6.0 Phosphorus Fertilizer Sources, Additives, and Microbial Products

Key Messages:

- Phosphorus fertilizer sources must provide available orthophosphate ions in the solution for plant uptake as required to optimize crop growth.
- Phosphorus fertilizers will react with soil constituents to influence the availability of the fertilizer P to the plant.
- Monoammonium phosphate (MAP, e.g., 11-52-0) is the most popular source of P fertilizer used on the Northern Great Plains, due to its high availability under high pH conditions, while ammonium polyphosphate (APP, e.g., 10-34-0) is a common and readily available fluid P source. Both sources capitalize on the benefits of modest amounts of ammonium-N in their formulation, which increases P crop uptake of P, without a high risk of toxicity when placed in the seed-row.
- Novel P fertilizer formulations, additives, coatings or use of microbial products have generally not shown increased effectiveness over MAP and APP under field conditions on the Northern Great Plains.
- Use of reclaimed P from wastewater streams as fertilizer products is beneficial for “closing the loop” to recycle P within the food system, lengthen the lifespan of P reserves and reduce negative environmental impacts of wastewater P loading to surface water.

Summary

Phosphorus fertilizer sources should provide available phosphate to the plant as required to optimize growth. Plants use orthophosphate ions from the soil solution, so fertilizer materials must dissolve before they become plant-available. As the fertilizer P dissolves and moves into the soil solution, it initiates a series of reactions with calcium and magnesium in neutral to alkaline soils and with iron and aluminum in more acid soils to form increasingly less soluble compounds. The reaction of phosphate with soil constituents will influence the volume and nature of the reaction zone around the fertilizer granule and the ability of the plant to access the fertilizer P. Fertilizer source will also interact with the plant to affect rooting and rhizosphere chemistry. The effectiveness of various fertilizer sources will be affected by the initial content and release of plant-available P, by the type and speed of reactions of the soluble P with soil constituents, and by interactions with the plant rhizosphere.

Phosphate rock is the original source for production of most agricultural fertilizers and contains a range of apatite minerals. Phosphate rock is relatively insoluble, but its solubility and effectiveness as a fertilizer varies, depending on its composition and particle size. Sedimentary forms of phosphate rock tend to be more soluble than igneous sources, due to their chemical composition and finer particle size. Solubility of rock phosphate decreases with increasing soil pH and calcium content, so its availability is particularly low on the high pH, calcareous soils that commonly occur on the Northern Great Plains and it is rarely used as a fertilizer in conventional farming in this region. Rock phosphate use is more common in organic farming

because it is considered a permissible fertilizer source, while other more soluble phosphate fertilizers are prohibited.

The common commercial phosphorus fertilizers are produced from rock phosphate that is treated with acid to increase its solubility. Impurities are removed through beneficiation and the ore is ground and reacted with acid to form phosphoric acid that is used directly or more commonly as a step in the production of other less corrosive products. The first improved phosphate fertilizer produced was single superphosphate (SSP), which dates to a patent issued in 1845. Both SSP and triple superphosphate (TSP) are soluble and contain monocalcium phosphate but TSP has a higher phosphate analysis of approximately 40 to 46%, as compared to 18 to 20% for SSP.

Monoammonium phosphate (MAP, e.g., 11-52-0) is the most common form of phosphorus fertilizer used on the Northern Great Plains. The chemical analysis is $NH_4H_2PO_4$, with the P present as orthophosphate. MAP is a highly water-soluble, granular form of P that provides both ammonium and phosphate ions for plant uptake, containing about 10-12% N and 48 to 61% phosphate. The solution around the fertilizer granule is moderately acidic, which will increase the availability of the phosphate on neutral to high pH soils. MAP also contains ammonium ions that increase crop uptake of phosphate by decreasing pH in the rhizosphere and reducing precipitation of phosphate, as well as by encouraging root proliferation in the fertilizer reaction zone.

Diammonium phosphate (DAP, e.g., 18-46-0) contains from 18 to 21% N and from 46 to 53% phosphate with the chemical analysis $(NH_4)_2HPO_4$. As with MAP, the phosphate in DAP is in the form of orthophosphate and it contains ammonium that can improve P uptake by plants. While DAP has a higher concentration of N than does MAP, it has a disadvantage on calcareous soils because its solution pH is higher than that of MAP. The high pH of DAP and its high ammonium content create a high solution concentration of ammonia that can lead to toxicity if too high a rate is placed too close to the seed-row. The higher pH of DAP as compared to MAP may also make it less plant-available on calcareous soils but more available on acid soils. Movement of DAP away from the fertilizer granule is less than with MAP making it a less effective fertilizer source especially on calcareous soils.

The most common fluid phosphate fertilizer on the Northern Great Plains is **ammonium polyphosphate (APP)**, which provides both polyphosphate and orthophosphate forms of P. The analysis of ammonium polyphosphate is usually 10-34-0 or 11-37-0. As with MAP and DAP, the presence of ammonium in the fertilizer will increase the P availability. Plants take up P as orthophosphate but because enzymes in the soil rapidly convert polyphosphates to orthophosphate, the polyphosphate in APP is quickly available to the crop. In some situations, the efficacy of APP may be greater than granular fertilizer forms because it is applied in a fluid form. Research in Australia has shown greatly improved efficiency by using fluid formulations such as APP or even dissolved MAP solutions instead of dry granular fertilizer. With fluid sources, the fertilizer was not precipitated as rapidly as with granular forms, and the size of the reaction zone was larger, increasing the fertilizer availability. However, this benefit has not been observed consistently in trials in the Northern Great Plains and may be greater on the very dry, highly calcareous soils in Australia than on the soils in this region.

Fertilizer formulation can influence P availability. Blending phosphate with ammonium and sulphate can increase the solubility and mobility of phosphate in calcareous soils. A homogenous blend of monoammonium phosphate, ammonium sulphate and elemental sulphur formulated in a single granule is marketed with the idea that acidification of the reaction zone during oxidation of the elemental sulphate and the presence of sulphate ions may increase the availability of the MAP, although field studies have not shown a significant benefit in P availability over traditional MAP.

Fertilizer coatings and additives are being marketed to improve the effectiveness of fertilizer P. A maleic-itaconic co-polymer additive can be applied to either granular or liquid P fertilizer with the aim of sequestering antagonistic metals in the soil around the fertilizer granule to reduce the tie-up of phosphorus. However, field studies in the Northern Great Plains have not generally shown a benefit from this mechanism.

Polymer coatings on granules may control the release of P into the soil solution to slow the formation of sparingly soluble P compounds and increase the supply of crop-available P. Polymer-coated P compounds are not commercially available, but in field trials they performed similarly to uncoated products in promoting yield, with the benefit of producing significantly lower risk of seedling damage.

A range of reclaimed and by-product P compounds, including struvite, have been evaluated as fertilizer sources. These are attractive because use as a fertilizer can recycle P that would otherwise end up in the waste stream. Most of these compounds would serve as a slow-release P source, with effectiveness depending on the long-term solubility.

Humic acids are not direct sources of P but have been investigated for their ability to slow the precipitation of phosphate on calcareous soils. While humic acid supplements have shown promise in laboratory incubation studies, benefits have not been as consistent in pot or field studies, possibly because very high rates are needed to be effective.

Two major types of microbial products are marketed in the Northern Great Plains to improve P availability. ***Penicillium bilaiae*** has been sold as an inoculant to improve the availability of soil P. This organism is a fungus that occurs naturally in agricultural soils and is said to improve P availability by secreting organic acids that can solubilize P. Benefits of *Penicillium bilaiae* have been erratic under field conditions and it seems to be unreliable as a method for improving P nutritional status of crops on the Northern Great Plains. **Mycorrhizae** are associations between fungi and the plant root that play a key role in the soil microbial community and are of great importance to a wide range of crop and wild plant species. Mycorrhizal fungi are naturally present in soils and their ability to colonize crops is affected by crop type, tillage, cropping system and P status of the plant. Crops differ in their response to mycorrhizae with canola being non-mycorrhizal while corn and flax are highly mycorrhizal. Mycorrhizal inoculants are commercially used in horticulture and forestry as well as in organic production systems; however, their effectiveness in commercial cropping systems on the Northern Great Plains has been limited. Although mycorrhizae clearly aid in P uptake for many crops the mycorrhizal populations provided in currently available inoculants may not be an improvement over a well-established native population.

Detailed Information

Phosphorus fertilizer sources are selected to provide available forms of P to the plant as required to optimize growth. Plant roots absorb orthophosphate ions that are present in the soil solution, so fertilizer materials must dissolve before they become plant-available. The availability of the P in different P fertilizer sources is therefore directly related to the solubility of each P source, with the most plant-available forms including those that are water-soluble and those that will dissolve in an ammonium citrate solution (Chien et al. 2011). However, the interactions between roots, nutrients and soil may alter the solubility of P fertilizers in the rhizosphere in ways that are not easily measured with traditional chemical analyses.

As the fertilizer P dissolves and moves into the soil solution, it initiates a series of reactions. The phosphate in the soil solution will react with calcium and magnesium in neutral to alkaline soils and with iron and aluminum in more acid soils to form increasingly less soluble compounds (Chien et al. 2011; Racz and Soper 1970; Racz and Soper 1967). The reaction of phosphate with soil constituents will influence the volume and nature of the reaction zone around the fertilizer granule, influencing the ability of the plant to access the fertilizer P (Bertrand et al. 2003; Bertrand et al. 2006; Lombi et al. 2004). The effectiveness of various fertilizer sources will therefore be affected both by the initial content of plant-available P and by the type and speed of reactions of the soluble P with soil constituents.

