decreases</u> dissolution, e.g., for dissolution of strengite:

$$FePO_4 \cdot 2H_2O + H_2O \leftrightarrow H_2PO_4^- + \mathbf{H^+} + Fe(OH)_3$$
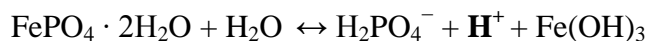
Precipitation of phosphate will increase with increasing concentration of the reacting ions. So, in high pH soils, increasing concentration of Ca, Mg or phosphate will increase precipitation. On low pH soils, increasing concentrations of Fe, Al or phosphate will increase precipitation.

Speed of reaction will increase with increasing temperature, whether it is precipitation or dissolution (Sheppard and Racz 1980). So, increasing temperature will increase the rate of dissolution of residual or native P or secondary minerals that are present in the soil, increasing the rate of release of orthophosphate into the soil solution. At the same time, increasing temperature will also increase the rate of precipitation of soluble P to less soluble forms, hastening the retention of recently applied P into less available forms.

When fertilizer P is added to the soil, there is an extreme change in the concentration of P in the immediate vicinity of the application site that initiates a series of adsorption and precipitation reactions that affect both the short- and long-term availability of the P in the reaction zone. If a solid fertilizer granule is added to the soil, it must dissolve before the phosphate enters the soil solution and becomes available. The release of phosphate from water-soluble fertilizers is rapid, with the initial dissolution and movement of P out of the granule occurring within a few days (Hedley and McLaughlin 2005; Lombi et al. 2004; McLaughlin et al. 2011). Phosphate fertilizers are hygroscopic, so will attract water vapour from the soil air-filled space, as well as soil porewater that will move towards the fertilizer through mass flow and capillary flow, dissolving the granule (Hettiarachchi et al. 2006; McLaughlin et al. 2011). At the same time, highly concentrated P solution will diffuse along the osmotic gradient, away from the granule, towards areas of lower concentration outside of the fertilizer reaction zone. The reactions of the fertilizer granule or droplet and the outward movement of the P solution result in a series of zones where P concentration decreases with increasing distance from the application point. The residual granule or droplet and the immediate surrounding area contain insoluble P compounds from the original fertilizer and the compounds that have precipitated from the highly concentrated fertilizer solution (Hedley and McLaughlin 2005; Kar et al. 2012). Beyond this is a zone of soil next to the granule where the capacity of the soil to adsorb P has been saturated, and precipitates have formed from the reaction of the fertilizer solution with the metal ions and organic matter released from the soil. Beyond this is an area where the P adsorption capacity of the soil has not been saturated.

The formation of compounds in the residual granule and the fertilizer-soil interface immediately surrounding it is affected primarily by the type of solution formed by the applied fertilizer and the available moisture from the soil (Hedley and McLaughlin 2005; Sample et al. 1980). The properties of the water-soluble P compounds most commonly contained in phosphate fertilizers are given in Table 2. The highly concentrated saturated solution may dissolve soil minerals and release cations such as Al, Fe, Ca and Mg. The high concentration of phosphate ions and reacting cations in the solution will lead to the precipitation of Al, Fe, and Ca phosphates (Hedley and McLaughlin 2005; Hettiarachchi et al. 2006; McLaughlin et al. 2011; Sample et al. 1980). The types of precipitates that have been identified during the reactions of various phosphate fertilizers in soils has been reviewed by Sample et al. (1980) and by Hedley and McLaughlin (2005). Mass flow of reacting cations in the soil water moving towards the granule may increase the precipitation of phosphate at the granule application site, particularly on calcareous soils, reducing the movement of phosphate away from the granule and reducing the volume of the fertilizer reaction zone.

Table 2. Phosphate compounds commonly found in fertilizers and composition of their saturated solutions (Sample et al. 1980)

| Compound | Formula | Composition of saturated solution | | | Accompanying cation, moles/liter | | Refer-ence[†] |
		Solution symbol	pH	P, moles/liter			
Highly water-soluble compounds							
Monocalcium phosphate	$Ca(H_2PO_4)_2 \cdot H_2O$	TPS	1.0	4.5	Ca	1.3	A
		MTPS	1.5	4.0	Ca	1.4	A
Monoammonium phosphate	$NH_4H_2PO_4$	MAP	3.5	2.9	NH_4	2.9	A
Monopotassium phosphate	KH_2PO_4	MKP	4.0	1.7	K	1.7	A
Triammonium pyrophosphate	$(NH_4)_3HP_2O_7 \cdot H_2O$	TPP	6.0	6.8 ($3.4\,P_2O_7$)	NH_4	10.2	B
Diammonium phosphate	$(NH_4)_2HPO_4$	DAP	8.0	3.8	NH_4	7.6	A
Dipotassium phosphate	K_2HPO_4	DKP	10.1	6.1	K	12.2	A
Sparingly soluble compounds							
Dicalcium phosphate	$CaHPO_4$ $CaHPO_4 \cdot 2H_2O$	DCP	6.5	~0.002	Ca	0.001	C
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	HAP	6.5	$\sim 10^{-5}$	Ca	0.001	C

[†] A: Lindsay et al. (1962); B: unpublished TVA data; C: based on Farr (1950), assuming pH = 6.5 and Ca = $0.001M$.

