SPECIATION OF PHOSPHORUS IN REDUCED TILLAGE SYSTEMS: PLACEMENT AND SOURCE EFFECT

by

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Abstract

Phosphorus (P) management in reduced tillage systems has been a great concern for farmers. Conclusive results for benefits of deep banding of P fertilizers for plant yield in reduced tillage system are still lacking. Knowledge of the dominant solid P species present in soil following application of P fertilizers and linking that to potential P availability would help us to design better P management practices. The objectives of this research were to understand the influence of placement (broadcast- vs. deep band-P or deep placed-P), fertilizer source (granular- versus liquid-P), and time on reaction products of P. Greenhouse and field based experiments were conducted to study P behavior in soils. Soil pH, resin extractable P, total P, and speciation of P were determined at different distances from the point of fertilizer application at 5 weeks (greenhouse and field) and 6 months (field) after P application (at rate 75 kg/ha) to a soil system that was under long-term reduced tillage. X-ray absorption near edge structure spectroscopy technique was used to speciate reaction products of fertilizer P in the soil. The reaction products of P formed upon addition of P fertilizers to soils were found to be influenced by soil pH, P placement methods, and P sources. Acidic pH (below~5.8) tended to favor formation of Fe-P and Al-P like forms whereas slightly acidic near neutral pH soils favored formation of Ca-P like forms. Scanning electron microscope with energy dispersive X-ray analysis of applied fertilizer granules at 5-wk showed enrichment of Al, Fe and Ca in granule- indicating these elements begin to react with applied P even before granules dissolve completely. The availability of an applied P fertilizer was found to be enhanced as a result of the deep banding as compared to the surface broadcasting or deep placed methods. Deep banded liquid MAP was found to be in more adsorbed P like forms and resulted greater resin extractable P both at 5 wk and 6 month after

application. Deep banding of liquid MAP would most likely result both agronomically and environmentally efficient solution for no-till farmers.

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Chapter 1 - Literature Review

1.1 Historical Background

Phosphorus (P) is an important element for all life forms. It was discovered by Henning Brand, a German alchemist, in 1669 by isolating it from the urine. The name came from Greek words *phos* meaning 'light' and *phorus* meaning 'bearing'. Before the development of fertilizer industry, the crop production was mainly relied on natural levels of P in soil and additions of organic manures and human excreta. Thousands of years ago, to increase crop production Chinese farmers used bones and the Incas in Peru used phosphoguano. Historically, slash and burn had been a common practice for nutrient recycling in shifting cultivation; however, this practice is found to be depleting P in long run (Ketterings et al., 2000) due to heat induced P fixation. The change from traditional approach to modern concept of supplying nutrients to enhance crop productivity came in 1840. In 1840, Justus von Liebig discovered that when plants were fed nitrogen (N), potassium (K) and P in the required amounts they would grow even in nutrient depleted soil. This led to use of P as a plant nutrient and development of chemical fertilizer industry. With the increasing food demand the use of guano and rock phosphate increased over time. Phosphoguano was used as a raw material for P fertilizer in the early days; however, phosphate industry began after discovery of phosphate rock in South Carolina in 1859. By 1889, the phosphate rock mine supplied 90% of the worldwide phosphate fertilizer production (Kongshaug et al., 2000). Today phosphate rock from sedimentary deposits is still a main source of P fertilizer.

In 1842, John Bennet Lawes patented addition of sulfuric acid to phosphate rock to yield effective phosphate fertilizers known as superphosphates (Jacob, 1964). The chemical reaction is:

$$Ca_{10}F_2(PO_4)_6 + 7H_2SO_4 + 3H_2O \rightarrow 3Ca(H_2PO_4)_2 \bullet H_2O + 7CaSO_4 + 2HF$$

In areas of gypsum deposits, superphosphates are still common fertilizer sources for crop production. In early days use of ammonium phosphates was limited. However, after 1960's ammonium phosphates became the popular phosphate fertilizers. Ammonium phosphate is a salt of ammonia, which is produced by Haber –Bosch process, with phosphoric acid. The Haber – Bosch process significantly increased the production of ammonium phosphate fertilizers.

1.2 Role of Phosphorus

Phosphorus is a major nutrient essential for plant growth next to nitrogen. It is a structural component of DNA and RNA and plays vital role in transfer of energy. For plants, P stimulates early root growth, flowering, fruiting and hastens maturity. Phosphorus is often a limiting nutrient in crop production. The deficiency symptoms of P include stunted growth and abnormal dark green color. Purplish leaves in corn also indicate the deficiency of P, however sometime it may be misleading because purple leaves can also result due to plant genetic characteristics and insects damage.