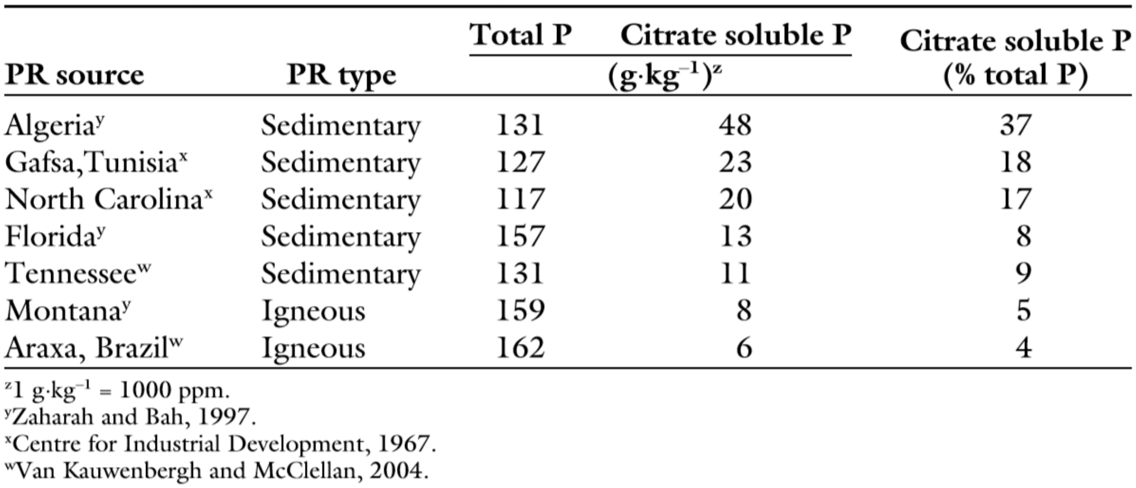
6.1 Traditional Sources of Phosphorus Fertilizer

6.1.1 Phosphate Rock

Phosphate rock is the original source for production of most agricultural fertilizers. Phosphate in rock phosphate is primarily present as apatites that include a range of calcium phosphate minerals ($Ca_5(PO_4)_3X$, where X is an anion such as fluoride). Rock phosphate also contains a range of impurities, including potentially toxic trace metals such as cadmium (Syers et al. 1986). Phosphate rock is relatively insoluble, especially on calcareous soils. However, the solubility of phosphate rock will vary, depending on the composition. The greater the isomorphous substitution of carbonate for phosphate in the structure, the less stable is the crystalline structure and the greater the ease of release of the phosphate into the soil solution for crop uptake (Chien and Menon 1995; Nelson and Janke 2007). Particle size will also influence solubility of rock phosphate, with solubility increasing as particle size decreases. Sedimentary forms of phosphate rock tend to be more soluble than igneous sources, due to both the different chemical composition and particle size (Table 1).

Efficacy of rock phosphate as a fertilizer source is directly related to its solubility, so there can be substantial variation in the fertilizer efficacy of various sources of rock phosphate (Chien and Menon 1995). For example, in studies conducted in Alberta, 17 rock phosphate sources were evaluated under greenhouse conditions for their effectiveness for crop uptake as compared to triple superphosphate (TSP) and monoammonium phosphate (MAP) (Kucey and Bole 1984). The most effective rock phosphate was approximately 88% as effective as TSP in a moderately acidic soil and 68% as effective as TSP in a slightly acidic soil when rock phosphate was added at 10 times the TSP rate, while several rock phosphates had no positive effect on wheat growth or P uptake (Kucey and Bole 1984). Partial acidulation of phosphate rock has been used as a way to increase its solubility and availability (Rajan 1987).

Table 1: Total and citrate-soluble phosphorus (P) concentration in phosphate rock (PR) from various sources (Nelson and Janke 2007).



PR source	PR type	Total P	Citrate soluble P	Citrate soluble P (% total P)
		(g·kg^{-1})[z]		
Algeria[y]	Sedimentary	131	48	37
Gafsa,Tunisia[x]	Sedimentary	127	23	18
North Carolina[x]	Sedimentary	117	20	17
Florida[y]	Sedimentary	157	13	8
Tennessee[w]	Sedimentary	131	11	9
Montana[y]	Igneous	159	8	5
Araxa, Brazil[w]	Igneous	162	6	4

[z] 1 g·kg^{-1} = 1000 ppm.
[y] Zaharah and Bah, 1997.
[x] Centre for Industrial Development, 1967.
[w] Van Kauwenbergh and McClellan, 2004.

Soil characteristics, most notably pH and calcium content, will affect solubility of rock phosphate. Dissolution of apatite follows the following reaction, using fluorapatite as an example:

$$Ca_5(PO_4)_3F + 6H^+ \leftrightharpoons 5Ca^{2+} + 3H_2PO_4^- + F^- \qquad \text{(Lindsay and Moreno 1960)}$$

Since H^+ is an ingredient for the dissolution reaction, increasing the solution concentration of H^+ on the left side of the equation will push the reaction towards dissolution of the rock phosphate, while increasing solution concentration of reactants on the right side of the equation will suppress dissolution. Therefore, a high concentration of H^+ ions, as occurs in acid soils, will increase the solubility of the apatite, so rock phosphate may be beneficial as a P source on acid soils (Choudhary et al. 1996; Choudhary et al. 1994; Ellis et al. 1955; Kucey and Bole 1984). However, high concentrations of calcium (Ca^{2+}), as in calcareous soils, will decrease solubility of rock phosphate, making it much less likely to be an effective P source on high pH, calcareous soils that make up a large portion of the land area on the Northern Great Plains. For example, studies conducted in Saskatchewan showed no increase in barley seed yield when rock phosphate was applied on a P-deficient calcareous soil, while use of triple superphosphate produced a substantial yield increase (Malhi et al. 2014). Calcium ions released from the dissolution of rock phosphate may adsorb to the soil cation exchange, removing them from solution and shifting the equilibrium towards dissolution. Therefore, agronomic effectiveness of rock phosphate may increase with increasing cation exchange capacity (CEC) in soil (Chien and Menon 1995).

Increasing organic matter content may also increase dissolution of rock phosphate, both because of the effects of organic matter on CEC and because the organic matter may form direct complexes with Ca^{2+}, again shifting the equilibrium towards dissolution.

Due to its lack of effectiveness as a phosphorus source, rock phosphate is rarely used as a fertilizer in conventional farming in the Northern Great Plains. Rock phosphate is slightly more commonly used in organic farming systems, because it is considered a permissible organic fertilizer source while other more soluble phosphate fertilizers are prohibited. Organic farming systems may differ somewhat from conventional systems in having more extended rotations, more use of N-fixing legume crops and more use of green manure crops. They also tend to have lower P concentrations in the soil than conventionally farmed fields (Entz et al. 2001). These factors may influence the effectiveness of rock phosphate as a P source.

6.1.1.1 Management to Increase Effectiveness of Rock Phosphate

Effectiveness of rock phosphate as a fertilizer is affected by management practices including tillage, placement, cropping sequence and time between application and crop uptake. Broadcasting and incorporation of rock phosphate will increase the contact between the fertilizer particles and the soil, increasing dissolution. Increasing the time between fertilizer application and crop demand will allow more time for the fertilizer to dissolve and thus increase efficacy. An exception could be on high P-adsorbing soils where the P retention reactions with soil constituents may be more rapid than the dissolution of the P from the rock phosphate (Chien and Menon 1995).

Since the solubility of rock phosphate is highly dependent on pH, factors that influence pH may also influence the solubility and hence the availability of rock phosphate for crop uptake. Lime application will decrease dissolution of rock phosphate by increasing both pH and calcium concentration (Chien and Menon 1995; Nelson and Janke 2007). Conversely, application of acidifying fertilizers such as elemental sulphur with rock phosphate may increase the dissolution and effectiveness of the fertilizer (Stanisławska-Glubiak et al. 2014), although the benefit may be greater on poorly buffered acid soils than on the more highly buffered, higher pH soils common on the Northern Great Plains (Evans et al. 2006).

Rock phosphate may be more effective for long-term supply of P to perennial crops than for use in annual crops, because the slow dissolution of the P over time may be able to supply the needs of the perennial crop over a number of years (Chien and Menon 1995). Also, plant species differ in their ability to access rock phosphate. Buckwheat appears to be particularly effective at accessing rock phosphate, while legumes are intermediate and grasses are relatively ineffective (Fried 1953). Crops that acidify their rhizosphere or that take up large amounts of Ca^{2+} tend to be relatively effective at accessing P from rock phosphate (Bekele et al. 1983; Hinsinger and Gilkes 1995). Studies on an alkaline artificial soil medium showed that lupins secreted H^+ and lowered the pH of the rhizosphere by approximately 2 units compared to the bulk soil, which led to increased solubilization of reactive rock phosphate (Hinsinger and Gilkes 1995).

The use of green manure crops to provide N in organic farming systems may have the additional benefit of mobilizing and releasing P from rock phosphate for the following crops in the rotation. A field study on an organic farm in Ontario examined the effect of residues from a buckwheat (*Fagopyrum esculentum*) green manure (GM) crop grown with an igneous and a sedimentary source of phosphate rock (PR) on soil P supply the following spring (Arcand et al. 2010). Application of a sedimentary phosphate rock application did not increase buckwheat dry matter production but did increase above-ground tissue P concentration. In the following spring, in situ soil P supply and Olsen P were increased in GM residue-applied soils, if the concentration of P in the residue was greater than 2.9 g P kg^{-1}. The quality of the GM residues in terms of P concentration had more influence on P availability than the quantity applied to the soil. However, the change in available P due to the GM application was not large enough to be of agronomic benefit.