Evidence from Australian studies indicates that if the fertilizers are applied in a solution or dissolved form, there is less movement of water carrying reacting ions towards the fertilizer, thus precipitation is reduced and P will move further away from the site of application (Bertrand et al. 2006; Hettiarachchi et al. 2006; Holloway et al. 2001; Lombi et al. 2004; Lombi et al. 2005). Evaluation of reaction products formed from granular as compared to fluid sources on a highly calcareous soil showed that P lability decreased near granules because of precipitation of octacalcium phosphate or apatite-like compounds while with fluid applications more P remained in a plant-available form similar to monocalcium phosphate (Lombi et al. 2004; Lombi et al. 2005; Lombi et al. 2006).

Use of solution P fertilizer has provided large increases in P use efficiency on dry, highly calcareous soils in Australia (Holloway et al. 2001), but the same benefits have not been demonstrated consistently on the Northern Great Plains. Field studies near Brandon, MB showed that monoammonium phosphate granular fertilizer (MAP) increased both dry matter yield and P uptake more than ammonium polyphosphate liquid fertilizer (APP) early in the growing season, but that APP had a greater benefit on final grain yield (Spratt 1973). Dry matter production and the uptake of P continued after the dough stage with APP but not with MAP. The author suggested that the hydrolysis of polyphosphate by roots later in the season may encourage later-season responses. However, later field studies in Manitoba and Alberta showed no difference in response of spring wheat yield to APP or MAP (Grant et al. 2007). Other field studies in Manitoba also showed that durum wheat (Grant et al. 2008) and canola (Grant and Relf-Eckstein 2009) showed similar responses to APP and MAP, while soybean did not respond significantly to either P source (Grant et al. 2008).

Blending soluble salts such as ammonium nitrate, ammonium sulphate, potassium nitrate, potassium chloride or potassium sulphate with the phosphate fertilizer can lead to the formation of structural analogues for the calcium phosphate during the reaction process. The analogues where K or NH_4 replace some of the Ca are more soluble than the unsubstituted calcium phosphates and so will move more quickly away from the granule, reducing the amount of P that remains in the granule residue (Hedley and McLaughlin 2005; Sample et al. 1980; Takagi et al. 1980). In contrast, adding $CaCO_3$ will increase the precipitation of relatively insoluble octacalcium phosphate or dicalcium phosphate dihydrate and increase the amount of P remaining near the granule.

The zone of soil immediately surrounding the fertilizer granule or droplet will contain a saturated P solution, characteristic of the type of fertilizer applied, that will saturate the P adsorption capacity of the soil. The greater the ability of the soil to retain P, the smaller will be the extent of the P-saturated zone. In the zone nearest the granule, precipitation reactions dominate, rather than adsorption. As P diffuses away from the granule, the concentration in the solution decreases to the point where it is no longer saturated and adsorption reactions become more important. In this region, P movement will be mainly by diffusion via the tortuous route through the soil water film around soil particles and through micropores (Figure 5).
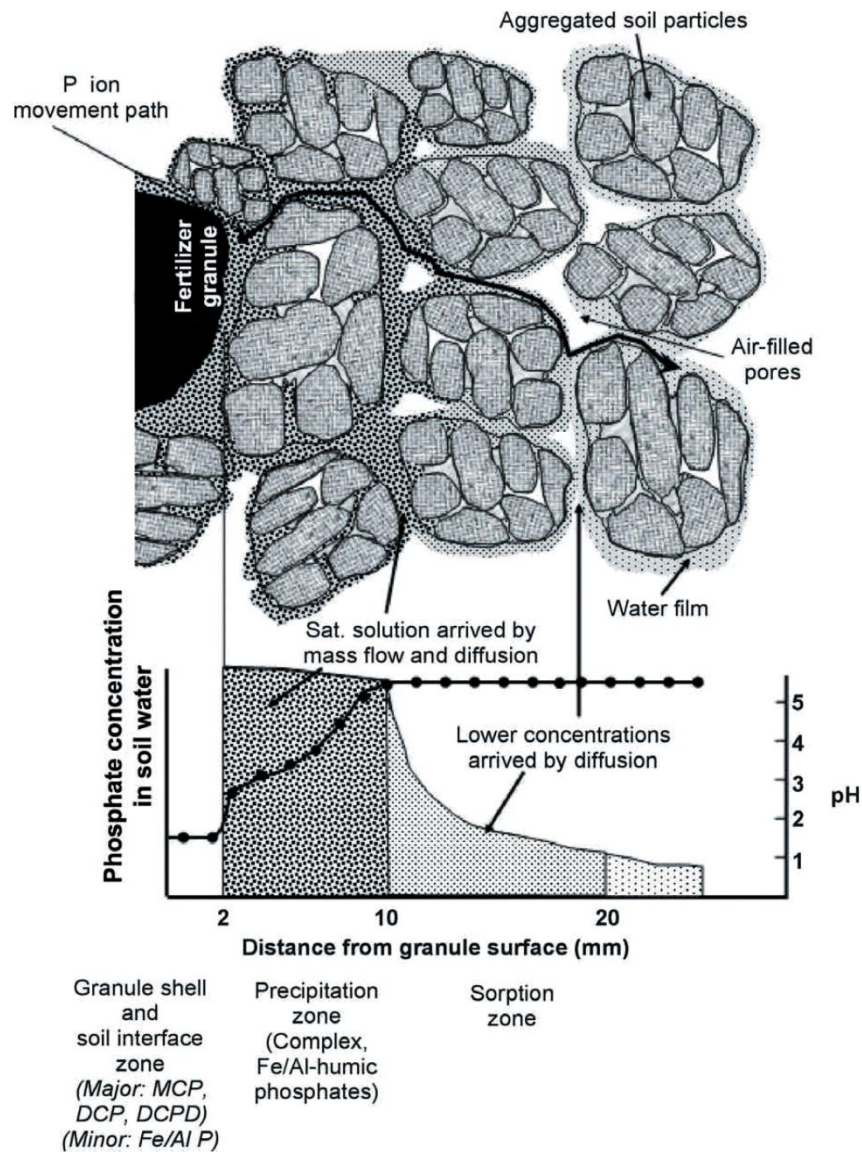
Figure 5. Diagrammatic representation of the movement of phosphate by mass flow and diffusion from a granule of triple superphosphate (or single superphosphate) through water-filled and water-lined large micropores in a well-aggregated soil. Note that the penetration of phosphorus (P) into aggregates is incomplete due to the slow rate of P diffusion in smaller intra-aggregate micropores and discontinuous micropores. (Not to scale.) Lower graph shows relative P concentration and pH (–•–•–) in soil water (Hedley and McLaughlin 2005).