1.3 Phosphorus Fertilizers

Phosphorus demand can be met by several fertilizers. Those can be divided into two main groupings, organic fertilizers and inorganic fertilizers.

1.3.1 Organic P Fertilizers

Organic P fertilizers have been used for long time before availability of commercial inorganic P fertilizers. Even with advent of P fertilizers, organic P fertilizer from crop residues, animal manures, and sewage sludges is very important. Phosphorus contained in organic sources is combination of both organic and inorganic P. Inorganic P in organic sources is readily available for plants use. Most of the organic P transforms into inorganic form depending upon soil moisture, temperature and pH over time via the process of mineralization.

1.3.2 Inorganic P Fertilizers

There are various commercial P fertilizer sources. Most of the inorganic P fertilizers come from rock phosphate. Once they are dissolved in water, orthophosphate becomes available for the plant uptake. Commonly used inorganic P fertilizers in USA are:

1. Ordinary or Single Super phosphate (SSP) (0-20-0): It is the oldest source of P fertilizer and is less popular now. It has been replaced by other commercial P fertilizers.
2. Triple Super Phosphate (TSP) (0-46-0): It is the first high analysis P commercial fertilizer. However, its production declined in favor of ammoniated fertilizers since 1980.
3. Diammonium phosphate (DAP) (18-46-0): currently DAP is the world’s major solid P fertilizer. It is produced by reacting one mole of phosphoric acid with two moles of ammonia and the chemical reaction for DAP is:

$$H_3PO_4 + 2NH_3 \rightarrow (NH_4)_2HPO_4$$

4. Monoammonium Phosphate (MAP) (11-52-0): Monoammonium phosphate is produced by adding one mole of ammonia to one mole of phosphoric acid. The chemical reaction is:

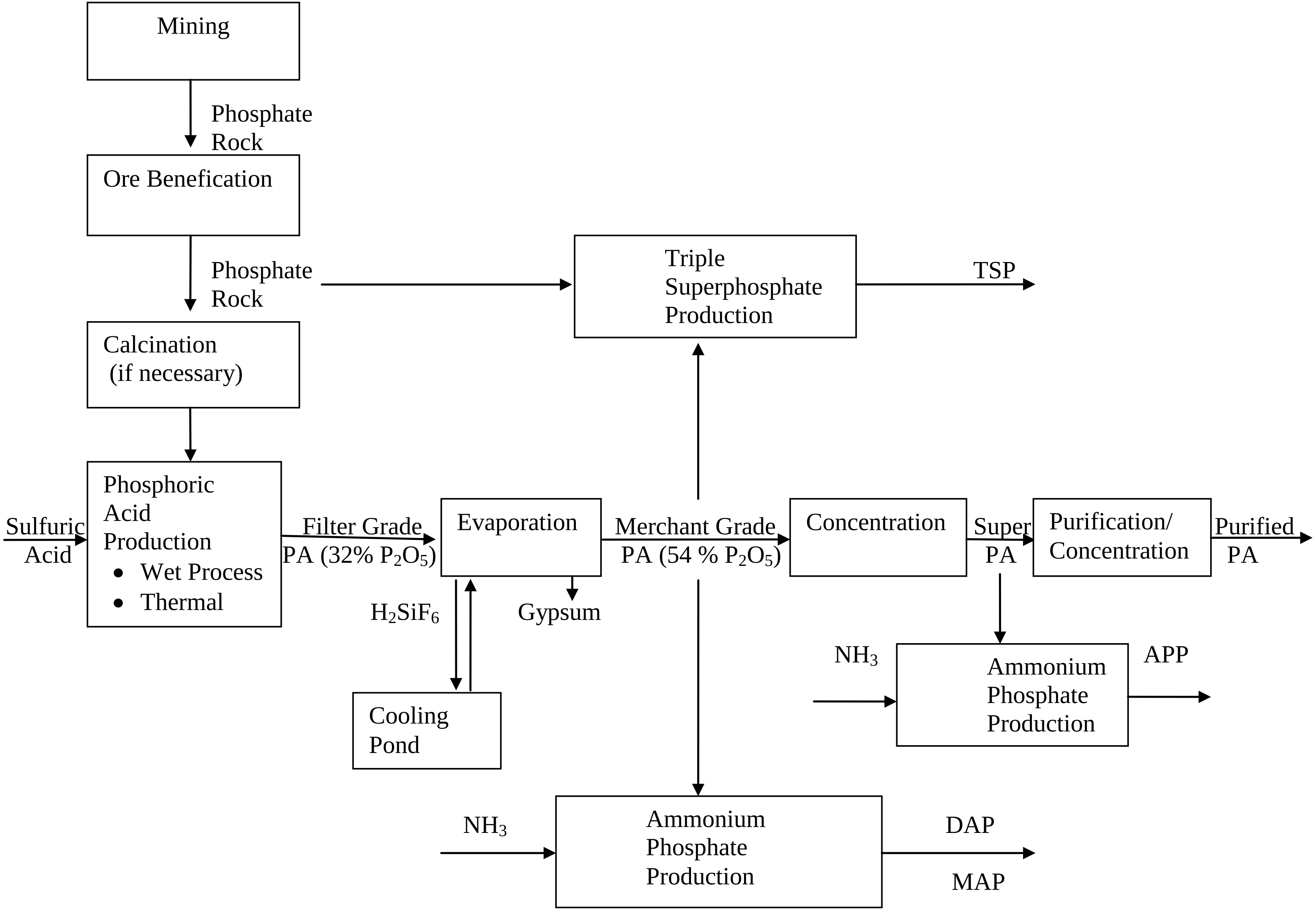
$$H_3PO_4 + NH_3 \rightarrow (NH_4)H_2PO_4$$