Studies on neutral to alkaline soils on organic farms in Montana evaluated the ability of spring pea, buckwheat and yellow mustard grown as green manure crops, compared to summer fallow, to mobilize P from applications of rock phosphate (Rick et al. 2011). Three rates of pelletized rock phosphate were applied in the three green manure crops. The following year, winter wheat was grown. The biomass yields of the green manure crops were not affected by the rock phosphate application, although P uptake was higher with rock phosphate application than in the control. Winter wheat grain yields were not affected by the green manure crops but were approximately 10% higher where P had been applied at the highest rate to the preceding crops. Among the green manure crops, spring pea had about three- to five-fold higher P uptake than mustard or buckwheat, but there was no effect of green manure crop on wheat, indicating that the extra P in the pea biomass was not an advantage, possibly because the pea had higher water use than the other crops. It may also be that the P from the crop residue was immobilized rather than mineralized and therefore might be of long-term rather than short-term benefit. On these neutral to alkaline soils, the phosphate rock was not highly available, nor did the preceding crop improve availability, compared to summer fallow.

The P-solubilizing fungus *Penicillium bilaiae* (also known as *Penicillium bilaii* or *Penicillium bilaji)* may increase the availability of rock phosphate, presumably by effects on soil acidity (Takeda and Knight 2006; Takeda and Knight 2003). In Alberta studies on a neutral pH soil, addition of *Penicillium bilaiae* with rock phosphate and straw increased P uptake and yield of wheat in greenhouse and field studies and of bean in greenhouse studies (Kucey 1987). Mycorrhizal fungi, which are naturally present in soils, were needed to optimize the benefit of the system. Similarly, in growth chamber studies using Saskatchewan soils, *Penicillium bilaiae* was able to enhance the solubility of rock phosphate (Takeda and Knight 2006; Takeda and Knight 2003). In unbuffered medium, the addition of *Penicillium bilaiae* increased the release of P from rock phosphate by about 5-fold, while in buffered medium, the increase was approximately 50-fold. Buffering the media increased the organic acid production. The increase in organic acid production was also related to a decrease in Ca concentration in the media, suggesting that the oxalate and citrate complexed with the Ca, reducing the reaction of P and Ca and hence increasing P solubilization.

6.1.2 Commercial Phosphate Fertilizers

The common commercial phosphorus fertilizers are produced from rock phosphate that is treated to increase its solubility. Normally, impurities such as sand, clay, carbonates, organics and iron oxide are initially removed from the rock phosphate ore through a process of beneficiation. The beneficiated ore is then ground and reacted with acid to form more soluble, plant-available commercial fertilizers. Phosphoric acid (H_3PO_4) is formed by reacting rock phosphate with sulphuric acid (Follett et al. 1981). The impure phosphoric acid contains gypsum that must be filtered out. The phosphoric acid is then heated to drive out water and increase the P concentration. High quality phosphoric acid can be used directly as a liquid fertilizer source (0-55-0), although its corrosive nature can cause problems in handling. It is more commonly used in the production of other fertilizer materials.

6.1.2.1 Dry Granular Phosphate Fertilizers

Single superphosphate (SSP, e.g., 0-20-0-10) is also known as normal superphosphate (NSP) or ordinary superphosphate (OSP) and was the first improved phosphate fertilizer produced, dating back to a patent issued in 1845 (Follett et al. 1981). Single superphosphate is produced by blending ground, beneficiated rock phosphate with sulphuric acid of about 60-72% concentration and allowing the mixture to react for several weeks until the apatite in the rock is converted to monocalcium phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$) and gypsum. The resulting fertilizer is low analysis, ranging from about 18 to 20% P_2O_5, which makes it costly to transport per unit of available P. Single superphosphate is reasonably soluble and serves as a source of available S as well as P, but is not a common fertilizer source in the Northern Great Plains.

Triple superphosphate (TSP, e.g. 0-45-0) has a higher phosphorus concentration than SSP, containing about 40 to 46% P_2O_5. As with SSP, the P in TSP is in the form of monocalcium phosphate, but TSP does not contain gypsum. The TSP is produced by reacting rock phosphate with phosphoric acid. It is highly water soluble and is agronomically similar in availability to SSP.

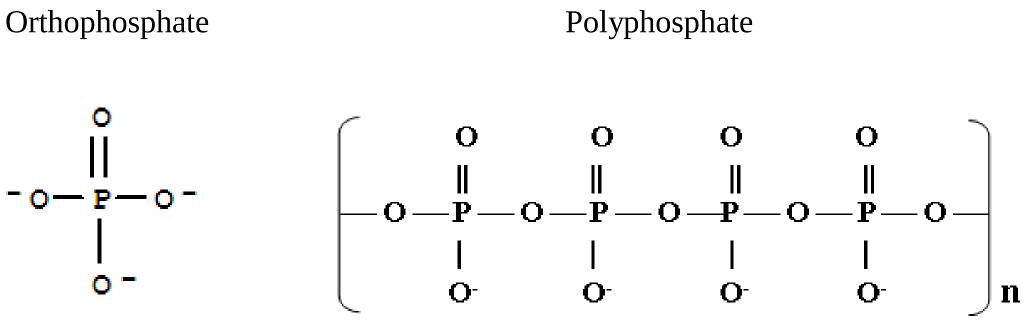
Monoammonium phosphate (MAP, e.g., 11-52-0) is the most common form of phosphorus fertilizer used on the Northern Great Plains. It is produced by reacting a 1:1 ratio of ammonium and phosphoric acid and solidifying the resulting slurry into granules. Monoammonium phosphate has an analysis of between 48 and 61% phosphate and 11 to 12% nitrogen, with the chemical analysis $NH_4H_2PO_4$ (Follett et al. 1981). The P is present in the form of orthophosphate (Figure 1). MAP is highly water soluble and provides both ammonium and phosphate ions for plant uptake. The solution around the fertilizer granule is moderately acidic, which will increase the availability of the phosphate on neutral to high pH soils. MAP also contains ammonium ions, which increase crop uptake of phosphate, by decreasing pH in the rhizosphere during root uptake and reducing precipitation of phosphate (Miller et al. 1970). Specifically, the uptake of ammonium by plant roots leads to the expulsion of H^+ that lowers pH in the rhizosphere and can reduce the formation of $CaHPO_4.2H_2O$ near the root surface. Ammonium has also been shown to increase root proliferation in the fertilizer reaction zone which would increase the ability of the plant to absorb the applied P (Miller and Ohlrogge 1958).

As a result of these attributes, monoammonium phosphate is well-documented as being superior to triple super phosphate for P fertilization of crops in the Northern Great Plains. For example, in 75 site-years of field trials on summer fallow fields in Saskatchewan from 1939 to 1943, the wheat yield response to monoammonium phosphate was 30% greater than to triple super phosphate (Mitchell 1946). Although these studies were not balanced for the N applied in the MAP, N responses would have been unlikely on summer fallow fields, given the large amounts of N mineralization in these soils at this time.

Diammonium phosphate (DAP, e.g., 18-46-0) is produced in a similar manner to monoammonium phosphate, but a 2:1 ratio of ammonium to phosphoric acid is used, resulting in a product containing from 18 to 21% N and from 46 to 53% phosphate with the chemical analysis $(NH_4)_2HPO_4$. As with MAP, the phosphate in DAP is in the form of orthophosphate (Figure 1) and ammonium is present in the fertilizer which can improve P availability to plants. While DAP has a higher concentration of N than does MAP, it has a disadvantage on calcareous soils because its solution pH is higher than that of MAP. The high pH of DAP and its ammonium content leads to a high solution concentration of ammonia that can lead to toxicity if too high a rate is placed too close to the seed-row. The toxicity of DAP is greater than that of MAP at a given P concentration and the effect is accentuated by $CaCO_3$ (Allred and Ohlrogge 1964). The higher pH of DAP as compared to MAP may also make it less plant-available on calcareous soils but may make it more available on acid soils (Bouldin and Sample 1959). In short-term growth chamber studies on a calcareous Saskatchewan soil, uptake of P by oats was greater from MAP than from DAP (Beaton and Read 1963). In studies using ^{32}P-labelling in nine Manitoba soils, the movement of P away from the fertilizer pellet was greater with MAP than DAP (Lewis and Racz 1969). The extent and rate of phosphorus movement was greater in noncalcareous than calcareous soils for both sources of P when added as a pellet. The high pH and large amounts of calcium and magnesium found in the soil solutions of the calcareous soils resulted in a rapid precipitation of the added phosphorus very close to the pellet, restricting P movement.

6.1.2.2 Fluid Fertilizers

Ammonium polyphosphate (APP, e.g., 10-34-0) is the most common fluid phosphate fertilizer on the Northern Great Plains. APP contains both polyphosphate and orthophosphate forms of P (Figure 1). The first stage in the production of ammonium polyphosphate is the dehydration of phosphoric acid to form superphosphoric acid (Follett et al. 1981; IPNI 2010). The superphosphoric acid is then reacted with ammonia and water to form ammonium polyphosphate. Ammonium polyphosphate contains about 70-75% of its P in the form of polyphosphate, with the remainder being orthophosphate. The polyphosphates are polymers of orthophosphate, with most being in the form of pyrophosphate, which contains two linked phosphate molecules. However, longer phosphate chains will also be present. The analysis of ammonium polyphosphate is usually 10-34-0 or 11-37-0. The presence of ammonium in the fertilizer will increase the P availability as discussed in the section on MAP.