As the distance from the application site increases, the concentration of P in solution decreases due to dilution, precipitation and adsorption until the P concentration in solution approaches background soil levels (Kar et al. 2012). The distance from the fertilizer granule where the P concentration is elevated is normally very small, in the range of a few millimeters. The volume

of the reaction zone around the granule where P concentration is increased will be important in affecting plant uptake because a larger volume provides a greater opportunity for roots to grow and access the P. The volume of the reaction zone will be influenced by the P retention characteristics of the soil and factors affecting P retention. The greater the retention capacity of the soil, the lower the P concentration will be in the solution where diffusion is occurring, the slower diffusion will be and the smaller will be the volume of soil where the P concentration is increased to enhance crop P uptake. Soils with a larger adsorbing surface area will have a greater adsorption capacity; clay soils, for example will tend to have greater adsorption than sandy soils.

Adsorption capacity will be large on acid soils with high concentrations of Fe and Al oxides. The Fe and Al oxides will adsorb more P at low than neutral pH. However, if acid soils are limed to increase the pH, Al^{3+} will precipitate as $Al(OH)_3$, creating more reactive surfaces and hence increasing adsorption. On high pH soils, adsorption will increase with increasing levels of $CaCO_3$ or $MgCO_3$.

Adsorption will also be influenced by other ions that compete for P adsorption sites, such as OH^- or HCO_3^-. Organic ions may also compete for adsorbing surfaces, reducing adsorption (Sample et al. 1980). Adsorption capacity will be greater if the adsorption complex is not highly saturated, so for example, there can be greater P adsorption during the early years of P fertilization rather than on soils with a long history of fertilization.

The initial reactions of P fertilizers with the soil described above are relatively rapid, taking place in hours to weeks (Sample et al. 1980). Rapid initial surface adsorption of P can be followed by diffusive penetration of P into soil aggregates where it is adsorbed on internal surfaces (Syers et al. 2008). Similarly, the metastable compounds that are precipitated from the saturated solutions soon after fertilizer application will continue to react to form increasingly more stable and less soluble products. In acid soils, the initial amorphous Fe and Al phosphate and Ca phosphate reaction products are thought to change ultimately to variscite-like and strengite-like crystalline compounds (Sample et al. 1980). On alkaline and calcareous soils, DCPD can change to OCP and other less soluble Ca and Mg phosphate forms over a period of months, with the ultimate reaction products thought to be hydroxy- and fluorapatites (Racz and Soper 1967). Although P transformation that occur when P fertilizer is added to the soil reduce plant availability over time, analysis of P recovery from long-term cropping studies indicates the retention of P in soils is largely reversible and that a large proportion can be recovered in following years (Johnston et al. 2014; Selles et al. 2011; Selles et al. 2007; Syers et al. 2008).

3.3 Residual value of fertilizer P

It is often said that the phosphorus use efficiency (PUE) of applied P fertilizer is low, with the amount of P being taken up by the crop in the year of application rarely being greater than 25% (Syers et al. 2008). However, the P that is not utilized by the crop in the year of application is primarily retained in the soil by the reactions described in the previous section, particularly on

dryland soils where leaching and run-off losses are relatively small. Studies around the world have shown that long-term applications of P fertilizers can influence the amount and form of P present in the soil. In general, the majority of the increase in soil P from addition of P fertilizer occurs as inorganic P, adsorbed or precipitated to Al, Ca and Fe although organic forms of P increase somewhat (McLaughlin et al. 2011). Long-term application of P at rates in excess of crop removal or the addition of large one-time applications of P fertilizer can increase the soil residual P. In the past, it was often suggested that retention or "fixation" rendered the P unavailable to crops. However, the residual P present in the soil can remain or become available for crop uptake and serves as a slowly available source of P for growing crops (Spratt and Read 1980; Syers et al. 2008).