5. Ammonium Polyphosphate (APP) (10-34-0) or (11-37-0): It is a major liquid P source produced by reaction of super phosphoric acid, ammonia and, water. It consists of variety of polymers. Out of total P, 70 to 75 % of P is polyphosphate and remainder is orthophosphate. It is assumed to have chelating and sequestering ability and hence more available than granular form of P fertilizers.

(IPNI, 2010)

Today various types of phosphate fertilizers are available in the market and are produced by using various methods. The production mechanisms for different phosphate fertilizers are shown in the Figure 1.1.

Figure 1.1Phosphoric acid manufacturing and phosphate fertilizer production process (Source: US EPA, 1993).



1.4 Soil P Cycle

The cycling of P in soil system is illustrated in Figure 1.2. The main sources of P in soil are inorganic fertilizers, organic waste products and manure. Organic form of P is made available to plants through mineralization process by transformation of organic P to inorganic P forms. Inorganic forms of P in soil solution in orthophosphate form are available forms of P in soil and are taken up by plants. With time P becomes unavailable due to reaction with soil minerals and cations. The losses of P from soil include leaching and runoff to water bodies. This loss of P from over application of inorganic P fertilizers is considered to be the major cause of eutrophication of aquatic systems (Sharpley et al., 1996; Maguire et al., 2000; Sims et al., 2000).

1.4.1 Forms of Phosphorus in Soil

In soil P may occur in soil solution form, solid forms (bound to Al, Fe, Ca), and adsorbed form on mineral surface. Not all the forms of P are available to the plants and the availability of P mainly depends on type of mineral it is bonded or part of, and soil pH. Phosphorus in soil can also be divided as (1) solution P- dissolved P readily available for plant uptake, (2) labile P- adsorbed P on soil solids that can rapidly go to solution form, (3) nonlabile P-very slowly releasing or transforming to labile or solution P and comprised of inner-sphere adsorbed P and precipitated P.