Orthophosphate

Polyphosphate

Figure 1: Linear structure of orthophosphate and polyphosphate

Plants take up P only in the orthophosphate form and are unable to take up intact polyphosphates. However, polyphosphates are quickly hydrolyzed to orthophosphate by chemical and biochemical reactions in the soil, with the rate of conversion influenced by factors such as soil pH, temperature and moisture content (Dick and Tabatabai 1986; Racz and Savant 1972). Incubation studies using two Manitoba soils showed that hydrolysis of polyphosphates was very rapid (Chang and Racz 1977). Hydrolysis rate of pyrophosphate and tripolyphosphate increased linearly with increased temperature at temperatures of 5 to 50° C. About 40 to 70% of the added polyphosphate hydrolyzed in 120 h at 5° C, whereas about 80 to 95% hydrolyzed in 120 h at 35° C. Increases in incubation temperature also increased the total amount of added polyphosphate hydrolyzed at the end of the incubation period. Hydrolysis was slowed by retention of the added polyphosphate by soil constituents. Polyphosphate hydrolysis was greater in the noncalcareous Newdale soil than in the calcareous Lakeland soil. Increasing the amount of polyphosphate applied to the soils increased the rate of orthophosphate production. Hydrolysis was rapid both at field capacity and under flooded conditions (Racz and Savant 1972). The rates of polyphosphate hydrolysis and total amounts of polyphosphate hydrolyzed shortly after application would normally be great enough to supply plants with their P requirement and would not constrain the early season crop uptake of P (Chang and Racz 1977; Dick and Tabatabai 1986; Khasawneh et al. 1979; McBeath et al. 2006). Therefore, there does not seem to be evidence that increasing the proportion of orthophosphate in fluid formulations increases the nutritional value of the P fertilizer.

An additional advantage to APP is its suitability for uniform blending with other nutrients. Polyphosphates are able to form metallic-cation multivalence chelate coordination complexes that are more soluble than the salts and oxides of the metals, thus increasing the concentration of micronutrient that can be present in the fertilizer solution (Cichy and Folek 2005; Havlin et al. 2014). Therefore, using ammonium polyphosphate can act as an effective carrier for trace elements such as zinc, by increasing the amount of nutrient that will remain in solution. Increasing the volume of solution that is used for micronutrient application by blending the micronutrient with the macronutrient solution will also increase the uniformity of micronutrient distribution, compared to applying the micronutrient separately.

The efficacy of APP may be influenced in part by the fact that it is applied in a fluid form. Research in Australia has shown greatly improved efficiency by using fluid formulations such as APP or even dissolved MAP solutions instead of dry granular fertilizer (Bertrand et al. 2003; Bertrand et al. 2006; Holloway et al. 2001; Lombi et al. 2004; Lombi et al. 2005; McBeath et al. 2005; McBeath et al. 2007). Commercial fluid APP or applications of MAP or DAP in dissolved form were more effective than dry granular products in increasing yield on highly calcareous alkaline soils in field and pot studies (Holloway et al. 2001). On the dry, calcareous soils used in these studies, precipitation of P with Ca was rapid when the dry fertilizer forms were used, reducing P availability. More detailed evaluations showed that the P from the fluid forms diffused further from the site of application than did the P from the granular forms (Bertrand et al. 2006; Lombi et al. 2004; Lombi et al. 2005). The proposed reason for the improvement in effectiveness with fluid fertilizer sources was that soil moisture moving along the osmotic gradient towards the dry fertilizer granule carried Ca that rapidly precipitated the P, limiting the size of the fertilizer reaction zone and the ability of the plant to access the P. With fluid sources, the fertilizer was not precipitated as rapidly, and the size of the reaction zone was larger, increasing the fertilizer availability. In laboratory studies that compared the lability, solubility and mobility of three P products applied in a fluid form and three applied in a granular form on two calcareous and one alkaline non-calcareous soils, between 9.5 and 18% of the P initially present in the dry fertilizer granules did not diffuse into the surrounding soil over a five-week period (Lombi et al. 2005). The degree of granule dissolution was independent of the soil type. In contrast, P solubility, lability and diffusion were significantly greater when fluid products were applied to the calcareous soils, but not to the alkaline noncalcareous soil. Benefits in availability were also seen when MAP was applied as a dissolved solution rather than as a granule (Lombi et al. 2004).

In contrast to the studies in Australia, large differences between the behaviour of fluid versus granular sources have not consistently been observed in the Northern Great Plains. Field studies near Brandon, MB showed that MAP increased both dry matter yield and P uptake more than 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 between the response of spring wheat yield to APP or MAP (Figure 2) (Grant et al. 2007). In other field studies in Manitoba, 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). The effect of two liquid ammonium orthophosphates (6–24–6 and 9–18–9), APP and MAP on plant-available phosphate was assessed over time in laboratory studies conducted using soils collected from Manitoba (Goh et al. 2013). The water-soluble and bicarbonate-extractable phosphate was increased in the first few days after application by all four sources as compared to the control. The liquid products produced greater water-soluble and sodium bicarbonate-extractable P concentrations than MAP until the second day of incubation, while the 9-18-9 ammonium orthophosphate produced higher concentrations than MAP until day 4. However, the differences among the products disappeared quickly and the available P was similar among the products after 4 days of incubation. These brief, transient differences in availability among the different fertilizer forms would be unlikely to have a major effect on crop growth and final yield. The difference between the results of studies with fluid P in Manitoba as compared to Australia may be because the Australian soils were much more highly calcareous than are commonly found on the Northern Great Plains and the growing conditions in that region of Australia tend to be drier.

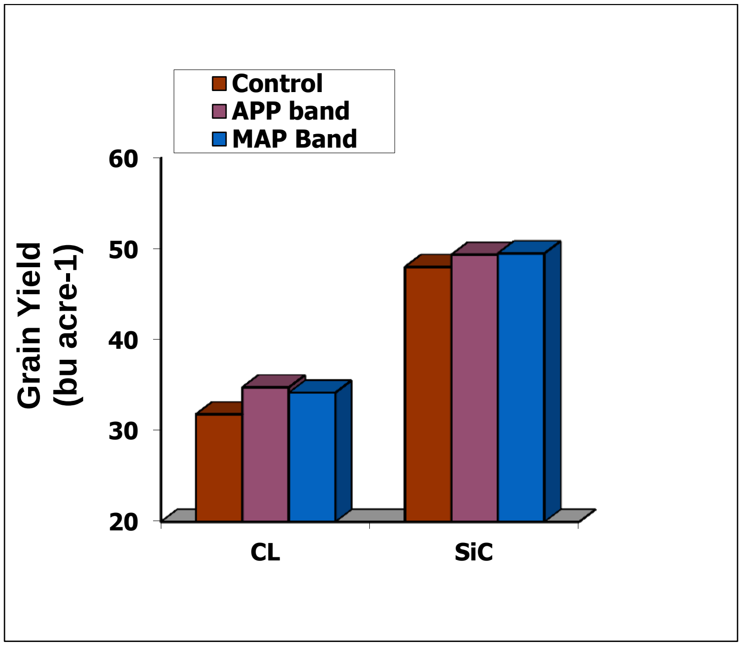


Figure 2. Effect of banded ammonium polyphosphate (APP) as compared to monoammonium phosphate (MAP) on grain yield of wheat on two Manitoba soils (Grant et al. 2007). Phosphorus response at the CL site was significant ($p<0.0382$) while differences between APP and MAP were never significant.

6.2 Fertilizer Special Formulations, Additives and Coatings

Crop uptake of phosphate from a fertilizer reaction zone is related to the concentration of phosphorus in the soil solution and the amount of roots present to access the fertilizer (Claassen and Barber 1976). Therefore, uptake can be increased by increasing the solubility of the fertilizer, the size of the reaction zone or proliferation of roots in the zone of high P concentration around the fertilizer granule. Phosphate ions in the soil solution will diffuse away from the area of high concentration around the fertilizer granule and interact with the cations in the solution. The distance that the phosphate ions move, and therefore the size of the reaction zone, will be affected by the type and concentration of ions that react with the diffusing phosphate ions. Adding products with the phosphate fertilizer to alter the solution chemistry and slow the soil reactions with the phosphate ion could therefore improve the availability of the fertilizer by increasing solution P concentration and/or increasing the volume of the reaction zone. In addition, as mentioned previously, some ions such as ammonium may increase root proliferation and/or lead to H^+ exudation and acidification of the rhizosphere, further increasing the ability of the plant to access fertilizer P.

Elemental S - Studies in the early 1950s looked at the effect of adding elemental S to MAP and dicalcium phosphate-nitrate to acidify the area around the fertilizer and potentially slow soil reactions with P (Mitchell et al. 1952). While growth chamber studies on a soil with pH of 7.4 showed a benefit in P availability from both P sources due to the addition of elemental S, field study results on soils with pH values of 8.4 and 7.2 did not. The authors speculated that oxidation of the elemental S was too slow under the cool soil conditions in the field to have an effect or that there were not enough S-oxidizing bacteria available to convert the elemental S rapidly. In a subsequent study, they added S-oxidizing bacteria to dicalcium phosphate-nitrate, which increased S oxidation and also the availability of the P (Mitchell et al. 1952). The action of S-oxidizing bacteria on elemental S in the fertilizer doubled the availability of dicalcium phosphate-nitrate, but even this more effective mixture of S and dicalcium phosphate nitrate was only about 30 per cent as effective as monoammonium phosphate (11-48-0) in supplying phosphorus to cereals under the conditions of the experiment. The MAP was much more effective than any of the calcium-based phosphate sources.