Residual benefits of large single-time applications of fertilizer P have been observed in several field trials across the Northern Great Plains. In the 1960s and 70s, at four sites on Chernozemic soils in Manitoba and Saskatchewan, a single large application of phosphate fertilizer at rates from 0 to 800 lb P_2O_5/acre (0 to 400 kg P/ha) was broadcast and incorporated at the initiation of the study (Read et al. 1973). The Manitoba sites were cropped with a wheat-flax rotation and the Saskatchewan sites in a wheat-fallow rotation. Yields were increased from the residual effect of the fertilizer application for the initial 8 years of the study, with higher yields and higher soil P concentrations occurring with the 400 and 800 lb P_2O_5/acre rates. Over the 8 years of cropping, 200 lb P_2O_5/acre was the most efficient treatment in increasing yield. By the final year of the study, the Olsen soil test extractable phosphorus level of the 200 lb P_2O_5/acre treatment was reduced to about 4 ppm which was comparable to the control and would be too low to support optimum crop yield. However, soils treated with 400 and 800 lb P_2O_5/acre still contained between 10 and 27 ppm of Olsen soil test extractable P and little response in yield to additional P fertilization would be expected (Bailey et al. 1977; Read et al. 1977).

Soil was collected from the field sites in the fall after three crops had been grown on the Manitoba sites and after one crop had been grown on the Saskatchewan site. These soils were used in greenhouse studies where 19 crops were grown to evaluate the persistence of the residual effect of the P applied (Read et al. 1973). The Olsen soil test extractable P concentration in the soil decreased to the level of the control after three to five crops on the 200 lb P_2O_5/acre treatment and after 11 to 13 crops on the 400 lb P_2O_5/acre treatment but was still higher than that of the control in the 800 lb P_2O_5/acre treatment, even after 19 consecutive crops. The recovery of applied P was calculated as the difference between P uptake from the fertilized treatments and from the check. The P uptake data from the soil in the field prior to bringing the soil into the greenhouse were combined with the uptake data for the greenhouse study to determine the total P recovery. A total of 87, 81 and 70% of the P applied was recovered in the harvested plant material from the 200, 400 and 800 lb P_2O_5/acre applications, respectively, indicating that the broadcast applications were used efficiently over time. Air-dried samples from the trials were evaluated in 1980 using the Hedley sequential extraction technique (Hedley et al. 1982; Wagar et al. 1986b). The proportion of P present as resin-extractable (consisting of the more soluble calcium phosphates such as DCPD and OCP and surface adsorbed P) declined from approximately 60% of the total P extracted in the samples taken in the first year of the study to approximately 30% in the samples taken in the 5th year of the study, then remained fairly

constant until year 8. Sodium bicarbonate-extractable P in the Hedley fractionation test (slightly different from soil test Olsen P) declined from about 12-16% of the P that could be recovered through the extraction procedures in the first year of the study to about 10-11% by year 8. By the end of the study, about 40-50% of the P applied remained in plant-available forms. Approximately 29% was in acid-extractable forms, possibly fractions that were metastable and slowly plant-available. There was also an indication that sodium-bicarbonate extractable P moved downward through the soil profile over time, possibly due to bio-cycling by plant roots, with higher concentrations in the fertilized as compared to unfertilized plots noted at the l5-30, 30-60, 60-90 and 90 to 120 cm depths (Read and Campbell 1981).

A six-year field study in Saskatchewan on a Dark Brown Chernozemic clay soil used single broadcast P applications at 5 rates from 0 to 320 lb P_2O_5/acre and annual seed-placed P applications at 5 rates from 0 to 40 lb P_2O_5/acre under continuous cropping (Wagar et al. 1986a). Broadcast P applications of 40, 80, 160 and 320 lb P_2O_5/acre increased the average yield by 9, 24, 33 and 35%, respectively. Yearly seed-placed P treatments of 5, 10, 20 and 40 lb P_2O_5/acre applied over the first 5 years of the study increased the average yield by 10, 15, 24 and 29% respectively. The broadcast application of 80 lb P_2O_5/acre increased yields over 5 years and had an average yield and P uptake comparable to that of the annual seed-placed applications of 20 and 40 lb P_2O_5/acre. Broadcasting 160 and 320 lb P_2O_5/acre increased yields over 6 years and soil levels of extractable $NaHCO_3$-P in the Hedley fractionation test were still high enough after 6 years to indicate that crop yields would be increased due to the residual benefit. The two higher rates of initial broadcast P applications increased both resin and sodium bicarbonate inorganic P, with about half of the recoverable inorganic P remaining in these forms by the end of the 5-year study (Wagar et al. 1986b). Significant amounts of the applied P were converted into organic P forms which persisted to the end of the study. Phosphorus was also found to have moved below the 15 cm depth at the higher rates of P application, possibly due to bio-cycling in plant residues or possibly leaching of organic P forms, as most of the subsurface P was in the organic form.

In a similar long-term field study conducted in Montana, superphosphate was applied once, at study initiation, at rates of 0, 45, 90, 180, and 360 lb P_2O_5/acre and crops were grown for the following 17 years without additional fertilizer P application (Halvorson and Black 1985a; Halvorson and Black 1985b). A wheat-fallow system was used for the first six wheat crops (*Triticum aestivum*) and then an annual cropping system including wheat, barley *(Hordeum vulgare)*, and safflower (*Carthamus tinctorius* L.), was used for remainder of the study. Fertilizer P recovery in the grain for the 45, 90, 180, and 360 lb P_2O_5/acre treatments averaged 32, 25, 23, and 13%, respectively, without N fertilization and 45, 38, 37, and 24% with 40 lb N/acre applied annually. Even after 17 years, the P recoveries at the higher P rates (> 90 lb P_2O_5/acre) were less than 50% of that applied and recovery of fertilizer P was still increasing at the higher P rates through harvest of the last crop in 1983. The researchers concluded that a one-time broadcast application of P fertilizer at rates as high as 180 lb P_2O_5/acre was an efficient way to manage P fertilizer (Halvorson and Black 1985b). However, in studies in Alberta, the residual benefit from application of a single application of 400 lb P_2O_5/acre as triple superphosphate had dissipated after 12 years of barley production (Karamanos and Kruger 2009).

While P content of the soil may be increased rapidly by large, single applications of P fertilizer, it may also be affected by repeated smaller applications. If the balance between P applied and P removed by the crop is positive, P will accumulate over time. A gradual increase in soil P due to long-term annual P applications has been demonstrated in many trials in the Northern Great Plains over the years. Field trials at seven sites across western Canada showed that application of MAP fertilizer at rates of 0, 40, 80 and 160 lb P_2O_5/acre each year from 2002 through 2009 increased both the labile (H_2O-P and $NaHCO_3$-P in the Hedley fractionation analysis) and non-labile (NaOH-P, HCl-P and Residual-P) fractions in surface soils (0-7.5 cm depth) (Grant et al. 2014; Obikoya 2016). When P application was stopped and crops grown for a three-year depletion phase, the labile P forms decreased but the non-labile fractions (HCl- and Residual-P) continued to increase.

In a study at Indian Head, SK, MAP was applied at 7 rates from 0 to 230 lb P_2O_5 per acre, banded with the seed of the summer fallow wheat crop in a wheat-wheat-summer fallow rotation for 20 years with the second wheat crop left unfertilized to evaluate the residual fertilizer effects (Spratt and McCurdy 1966). The sodium bicarbonate-extractable P increased with increasing rate of long-term P fertilizer application. When sub-plot P treatments of 20 lb P_2O_5 per acre tagged with ^{32}P were superimposed on the plots that had received long-term annual P rates, the increase in crop yield and the recovery of the tagged fertilizer P decreased as the past rate of P application increased, indicating that the crop was less reliant on annual applications of P fertilizer as the residual P in the soil increased. On an acid Dark Brown Chernozem at Scott, SK, MAP was applied to one side of split plots during the wheat phase of a wheat-fallow rotation from 1930 to 1987, for a total of 19 fertilizer application, at a rate of 15 lb P_2O_5 per acre until 1978 and at 25 lb P_2O_5 per acre from 1978 to 1987 (Ukrainetz 1990). The repeated application of relatively small amounts of P fertilizer led to an increase in resin-P of 59% and sodium bicarb-P by about 49% in the surface 15 cm as compared to the side that had not received P fertilizer. Resin P and Olsen P also increased to some extent to at least the 45 cm depth. The organic P forms were not substantially affected by fertilization. Over the 57 years of this study, a high proportion of the fertilizer P applied remained in labile forms in this acid soil.

If P removal is greater than P addition, P will move from stable to labile pools to compensate for the decrease in concentration, while P application in excess of removal will shift P towards accumulation of more stable forms (Liu et al. 2015; McKenzie et al. 1992a; McKenzie et al. 1992b; Syers et al. 2008). Effects of long-term management on phosphorus fractions were evaluated in a Chernozemic and a Luvisolic soil in Alberta that had been cultivated for 74 and 57 years, respectively (McKenzie et al. 1992a; McKenzie et al. 1992b). A comparison of the cultivated soils to adjacent uncultivated soils showed that cultivated crop production without application of P fertilizer led to a decline in sodium bicarbonate-extractable organic P (bicarb-P_o) and sodium hydroxide-extractable organic P (NaOH-P_o) as compared to the uncultivated soil. Hydrochloric acid-extractable inorganic P (HCl-P_i) also declined in all unfertilized systems on the Chernozemic soil and declined with unfertilized continuous cropping on the Luvisolic soil. Organic P fractions decreased more when fallow was included in the rotation than with continuous cropping, likely because the higher C return to the soil with continuous cropping slowed the decline of organic P. Cropping without P fertilizer led to movement of P from the