Non-Phosphate Salts - Many subsequent studies evaluated the effect of various non-phosphate salts on the solubility and movement of fertilizer P. In laboratory studies, movement of phosphate in columns containing a Ca^{2+}-saturated resin-sand mixture was reduced when KH_2PO_4 was applied with KCl (Akinremi and Cho 1993). The mobility and solubility of the applied P was reduced by Ca^{2+} ions displaced from soil exchange sites by the K^+ (Akinremi and Cho 1991a; Akinremi and Cho 1991b; Akinremi and Cho 1993). The decrease in mobility of P with KCl addition on high pH soils fits with models in other studies (Barber and Ernani 1991; Ernani and Barber 1991). Laboratory column studies also showed that the addition of $(NH_4)_2SO_4$ and $MgSO_4$ with MCP significantly increased P diffusion whereas $(NH_2)_2CO$ (urea) had little or no effect (Kumaragamage et al. 2004). Application of urea initially increased soil solution pH, favoring precipitation of calcium phosphate. In contrast, the sulphate ions competed with P for Ca, reducing the formation of Ca phosphates and increasing P solubility and mobility. Other column studies using cation exchange resin-sand mixtures containing $CaCO_3$ to simulate calcareous soils showed that adding ammonium sulphate (AS) or potassium sulphate (KS) salt to MAP or monopotassium phosphate reduced the pH of the system at a greater distance from the site of application than for the phosphate fertilizers applied alone (Olatuyi et al. 2009a; Olatuyi et al. 2009b). Adding AS or KS to the MAP increased the concentration of water-soluble P in the reaction zone by 43% and 21% respectively, while with monopotassium phosphate, the corresponding increases were 48% and 41%. The AS was likely better than the KS at enhancing P solubility because the NH_4^+ ion would replace less exchangeable Ca^{2+} than would the K^+, leaving less Ca^{2+} in the soil solution to react with the phosphate ions. In addition, combining sulphate sources with MAP could increase the solubility and mobility of phosphate in calcareous soils by pH reduction and competition between sulphate and phosphate ions for precipitation with soil Ca. In growth chamber studies, seed-placement of various forms of soluble S fertilizer sometimes slightly increased P availability as measured with PRS probes or by canola uptake, but the effect was small and not always significant (Ahmed et al. 2017).

Homogeneous Blends - A homogenous blend of monoammonium phosphate, ammonium sulphate and elemental sulphur formulated in a single granule is available on the Northern Great Plains. The product contains 13% N, 33 % plant-available phosphate, plus 7.5% S as sulphate and 7.5% S as elemental S, forms of S which may improve P availability on calcareous soils for reasons discussed previously. In addition, the presence of ammonium may also enhance phosphate availability through both chemical and biological mechanisms, as discussed previously (Miller et al. 1970; Miller and Ohlrogge 1958). However, there appears to be little benefit under field conditions for the novel product in terms of enhanced P availability, compared to conventional MAP. Field studies on five sites in Manitoba comparing the homogenous product to MAP determined that the midseason uptake of phosphate by wheat and canola showed a tendency to be slightly higher, numerically, with the novel product, but the differences were not statistically significant (Kroeker 2005). In growth chamber studies, P uptake was increased by either blending MAP and AS or by the use of the homogenous product, with the effect presumably being due to a crop response to the added sulphate-S in otherwise S-deficient soil (Kroeker 2005). Over a two-crop sequence in the growth chamber, total P uptake for both crops tended to be slightly higher, numerically, for the homogenous product than for MAP + AS, but the effects were not statistically significant. However, P uptake was higher with both the homogenous product and MAP +AS than with MAP alone, likely due in large part to an S response of the crops that led to greater yield and nutrient uptake. In studies conducted in Quebec, Ontario, Manitoba and Alberta, canola yield on P-deficient sites was similar with the homogenous product and MAP + AS, indicating that both P fertilizers were good sources of phosphate for canola (Grant 2013). The homogenous product led to less seedling damage when seed-placed with canola than did a blend of MAP and AS that provided the same ratio of total nutrients applied, without adjusting for the difference in availability between the forms of S in these two treatments (Grant 2013; Grenkow 2013; Grenkow et al. 2013).

Maleic-Itaconic Co-Polymer Additive - A maleic-itaconic co-polymer additive is available that can be applied to either granular or liquid P fertilizer. It is designed to sequester antagonistic metals in the soil around the fertilizer granule to reduce the retention of phosphorus and keep it in a plant-available form throughout the growing season. The suggestion is that the copolymer reduces P-binding by soil exchangeable Ca, Fe, and Al by reacting with these ions to form Ca-, Fe-, or Al-maleic and itaconic acids, thus reducing the formation of less soluble Ca, Fe or Al phosphates. However, calculation of the equilibrium constants for the Ca phosphates as compared to the maleic or itaconic acid complexes indicate that the product would not block formation of the phosphate compounds on either acid or high pH soils (Chien and Rehm 2016). The equilibrium constants of the various reactions of P with maleic acid and itaconic acids as well as with $CaHPO_4{\cdot}2H_2O$ (DCPD), an initial reaction product of soluble P fertilizers in calcareous soils, indicate that precipitation of P to form DCPD would occur before chelation with the copolymer (Chien and Rehm 2016). These theoretical calculations are in line with laboratory assessments of effects of the products on availability and mobility of P fertilizers (Degryse et al. 2013).

Studies using model systems showed that dissolved PO_4 concentrations in aqueous suspensions of ferrihydrite and poorly crystalline aluminium hydroxide (pxl-$Al(OH)_3$) at pH 6.2 increased with increasing additions of PO_4 and the maleic-itaconic co-polymer with greater effects shown for pxl-$Al(OH)_3$ (Doydora et al. 2017). The (hydr)oxides evaluated are models of high-capacity phosphate sorbents in soils. The primary mechanism for enhanced PO_4 solubilization by the co-polymer would be competitive adsorption between the co-polymer carboxyl groups and $H_2PO_4^-$ for either ferrihydrite or pxl-$Al(OH)_3$. A greater enhancement of dissolved PO_4 by the co-polymer in these model systems at higher PO_4 inputs suggests that a co-application of fertilizer and co-polymer that concentrates both materials in a smaller soil volume (e.g., a banded fertilizer application) would enhance plant-availability of P. However, the concentrations of the co-polymer used in these model systems were orders of magnitude higher than the current application rates recommended in the field.

Several studies on corn, winter wheat and potatoes conducted in the United States as well as studies with wheat in Alberta report benefits of using co-polymer with band-applied P (http://www.chooseavail.com/research.aspx, accessed December 20, 2018). Field studies conducted with irrigated corn in Kansas showed increased yield and P ear leaf concentration when the co-polymer was included to a starter fertilizer as compared to the starter treatment alone (Gordon and Tindall 2006). However, other independent field studies show no benefit from treatment with the co-polymer (McGrath and Binford 2012). Studies in Kansas on corn and winter wheat showed no benefits of using the co-polymer, even on sites where a P response occurred (Ward 2010). In two 3-yr trials in Alberta on wheat that included an unfertilized control and three rates of seed-placed P (13, 26 and 40 lb P_2O_5/acre) applied as MAP with or without the co-polymer and arranged in a randomized complete block design with six replications, neither a significant effect of treating MAP with the co-polymer nor a significant interaction between the co-polymer treatment and rate of P on the yield of wheat and P uptake was observed (Karamanos and Puurveen 2011). Studies on two soils in Manitoba showed no advantage of using the co-polymer as compared to untreated MAP or polymer-coated MAP (Grant 2011). A meta-analysis of published and unpublished studies on the co-polymer showed no benefit of the product (Chien et al. 2014). However, a subsequent meta-analysis including studies conducted up to and after those used by Chien et al. (2014) showed a benefit of the co-polymer under conditions of low soil test P, extreme pH and low rate of P application (Hopkins et al. 2018).

Polymer Coatings - Polymer coatings on granular P fertilizer may control the release of P into the soil solution to slow the formation of sparingly soluble P compounds and increase the supply of crop-available P (Grant and Wu 2008). Controlled release MAP, DAP, and APP were simulated under greenhouse conditions by making small, periodic additions of fertilizer P (Nyborg et al. 1998). The plants rapidly depleted the supplied P from the soil solution, minimizing the potential for precipitation. Where the P was gradually supplied to the plant over several weeks, P retention was reduced, and P uptake increased as compared to a single application of P at the start of the growing period. In an evaluation of an experimental polymer coated MAP, release of P from coated MAP was slower in soil than in water, decreased markedly with increasing thickness of polymer coating on MAP, and increased with increasing temperature (Zhang et al. 2000). Coating MAP improved P uptake, fertilizer efficiency and barley dry matter yield, but the performance of DAP was not consistently improved (Pauly et al.

2002). Under field conditions in Manitoba, both coated and uncoated MAP were effective at increasing spring wheat yield but there was no significant benefit of using coated MAP as compared to uncoated MAP (Grant 2002). Growth chamber studies with 10 different crops showed that use of controlled release polymer coated MAP increased the seedling safety so that rates of 70 lb P_2O_5/acre could be safely seed-placed as compared to about half of that for the uncoated product (Schoenau et al. 2007). Under field conditions on two sites in Manitoba, seedling damage occasionally occurred with agronomic rates of seed-placed MAP in canola, but not with a polymer coated MAP (Grant 2011). In greenhouse studies, using two soils collected from Manitoba fields, a polymer coated MAP produced yields similar to that of uncoated MAP, but led to lower seedling toxicity when seed-placed at higher rates of P (Katanda et al. 2016; Katanda et al. 2019).

6.3 Reclaimed and By-Product Sources of Phosphorus

Manures, composts and municipal biosolids are valuable sources of P for crop uptake. However, due to the focus of this review on management of commercial fertilizers, these raw forms of organic byproducts will not be dealt with in this review.

Struvite - Wastewater streams, including municipal wastewater and liquid livestock manure, contain large amounts of P. Struvite is a P-containing mineral that can be manufactured from municipal wastewater and hog manure (Ackerman et al. 2013; Degryse et al. 2017; Katanda et al. 2016; Talboys et al. 2016). The struvite ($MgNH_4PO_4 \cdot 6H_2O$) can then be used to recycle wastewater and manure P as a concentrated granular fertilizer. The higher P concentration in the struvite as compared to the wastewater or manure makes it more economical to transport from areas of P surplus to areas of P deficit. Studies from Rothamstad in southern England comparing the effectiveness of 11 different struvites to that of monocalcium phosphate showed that all supplied similar amounts of P to ryegrass (Johnston and Richards 2003). Some non-significant differences occurred among the different sources and the suggestion was that differences in crystal size might be affecting efficacy.