stable to the labile forms, depleting soil P to support crop uptake. Adding P fertilizer reduced the drawdown of soil P, and when P additions were increased to exceed P removal rates, increases in most inorganic soil P pools began to emerge (McKenzie et al. 1992a). With P addition, total P and all P_i fractions were higher than when P was not added, with the greatest difference being in more labile inorganic P forms (resin-, sodium bicarbonate- and NaOH-extractable P). On the Chernozemic soils, concentrations of these labile forms of inorganic P were higher on P-fertilized soils than on uncultivated soils, because recent P applications exceeded removal rates (McKenzie et al. 1992a). In contrast, on the Luvisolic soil, sodium bicarbonate-extractable inorganic P and sodium hydroxide-extractable inorganic P forms were lower on the fertilized than uncultivated soils, likely because the fertilizer P rates applied were low (McKenzie et al. 1992b). Fertilizer P alone had no effect on labile organic P forms but adding N fertilizer encouraged greater production of organic matter, increasing the proportion of labile organic to labile inorganic P forms. On the Luvisolic soils, concentrations of HCl-extractable inorganic P in the fertilized treatments were similar to or greater than in the uncultivated soil, indicating that the fertilizer P had been moving into the HCl-extractable inorganic P fraction. Continuous cropping with application of N and P produced the highest total-P levels of all treatments at both locations indicating that continuous cropping with balanced P applications had the most positive effects on P dynamics on both sites.

Changes in soil P over time will be a function of the P balance, calculated by the difference between P addition and P loss, with the main path of P loss being P removal in the crop. Where P input exceeds P removal, soil P fractions can increase and where removal is greater than input, P reserves will decline. In a 12-year field trial on an Orthic Brown Chernozemic soil near Swift Current, SK, changes in soil P were closely related to the difference between fertilizer P additions and P removal in the grain, which was mainly related to the grain yield (Selles et al. 1999). During a 7-yr period of low yields caused by dry conditions, Olsen-P increased, reflecting the positive P balance, while in the following four years when grain yield and crop removal of P were greater due to improved moisture conditions, Olsen-P concentration remained nearly unchanged.

In another long-term study at Swift Current, continuous wheat and a summer fallow-wheat-wheat rotation were grown with each receiving either P only or N plus P fertilizer from 1967 to 2005. In 1993, plots were split, and P withheld on half of the plot for the next 12 years of the study. The balance of fertilizer P minus P removed in the grain accounted for about 60% of the variability in Olsen-P accumulation over the experiment (Selles et al. 2011). Olsen-P in the 0 to 1 cm depth increased by 0.07 ppm for each kg per hectare of P applied in excess of removal on the continuous wheat and by 0.10 ppm in the fallow-wheat-wheat rotation during 39 years of P application. The higher value in the fallow rotation may reflect mineralization of P during the fallow year. Cumulative crop P removal over the entire 39-year cropping period where P was withheld during the last 12 years was equal to between 90 and 105% of the total P applied during the initial fertilization portion of the study, with greater removal where both N and P had been added compared to where only P had been applied. In other words, the residual P accumulated during the early years remained in an available form that was used by the crop when further P application was withheld.

Later studies on this site helped to determine the fate of the residual P. In 2010, after another five years of treatment application, the soil P was characterized in surface and subsurface layers using sequential fractionation, P K-edge X-ray absorption near-edge structure (XANES) and solution ^{31}P nuclear magnetic resonance (P NMR) spectroscopy (Liu et al. 2015). The residual P that had accumulated from 28 years of build-up was enough to support a further 15 years of wheat cultivation, with no difference in yield occurring between the fertilized and unfertilized sides of the plot in 2010. Levels of organic P forms in the soil were not decreased in the unfertilized as compared to fertilized soil. However, the Olsen-P levels in the surface soils in the unfertilized sides of the plots decreased compared with 1995 while the levels in the fertilized sides of the plots were similar to the levels in 1995. So, cropping without fertilization depleted the Olsen-P levels while cropping with fertilizer application maintained the Olsen-P pool. Applied fertilizer P was apparently removed through crop uptake, adsorbed by Fe/Al (hydr)oxides or precipitated as Ca-P minerals. With continuous P fertilization, P accumulated in the surface soil as inorganic Fe-P rather than Al-P. In the unfertilized soils, inorganic Al-P fractions as well as hydroxyapatite and $Ca_3(PO_4)_2$ decreased, indicating possible release for crop uptake or conversion to other P forms. There was an increase of Fe (hydr)oxides-associated P between 1995 and 2010 in both the fertilized and unfertilized soils indicating that this may be an intermediate P reservoir for crop production. When P fertilization stops, it is likely that the plants will access the P left behind in the soil and reduce the labile soil P pools.

Benefits from P fertilizer remaining in the soil can persist for many years. In field studies on low (10 ppm) and high (22 ppm) testing clay loam soils in Minnesota, broadcast P applications of 0, 50, and 100 lb P_2O_5/acre applied annually and 150 lb P_2O_5/acre applied every third year for 12 years in a corn-soybean rotation provided residual benefits for 8 years after fertilizer application ceased (Randall et al. 1997a; Randall et al. 1997b). In studies on a thin Black Chernozem loam soil in Crossfield, Alberta, soil samples were taken in 1997 in smooth bromegrass fields that had been fertilized with P as triple superphosphate broadcast at 0, 32, 66, 110, 132, 220 and 264 lb P_2O_5/acre for 10 years from 1968–1977 (i.e., 20 years prior to sampling) and on soils that had not been fertilized (Malhi et al. 2003). Increases in extractable P (in 0.03 M NH_4F +0.1 N HCl solution) in the soil reflected 10 years of P fertilization relative to no P fertilization, even though applications had been terminated 20 years prior to soil sampling. The magnitude and depth of increase in extractable P (in 0.03 M NH_4F +0.1 N HCl solution) paralleled N and P rates. Most of the increase in extractable P (in 0.03 M NH_4F +0.1 N HCl solution) occurred in the top 10-cm soil layer and almost none was noticed below 30 cm depth. Other studies with established forage grass or alfalfa stands also showed that most surface-applied P remained in the surface 5 cm and did not move below 15 cm (Malhi et al. 1992). The relatively small amounts of the surface applied P that moved downward to deeper soil depths could be due to some leaching of inorganic P, of organic P forms or biocycling in plant roots. Nitrogen fertilization led to soil acidification that increased extractable P and could have increased the leaching of P. Therefore, application of higher than recommended rates of N and P can increase P remaining at the soil surface and shallow depths, increasing availability of P but also potentially increasing the risk of movement of P to water bodies for many years after application is terminated.