Pot studies at the University of Manitoba showed that although P uptake was similar for hog manure-derived struvite and commercial fertilizers at P_2O_5 rates of 38 mg/pot or lower, biomass yield per unit of P taken up was smaller for the struvites (Ackerman et al. 2013). The lower yield as compared to commercial fertilizers may be due to lower initial solubility of the struvites in the alkaline (pH 7.7) soil used in this experiment, which gave an early stage growth advantage to canola fertilized with conventional or polymer coated MAP. Alternately, the banding method used in the Ackerman study may have reduced the dissolution of the struvite as compared to mixing the struvite through the soil as was used as the method of application in other studies (Degryse et al. 2017). Reducing the contact between the struvite and the soil through banding would slow dissolution of the fertilizer.

When struvite is used in canola–wheat rotations, there is a potential for greater residual P availability for subsequent canola crops than with MAP or coated MAP. In the greenhouse bioassay conducted by Ackerman et al. (2013), the soil was left to rest for only 14 d, was not subjected to freeze–thaw or wet–dry cycles, and the crops were not grown to maturity. Longer-term field-scale studies would allow a more complete evaluation of the P availability through the growing season and the residual benefits from the product. In addition, the P-release rate from struvite in different soils needs to be evaluated to provide a better understanding of the mechanisms of P transfer from this P source.

Other pot studies from University of Manitoba evaluated coated MAP as compared to struvite and uncoated MAP for seed safety and efficiency in canola and wheat grown in rotation on two Manitoba soils (Katanda et al. 2016; Katanda et al. 2019). The struvite was applied as granules formed by moistening the finely ground struvite powder, air-drying the resulting paste and cutting it into uniform granules that were similar in size to those of MAP. The fertilizers were applied either in the seed row or in a sideband at two rates. Dry matter yield in the first wheat and canola crops were similar for all three fertilizer sources but seedling damage in canola was greater with MAP than with the more slowly available products when seed-placed at the higher P rates. Struvite had more residual benefit than MAP, with dry matter yield being higher than with MAP in the second crop after application and higher than with either MAP or controlled release MAP in the third crop.

Many studies have used a powdered form of struvite, but commercial fertilizer forms would likely be in granular form to facilitate blending and handling. Growth chamber studies conducted in Australia compared granular MAP, a commercial granular struvite and several other synthesized struvites (Degryse et al. 2017). The P in MAP was almost completely soluble in water while the commercial struvite was only 3% soluble. The struvites in this experiment differed in the amount of Mg that they contained. In water, the differences in Mg had little effect on solubility of the struvites, but in the soil, the presence of extra Mg reduced the solubility and movement of the struvite, reducing the volume of the reaction zone. There was much less diffusion with the struvites than with the MAP when the products were applied as granules. However, when the products were ground and mixed through the soil, the solubility of MAP and struvites were similar. The pattern of movement for the struvite and the MAP followed the pattern of dissolution. The greatest movement of MAP occurred in the first few days after application and then decreased as the phosphate reacted with the soil. In contrast, diffusion for the struvite proceeded slowly and gradually as the struvite dissolved. In pot studies, P availability was much lower for the granular struvites than for MAP, especially on the high pH soils where granular struvite provided no increase in yield and P uptake over the untreated control (Degryse et al. 2017). Similarly, in studies conducted in Brazil using soils from Brazil and the United States, mobility of P from three small struvite granules was less than from a MAP granule (do Nascimento et al. 2018). However, as mentioned previously, in other studies, if struvites are ground and mixed through the soil, yield and P uptake can be similar to that of the MAP (Degryse et al. 2017).

Struvite would presumably be similar in effectiveness to soluble fertilizers once it dissolves, but the time to reach near-complete dissolution may range from days to years depending on fertilizer, soil and plant properties (Degryse et al. 2017). Large granule size, high excess base content, and high pH would slow the dissolution (Degryse et al. 2017; Everaert et al. 2017). Plant roots would also affect the dissolution rate though uptake of P and by modifying the chemistry of the rhizosphere. In laboratory assays, the initial rate of dissolution of a commercial granular product and the equilibrium concentration of P in the solution was increased by adding organic acid anions to the buffered solutions (Talboys et al. 2016). In subsequent pot experiments using a P-deficient soil collected in Wales, buckwheat (*Fagopyrum esculentum* L.) a plant that exudes a high amount of organic acids, absorbed similar amounts of P from struvite and DAP. In contrast, wheat, which does not exude many organic acids, had plant P uptake from struvite that was only about 30% as much as from DAP. Early season uptake of struvite was lower than uptake from DAP but blending mixtures of struvite and DAP where struvite was no more than 20% of the blend provided comparable levels of P uptake to the full DAP treatment. Therefore, blending some struvite with more soluble traditional P sources may be able to supply enough P for early crop growth but also provide a slow release source that will release P throughout the growing season.

Layered double hydroxides - Layered double hydroxides (LDH) are inorganic anion exchangers, typically consisting of layered hydroxides of divalent and trivalent cations that hold anionic species in the interlayer galleries and at the outer surface of the crystallites by competitive electrostatic interactions (Everaert et al. 2017). They are highly selective for HPO_4^{2-} anions and have been suggested as a mechanism to remove P from waste streams. The P-exchanged layered double hydroxide that is recovered from the waste stream has potential as a slow release P fertilizer (Everaert et al. 2017; Everaert et al. 2016). In a neutral or alkaline soil, ion-exchange of the interlayer or surface bound HPO_4^{2-} will allow LDH to release P slowly into the soil solution, while in an acid environment, there may also be phosphate release by dissolution of LDH. Phosphorus uptake by barley from an LDH powder treatment on an acidic soil from Kenya was up to 4.5 times greater than from a soluble KH_2PO_4 treatment, likely because of a beneficial liming effect from the LDH. In a calcareous soil from Spain, P uptake by barley from the LDH was less than from KH_2PO_4 at the higher P rates and similar at low P rates (Everaert et al. 2016). In subsequent studies using two Australian soils, when granulated forms of the LDH were evaluated in pot trials with wheat, the granular product produced lower crop yields and P uptake than did granular MAP due to slow dissolution or P release from the SRF granules (Everaert et al. 2017). As in Everaert's previous experiments with LDH and KH_2PO_4, when the LDH was applied as a powder, its agronomic performance was much better than in the granular form, slightly better than MAP on an acid soil, possibly because it had a liming effect, but slightly worse than MAP on an alkaline soil. All of the powdered fertilizers produced less P availability than granular MAP, with the advantage of the granular P likely related to more precise placement of the fertilizer granule close to the seed. The agronomic performance of LDH in soils from the Northern Great Plains is not known.

Humic Acids - Although they are not considered direct sources of P, humic and fulvic acids (HA and FA) have been investigated as substances to increase P availability by supplementing the organic acid content of the soil to slow the precipitation of sparingly soluble calcium phosphates (Delgado et al. 2002). In laboratory incubation studies, a mixture of humic and fulvic acids (HFA, which contained 11% HA and 4% FA) was applied at 0, 1, 2, and 5 g/kg to six calcareous soils with different levels of salinity and Na saturation (these rates of application were equivalent to approximately 0, 2000, 4000, and 10,000 lb of product per acre to a 6 inch depth of topsoil).

The soils were then fertilized with 200 and 2000 mg P/kg soil as MAP (Delgado et al. 2002). The recovery and forms of P were studied after 30, 60 and 150 days, using sequential chemical fractionation and ^{31}P NMR spectroscopy. Application of the HFA increased the amount of applied P recovered as Olsen P in all the soils except the soil with the highest Na saturation. The HFA appeared to inhibit the precipitation of poorly soluble Ca phosphates, with the ^{31}P NMR spectra showing reduced formation of apatites and more formation of amorphous Ca phosphate and dicalcium phosphate dihydrate (DCPD). The increase in the recovery of applied P due to HFA shows that application of organic matter soil amendments may improve the efficiency of P fertilizers and may also explain how manures and other organic amendments that contain P can be more efficient than inorganic P fertilizers in increasing available P in calcareous soils.

While humic acid supplements have shown promise in some laboratory incubation studies, benefits have not been consistent, especially in pot or field studies. Laboratory studies using soils from Brazil and the United States showed that mobility of P from humic-acid coated MAP was lower than from uncoated MAP on soils with a high Fe content, but did not affect mobility in the other soils tested (do Nascimento et al. 2018). A three-year field study conducted on calcareous low organic matter soils at University of Idaho to investigate application of low rates of humic acid to liquid P bands in potatoes showed a tendency for increased petiole P and higher yields of large no. 1 tubers compared to liquid P alone (Hopkins and Ellsworth 2005; Hopkins and Stark 2003). In contrast, lysimeter measurements of soluble P near a simulated fertilizer band was not affected by treatment of MAP fertilizer with one of two humic acid products on either a calcareous silty clay loam or a noncalcareous sandy loam soil collected from Montana fields through most of a 48-day incubation period (Jones et al. 2007). The second product in the Montana study increased the soluble P concentration 1.5 inches (3.8 cm) below the band in the calcareous soil at 16 and 32 days, indicating that the second product may have increased P solubility. The rates of HA used in the Montana study were about 100 to 300-fold lower in the area around the band than those used in the incubation study by Delgado et al. (2002) discussed previously. Pot studies using the same two Montana soils showed that additions of low rates of two humic acid products did not improve use of phosphate fertilizer or increase yield of spring wheat on either a calcareous or non-calcareous soil (Jones et al. 2007). The lack of response at low rates of HA application may indicate that HA may only be effective at high rates of application.