While excess applications of P that accumulate in the soil surface can lead to risk of P movement to water bodies, decline of P over time due to P removal greater than application can lead to P depletion and loss of soil productivity. The long-term studies described above show that P will move from the non-labile pools to replenish the labile pools in response to plant uptake (Liu et al. 2015; McKenzie et al. 1992a; McKenzie et al. 1992b; Selles et al. 2011; Selles et al. 1999). However, the soil P pools are not infinite and as they decrease, the ability of the soil to supply P to meet crop demand will decline. The "maintenance", "balance" or "long-term sustainability" strategy for P fertilizer management suggests targeting a critical desired soil P level by either adding P greater than crop removal if available soil P is low, or less than crop removal if soil P is high. When the target soil test P level is reached, P fertilizer can be applied to match crop removal to maintain the target soil P.

Phosphorus depletion can be of particular concern in organic crop production systems, where options for P application are restricted. Therefore, many organic farms experience declines in soil P status. A survey of 14 organic farms in the eastern part of the Northern Great Plains showed that soil test P levels were frequently low, with available soil P levels that ranged from deficient (2 ppm) to adequate (27 ppm) (Entz et al. 2001). While the range in soil test P was wide, the average P level in the study was 7 ppm. This compares to soil tests for non-organic commercial fields where 76 and 89% of soil samples taken in Manitoba in 1997 and 1998, respectively, tested greater than 10 ppm. In the University of Manitoba's long term organic rotation at Glenlea, available soil P in the high-yielding organic grain-forage rotations decreased over the first thirteen years of the study, with organically managed soils having lower concentrations of readily available P than conventionally managed soils, while the non-labile forms were similar in the two management systems (Welsh et al. 2009). The lower yielding organic grain-only rotations had lower P removal than the conventional system, resulting in a slightly lower concentration of available-P forms in the soil. The high yielding organic forage-grain rotation decreased available-P forms to below an agronomic response threshold, demonstrating that high-yielding organic rotations that export large amounts of P can lead to P depletion of the soil over time, in the absence of P inputs.

3.4. Assessing P Use Efficiency

As stated previously, phosphorus fertilizer use efficiency (PUE) measured in the year of application will rarely exceed 25% (Johnston et al. 2014; Syers et al. 2008). Traditional methods of measuring nutrient use efficiency that can be applied to PUE are listed in Table 3. However, these methods of evaluation do not normally consider the benefits from residual P.

Use of ^{32}P-labelled P fertilizer can directly show how much of the fertilizer applied moves into the plant and can provide an accurate indication of the short-term use efficiency of fertilizer sources. The half-life of ^{32}P is approximately two weeks, so this technique is limited to studies that are less than about 3 months. While this is a powerful technique for directly studying the fate of applied P, the short half-life, radioactivity hazards and expense of this method limit its application in agronomic field trials.

Table 3. Common methods of calculating nutrient use efficiency (Fixen et al. 2015)

Term	Calculation*	Question addressed	Typical use
Partial factor productivity	$PFP = Y/F$	How productive is this cropping system in comparison to its nutrient input?	As a long-term indicator of trends.
Agronomic efficiency**	$AE = (Y-Y_0)/F$	How much productivity improvement was gained by use of nutrient input?	As a short-term indicator of the impact of applied nutrients on productivity. Also used as input data for nutrient recommendations based on omission plot yields.
Partial nutrient balance	$PNB = U_H/F$	How much nutrient is being taken out of the system in relation to how much is applied?	As a long-term indicator of trends; most useful when combined with soil fertility information.
Apparent recovery efficiency by difference**	$RE = (U-U_0)/F$	How much of the nutrient applied did the plant take up?	As an indicator of the potential for nutrient loss from the cropping system and to access the efficiency of management practices.
Internal utilization efficiency	$IE = Y/U$	What is the ability of the plant to transform nutrients acquired from all sources into economic yield (grain, etc.)?	To evaluate genotypes in breeding programs; values of 30-90 are common for N in cereals and 55-65 considered optimal.
Physiological efficiency**	$PE = (Y-Y_0)/(U-U_0)$	What is the ability of the plant to transform nutrients acquired from the source applied into economic yield?	Research evaluating NUE among cultivars and other cultural practices; values of 40-60 are common.