Leonardite, an oxidized form of lignite that overlies the more compact coal in coal mines, is a rich source of humic acid (Akinremi et al. 2000). Rather than being viewed as a P source, it has been suggested that as an organic amendment, it may increase the availability of P and other nutrients, particularly on low organic matter soils. In greenhouse trials at the University of Manitoba, leonardite did not provide a benefit for wheat or green beans, crops that have a lower S requirement than canola. However, the dry matter yield and uptake of N, P, K and S for canola, a crop with a large requirement for S, was increased by the application of leonardite as an indirect result of the influence of S supplied by leonardite. Both the dry matter yield and the nutrient concentrations of canola increased with increasing rates of leonardite, indicating that nutrient uptake by canola was facilitated at high rates of leonardite. However, there was no response to leonardite observed if N and P were not applied as well, or if S was applied, indicating that the response to leanardite was an S response that required an S deficiency and an adequate supply of other nutrients to occur.

Ash - Gasification is used for disposing various types of organic waste, including bone meal, meat and dried distillers grain (Alotaibi et al. 2013). The resulting ash is rich in P and may be suitable for use as a P fertilizer. Growth chamber studies in Saskatchewan evaluated the effect of meat and bone meal ash and dried distillers grain ash as compared to MAP as a P source for canola (Alotaibi et al. 2013). The ash from the distillers' dry grain was an effective P source and produced a yield response similar to equivalent rates of MAP, while the meat and bone meal ash was less effective.

Wood ash, a by-product of the forestry industry, can be used for land application, largely as a liming material due to its very high pH (Arshad et al. 2012). Wood ash varies widely in mineral composition but can contain significant amounts of P (Vance 1996). The solubility and availability of the P in wood ash may be low and contribution of wood ash to crop uptake of P will reflect the concentration in the ash, the solubility of the P present and the impact of pH-induced changes in soil nutrient availability. In studies in northern Alberta, application of wood ash to an acid soil at liming rates increased crop yield more than application of lime (Arshad et al. 2012). Extractable P was higher in the top 2 inches (5 cm) of the wood ash treated soil than in the lime-treated soil, but the two treatments did not differ in crop P uptake. While wood ash may serve as a source of P, the major benefit appears to be in improving crop growth and P availability through alleviation of soil acidity.

Biochars - In many soils around the world, including Chernozemic soils in the Northern Great Plains, carbon residues from natural or human-initiated burning events can make up a substantial proportion of the soil carbon (Atkinson et al. 2010; Schmidt et al. 1999). This carbon contributes to the nutrient and water-holding capacity of the soil. Application of biochars to soils is being investigated as a way of using waste biomass to sequester carbon and improve soil quality.

Biochars are highly condensed carbon products formed from pyrolysis through the incomplete burning of biomass at low levels of oxygen (Atkinson et al. 2010; Solaiman et al. 2019). The C compounds in biochars are highly stable and can remain in the soil for decades to centuries, improving soil physical, chemical and biological quality. Biochars were historically used to improve soil quality on low organic matter soils, providing a great benefit in tropical soils such as the "Terra preta" in the Amazon basin (Atkinson et al. 2010; Cunha et al. 2009; Glaser et al. 2001). Biochars can also contain varying amounts of nutrients, including P (Atkinson et al. 2010; Solaiman et al. 2019). Conversion of biomass to biochar will increase the proportion of P in the material.

Greenhouse studies using a 1% addition of biochars produced from different feedstocks showed that biomass production and P uptake of wheat was positively correlated with the P concentration of the biochar (Solaiman et al. 2019). However, biochars may also influence P availability through effects on pH, microbial activity, anion exchange capacity and the activity of other cations that affect P availability (Atkinson et al. 2010). While the benefits of biochar application have been demonstrated on many low organic matter tropical soils, relatively little research has been conducted on temperate soils that are naturally higher in soil organic matter (Atkinson et al. 2010; Hangs et al. 2016). Greenhouse studies in Saskatchewan evaluated the effect of biochar produced from willow feedstock applied at 2 % w/w; incorporated within a 10-cm depth, on a black and a brown Chernozemic soil (Hangs et al. 2016). Effects on pH were minimal but biochar increased the CEC by ≈13 %, water holding capacity by ≈16 % and porosity by ≈11 % while decreasing bulk density by ≈11 % and water-filled pore space by ≈15 %. These improvements in soil quality could indirectly influence P dynamics.

6.4 Microbial Products

Penicillium bilaiae and mycorrhizal inoculants are the two major types of microbial products that are marketed in the Northern Great Plains to improve P availability.

***Penicillium bilaiae* -** *Penicillium bilaiae* has been sold in the Northern Great Plains as an inoculant to improve the availability of soil P. It is a fungus that occurs naturally in agricultural soils and is said to improve P availability by secreting organic acids that can solubilize P. It is also referred to in the literature as *Penicillium bilaii* or *Penicillium bilaji*.

Laboratory and greenhouse studies have shown enhanced P uptake with the use of P. bilaiae (Kucey 1988; Kucey and Leggett 1989). Other *Penicillium* species have also been shown to have P-solubilizing effects (Wakelin et al. 2007; Wakelin et al. 2004). Studies on field peas in Saskatchewan and Alberta showed that P. bilaiae increased root growth and P concentration in the tissue in one site-year on P-deficient soils, possibly because of the effect of the fungus in stimulating root growth (Vessey and Heisinger 2001). In greenhouse studies with wheat, *P. bilaiae* increased solubilization of inorganic P and increased the amount of P in solution through a decrease in the solution pH (Asea et al. 1988). The improved P supply led to an increase in wheat dry matter yield and P uptake. In nutrient solution studies, neither P nor *P. bilaiae* influenced the root length or mean root diameter of field pea roots, but the proportion of the root with root hairs was higher with inoculation (Gulden and Vessey 2000). The differences in root morphology and the stimulation of P uptake were related.

In studies conducted under field conditions on the Northern Great Plains crop yield responses to use of P. bilaiae have been mixed. Some field studies have shown a benefit from *P. bilaiae.* A total of ten field trials were established throughout the major alfalfa-producing regions of Saskatchewan in 1994 to determine the effects of inoculating alfalfa seed on the early season vegetative growth and P uptake, and forage yield response of alfalfa over a range of soil and climatic conditions (Schlechte et al. 1996). Increased alfalfa dry matter production, P uptake, and forage yield responses occurred following inoculation with *P. bilaiae*, most likely due to increased P availability from the solubilization of otherwise unavailable soil P (Beckie 1997; Beckie et al. 1998). In subsequent alfalfa trials in Saskatchewan, the *P. bilaiae* treatments generally did not increase, and in some cases seemed to decrease, biomass yield, although in one site application of *P. bilaiae* + 20 kg P_2O_5 increased yield (Farden and Knight 2005).

Field studies with annual crops have also shown inconsistent benefits to use of *P. bilaiae*. In nine site-years of a study with wheat in Manitoba and Alberta, there was no significant increase in grain yield due to use of *P. bilaiae* (Grant et al. 2002). In 47 site-years of experiments with hard red spring wheat across western Canada, yield increases with fertilizer P occurred in 33 site-years, while there were five increases in yield and nine decreases in yield with *P. bilaiae* inoculation (Karamanos et al. 2010). These responses could not be attributed to extractable P soil concentration, soil organic matter or texture, or weather conditions and were considered random events. In studies conducted at four sites in North Dakota, fertilization with P consistently enhanced early season growth, main stem development, tillering and P uptake while seed inoculation with *P. bilaiae* had little or no effect on these measurements (Goos et al. 1994). Grain yields were significantly increased by P fertilization and by *P. bilaiae* inoculation at one site. The reason why *P. bilaiae* inoculation increased yield at this location is not evident, as it did not increase plant growth and P uptake earlier in the season. Averaged across all four sites, *P. bilaiae* inoculation increased wheat yields by 1 bu/acre (66 kg/ha) (Goos et al. 1994).

In studies in Manitoba and Saskatchewan, *P. bilaiae* had small and infrequent effects on early-season plant P uptake, seed yield, and seed P concentration and content of canola (Mohr et al. 2013). Inoculation with *P. bilaiae* produced a small increase in early season P concentration in 4 of 9 site-years, but increased canola yield in only one site-year and decreased canola yield in one site-year while P application increased canola yield in 6 of 9 site-years (Mohr et al. 2013). Phosphorus fertilizer application generally resulted in comparatively more consistent and marked increases in early-season P uptake, yield, and seed P concentration and content. Similarly, there was no yield benefit of using *P. bilaiae* on flax in nine site-years of field studies in Manitoba (Grant et al. 2005; Grant et al. 2000). Field trials have demonstrated no consistent effects of *P. bilaiae* on the growth, development and seed yield of lentil in field trials in Saskatchewan (Gan et al. 2005). Studies on corn and winter wheat in Kansas also showed no benefit to the use of *P. bilaiae* when applied with or without P fertilizer (Ward 2010). Therefore, it appears that *P. bilaiae* is unreliable as a method of improving P nutritional status of crops on the Northern Great Plains.