* Y = yield of harvested portion of crop with nutrient applied; Y_0 = yield with not nutrient applied; F = amount of nutrient applied; U_H = nutrient content of harvested portion of the crop; U = total nutrient uptake in aboveground crop biomass with nutrient applied; U_0 = nutrient uptake in aboveground crop biomass with no nutrient applied; Units are not shown in the table since the expressions are ratios on a mass basis and are therefore unitless in their standard form. P and K can either be expressed on an elemental basis (most common in scientific literature) or on an oxide basis as P_2O_5 or K_2O (most common within industry).

The difference method is commonly used to measure short-term and long-term phosphorus use efficiency in agronomic studies, either using the difference in yield between the fertilized and unfertilized treatments (agronomic efficiency $AE=(Y-Y_0)/F$ in Table 3) or the difference in P uptake between the fertilized and unfertilized treatments (apparent recovery or use efficiency $RE=(U-U_0)/F$). The P supply and yield of the unfertilized control will have a large effect on the efficiency calculated by these difference methods. In a severely P deficient soil, yield and P recovery will be low on the unfertilized soil and both yield, and P uptake will increase to a large extent with P application, other limiting factors being excluded, and the calculated efficiency will be high. In contrast, if the study is conducted on soils that are high in available P, there will be little or no yield response to P and the calculated efficiency will be low. Therefore, the

measured P efficiency will be largely dependent on the amount of plant-available P in the unfertilized soil. In addition, the P recovery in the crop is directly proportional to crop yield, which will be affected by a broad range of factors other than P availability. Crop type and genetics, rotation, rainfall, daylength, salinity or other soil constraints, presence of other nutrients, crop disease, weed competition, tillage management, seeding data and other environmental and management practices will influence crop yield and P uptake. Efficiency of P use will be low if crop yield is reduced due to factors unrelated to P availability.

The balance method ($PNB=U_H/F$ in Table 3) has been proposed recently as a method of considering the long-term residual benefit of P fertilizer (Johnston et al. 2014; Syers et al. 2008). In this, the uptake of P by the crop is divided by the amount of P applied and converted to a percentage. Considering PUE in this way relies on the assumption that the fertilizer P not used by the crop will remain in the soil in a form that can remain available to the plant in the short- or long-term. The P that is taken up by the plant in any year is the combination of P from the fertilizer applied that year plus P that is taken up from the soil reserves. A reliable assessment of P fertilizer efficiency using the balance method requires a long-term data set where P inputs and removals are measured annually for many years. The long-term efficiency of P fertilizer measured using the balance method is normally significantly greater than the 25% value often cited as the efficiency in the year of application and can approach 90% (Syers et al. 2008). However, the balance method assumes that all residual P in the soil results from previous fertilizer application, ignoring the naturally occurring P in the soil, which will lead to an over-estimation of PUE, especially if the natural P reserves are substantial (Chien et al. 2011; McLaughlin et al. 2011).

The balance method was used to evaluate the long-term recovery of P fertilizer in the long-term cropping study at Swift Current, SK that was described previously (Selles et al. 1995). Inputs exceeded removal in the treatments where P fertilizer was added. In the P-fertilized treatments, P removal in the grain increased linearly with the P applied. Fertilizer P accumulated in the soil primarily in plant-available forms (Liu et al. 2015; Selles et al. 2011). Changes in Olsen-P in the long-term study were directly proportional to the P balance in the treatment, with a change in P balance of 6 lb P/acre (14 lb P_2O_5/acre) producing a change of 1 lb/acre (0.5 ppm) in Olsen P (Selles et al. 2007). Efficiency calculated using the balance method in the 24 years of fertilization in this study averaged from about 50 to 65%, with the higher values occurring where both N and P were applied. When P fertilizer input was halted and crops were grown for 12 years on the previously fertilized soils without any additional P addition, total P recovery (calculated as 100*(total P removed in the grain/total P applied during the duration of the study)) was 105% of the initial P application on the NP systems and 90% in the P only system. Recovery of residual P was lower on treatments where yields were limited by N deficiency. Therefore, where P fertilizer additions are not lost through erosion or water movement, the P can remain in a plant-available form for many years.

The balance method is also useful in a long-term sustainability management system, where soil P is managed towards a critical P soil test level and then maintained by balancing P inputs with removal. The balance method calculates the P removed in the crop as a percentage of the P

applied as fertilizer. If the value is less 100%, P will be building in the soil, apart from any other pathways of permanent P loss. If the P is more than 100%, the P in the soil will be depleted. If the soil reserves are to be maintained or built and not depleted, they must be replenished through inputs from fertilizers or other P sources.

Gaps in Knowledge

More information is needed on:
- the dynamics of organic soil P and its contribution to plant-available P and to environmental P losses on the Northern Great Plains.
- evaluation of varying formulations, additives and coatings of P fertilizer, to improve short-term availability for crops. In particular, fertilizer products, additives or coatings that match the release of P into the soil solution with the rate of depletion by root uptake could reduce retention of P by soil and increase fertilizer use efficiency.
- the long-term efficiency of fertilizer P applications on different soils and environments, as well as the soil test P levels that indicate the agronomic, economic and environmental optimum overall, background P fertility in various cropping systems. Further information from new or continuing long-term experiments would help to clarify these issues.

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