Mycorrhizal Inoculants - Another class of microbial product being marketed on the Northern Great Plains is mycorrhizal inoculants. Mycorrhizal fungi form associations with the roots of many plants (Grant et al. 2005). Mycorrhizae play a key role in the soil microbial community and are of great importance to a wide range of domestic and wild plant species (Dai et al. 2014; Hamel 2004; Hamel et al. 2014; Hamel and Strullu 2006; Miller 2000; Miller et al. 1995). The plant provides photosynthate to the fungus and the fungus provides nutrients and possibly water to the plant. The external hyphae of arbuscular mycorrhizal fungi (AMF) extend from the root surface to the soil beyond the P depletion zone and so access a greater volume of undepleted soil than the root alone (Grant et al. 2005). Some hyphae may extend more than 10 cm from root surfaces (Jakobsen et al. 1992) which is a hundred times further than most root hairs. The length combined with the small diameter of hyphae (20–50 μm) allows the root-mycorrhizal system to access soil pores that cannot be explored by roots alone. Therefore, a root system that has formed a mycorrhizal network will have a greater effective surface area to absorb nutrients and explore a greater volume of soil than nonmycorrhizal roots. Mycorrhizae are naturally present in soils and extremely important in natural ecosystems, but their populations can be reduced by summer fallow, excess tillage, P fertilization and growing a non-mycorrhizal crop such as canola or sugar beet (Gavito and Miller 1998a; Grant et al. 2005; McGonigle et al. 2011; McGonigle et al. 1999; Miller 2000; Miller et al. 1995; Monreal et al. 2011). Some crops such as corn or flax are more dependent on mycorrhizal associations than crops such as wheat or barley and can show a negative response when grown after a non-mycorrhizal crop such as canola (Bittman et al. 2006; Grant et al. 2009a; McGonigle et al. 2011; McGonigle et al. 1999; Miller 2000).

Inoculation with a mycorrhizal fungus may be able to increase mycorrhizal colonization, especially under conditions where the background level of mycorrhizal spores is low. Inoculants are commercially used in horticulture and forestry as well as in organic production systems; however, their effectiveness in commercial cropping systems on the Northern Great Plains has been modest, at best.

In studies conducted in Saskatchewan, seed yield of N-fertilized barley increased substantially with application of triple superphosphate (TSP) on a P-deficient soil, but there was only a slight increase in yield from application of an AMF inoculant (Malhi et al. 2014). Similarly, field trials conducted over three years at two locations near Brandon, MB and one near Lacombe, AB, assessed the effects of combinations of AMF inoculant and APP on mycorrhizal colonization, wheat yield and P uptake (Grant et al. 2006). Mycorrhizal colonization of wheat roots was increased by application of a mycorrhizal inoculant but biomass production was reduced and grain yield generally unaffected by inoculation (Grant et al. 2006). Grain yield tended to be greater when P fertilizer was used alone than when mycorrhizal inoculant was used alone. Effect of inoculant when applied with P fertilizer varied, causing increased yield at some sites and decreased yield or no effect at others. Decreased yields from inoculation may have occurred because wheat did not require the mycorrhizal association to access adequate P, so colonization was detrimental to the plant (Dai et al. 2014; Ryan and Angus 2003; Ryan and Graham 2002). If there is no advantage to the plant from the mycorrhizal colonization, the fungus may depress yield potential by using the photosynthate of the crop.

The conditions historically used in plant breeding of wheat may have affected the response of wheat cultivars to AMF. Growth chamber trials were conducted in Saskatchewan to evaluate effect of soil P availability on AMF symbiosis in modern and historic wheat cultivars (Germida et al. 2001). At low P availability, historic cultivars had a higher level of AMF root colonization than modern cultivars, whereas at high P availability the modern cultivars were more extensively colonized. The AMF associated with historic cultivars could benefit the host plant through increased nutrient uptake, but the tissue P concentration and P uptake efficiency of the modern cultivar was higher, indicating that modern wheat cultivars were less dependent on AMF for P nutrition than were historic cultivars.

Crops such as corn, flax, or pulse crops that are dependent on AMF inoculation may be affected when soil levels of inoculum are reduced by tillage, fallow or crop sequence (Dai et al. 2014; Hamel et al. 2014). Growth chamber studies using soil containing native AMF and fertilized with 0, 5, 10, 20 ppm of added P evaluated the growth responses of lentil (*Lens esculenta* L. cv. Laird) and two wheat cultivars (*Triticum aestivum* L. cv. Laura and Neepawa) to *Glomus clarum*

NT4 (Xavier and Germida 1997). Lentil was more dependent on mycorrhizae than wheat and responded to an AMF inoculant for the soil receiving low rates of P fertilizer even in soil containing high concentrations of indigenous AMF. In outdoor container studies using four Saskatchewan soils transported and tested at four different locations, a commercial AMF bio-fertilizer was applied to field pea in the first year of the study and residual benefits were evaluated in a wheat crop the next year and a field pea crop the year after that (Islam et al. 2014). Inoculation increased the amount of mycorrhizal infective propagules present in all soil-climate combinations after the initial pea harvest, but there were no consistent residual benefits in the following two crops. Other growth chamber and field studies in Saskatchewan evaluated AMF colonization of flax roots and the effectiveness of AMF inoculants in improving flax P status (Walley and Germida 2015). Flax is a crop that tends to be reliant on mycorrhizal interactions (McGonigle et al. 2011). Flax typically supported a relatively high level of AMF colonization in both growth chamber and field studies, showing the importance of this association for flax nutrition and growth (Walley and Germida 2015). Application of the AMF inoculant containing a non-indigenous form altered the AMF root community composition, showing that the introduced AMF was able to compete with native AMF communities to colonize flax roots. Some growth parameters such as root growth, midseason biomass, or nutrient uptake improved with AMF inoculation in some instances, but the responses were not frequent or predictable and there were no significant seed yield responses in the growth chamber or field and no economic benefits for AMF inoculation.

Similar results occurred in a field demonstration at Indian Head, SK that failed to show any benefits to mycorrhizal inoculation for field pea, lentil or soybean (Holzapfel 2014). This demonstration was conducted following a spring wheat or barley host crop and in long-term no-till fields, factors that may encourage native AMF and so reduce reliance on and response to mycorrhizal inoculant (Gavito and Miller 1998b; Grant et al. 2005; McGonigle et al. 2011; McGonigle et al. 1999; Miller 2000; Miller et al. 1995; Monreal et al. 2011). Benefits for inoculation would be more likely to occur following non-host crops such as canola or summer fallow or when tillage disrupts mycorrhizal hyphal networks.

Another study in Saskatchewan examined inoculation of wheat, lentil, mustard and flax with commercial formulations of AMF and *P. bilaiae*, applied alone or in combination, for effects on seedling emergence, biomass production, and nutrient uptake on an organically managed soil and a conventionally managed soil (Knight 2011). When the inoculation treatments were applied at seeding, crops grown in the conventionally farmed soil were generally unresponsive to inoculation, except for lentil that showed increased yield and nutrient uptake with AMF inoculation. The lack of response of the other crops on the conventionally farmed soil could be because the nutrient content of the soil was higher than that of the organically farmed soil, so plants growing in the conventional soils were not nutrient limited. In the organic soil, biomass production of wheat and mustard in the year of inoculation increased with at least one of the inoculants and wheat showed higher nutrient uptake. Dual inoculation with the two organisms showed no advantage over single inoculation, and the two organisms were not complementary. Mustard showed a response to AMF inoculation, which was unexpected since mustard does not form mycorrhizal associations. In mustard, nutrient uptake was not affected so it may be that the

AMF had an indirect effect on other soil microorganisms that affected overall growth. Flax grown in the organic soil was unresponsive to inoculation with either organism, showing no difference in productivity or nutrient uptake. Lentil grew poorly in the organic soil and showed low AMF associations with colonization, which was approximately 1/3 of the colonization observed in the conventional soil. The lower colonization in the organic soil was reflected in the overall poor growth and low nutrient uptake. There was some carry-over of the inoculant effect into the second crop grown after inoculation, especially for wheat grown after flax or lentil but not mustard. Mustard also showed higher biomass and nutrient uptake from inoculant carryover when grown after lentil and wheat. Lentil also showed improved growth and nutrient uptake from inoculation of the preceding crop. However, none of the crops showed carryover benefits from inoculation of the preceding crop when grown after mustard, presumably because mustard is not an AMF host crop, which indicates that the carryover effect will occur only if new spores are produced by the crop-fungal association.

While inoculation of crops with AMF spores may have small and infrequent benefits for field crops, the AMF association is important to many crops, including flax, legumes and corn. Therefore, management practices that encourage AMF, such as reduced tillage or rotations with mycorrhizal crops preceding mycorrhizal-dependant crops would likely benefit yield (Grant et al. 2009b; McGonigle et al. 2011; Monreal et al. 2011). Furthermore, although AMF clearly aid in P uptake, and uptake of P from fertilizer may be enhanced by AMF inoculation, the AMF populations provided by currently available inoculants may not be an improvement over a well-established and maintained native AMF population.

Gaps in Knowledge

More information is required on:

- agronomic value of varying formulations, additives and coatings for P fertilizers. For example, development of more cost-effective coated P products would be beneficial, particularly for use as seed-placed starters in today's high yielding, diversified cropping systems.
- performance of fluid P forms on highly calcareous soils on the Northern Great Plains. While it appears that fluid and granular sources behave similarly on the Northern Great Plains, it would be interesting to determine if there are situations where fluids are more effective than granular products, as has been seen in Australia.
- recycled and by-product sources of P would be highly beneficial, so investigation of methods of increasing the solubility and availability of these products as fertilizer sources is worthwhile.
- performance of mycorrhizal inoculants for field crops. While the importance of mycorrhizae for plant growth is clear, performance of inoculants has been disappointing. It is not apparent whether native inoculants are adequate or if the commercial inoculants used have either been suboptimal or not competitive with local microbiota. So, it would be worthwhile to determine if more effective inoculants could be found. This would not necessarily save on crop inputs of P in the long term, since the rates of crop P removal must eventually be balanced with rates of P application. However, P-efficient mycorrhizal

associations could enable farmers to maintain lower levels of soil test P, which could reduce P loss to surface water due to runoff and erosion.

- influence of biochar amendments on prairie soils.

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