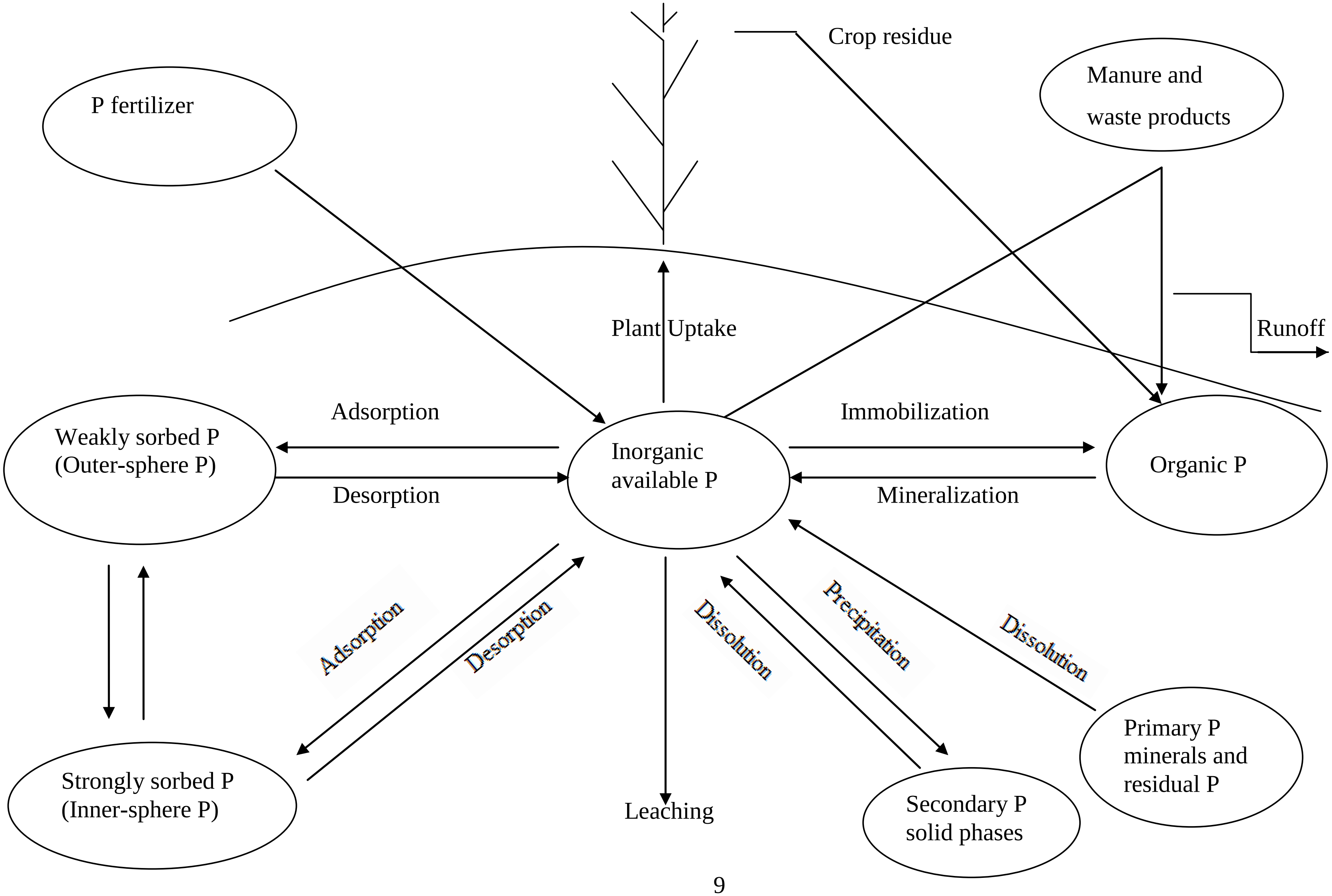
1.4.1.1 Soil Solution Phosphorus

The soil solution P is in equilibrium with soil solution inorganic P and dissolved organic P forms in soils. Phosphorus exists in soil solution mainly in inorganic dissolved form as primary (PO_4^{3-}) or secondary orthophosphates (HPO_4^{2-} and $H_2PO_4^-$) depending on the soil pH. In acidic soils, monovalent $H_2PO_4^-$ is dominant whereas alkaline solutions are dominated by divalent HPO_4^{2-} ions. Both the form of P is taken up by plants. Many phosphate compounds are not that soluble in water, so soluble or soil solution P is in relatively lower concentration in soils. The concentration of P in soil solution is very low ranging from 0.001 mg/L in very infertile soil to 1 mg/L in heavily fertilized soil (Brady and Well, 2002).

1.4.1.2 Solid Phosphorus

Solid P forms in soils include both inorganic and organic solid P although majority of P exists in soil mainly in inorganic forms. Inorganic forms of P in soil accounts for 50-70% of total P while organic forms accounts for 30-50% of total P (Carman et al., 2000). Inorganic forms of P in soil include both mineral P forms and adsorbed P forms. Adsorbed forms of P may be loosely bound or tightly bound. Sources of organic forms of P in soil are humus, animal manures, biosolids or other organic materials. Organic P in soil is found in the forms of inositol phosphate, phospholipids, phosphoglycerides, phosphate sugars, nucleic acids, and phosphonates (Pierzynski et al., 2000). With time this form of P is transform into available inorganic forms of P via process of mineralization which is a function of pH, temperature, and soil moisture. Immobilization is the process of conversion of inorganic P in soil solution to organic P. Based on the solubility and other soil characteristics such as pH and redox both organic and inorganic forms of P may be either plant available or unavailable.

Figure 1.2 The Phosphorus Cycle



1.4.1.2.1 Phosphate Minerals

Phosphorus in soil is found to be bound with iron (Fe), aluminum (Al), magnesium (Mg) and calcium (Ca) phosphates. At acidic pH, P is found to be bound with Al and Fe whereas at alkaline pH, Ca is a major cation binding P and hence altering its availability. The relative solubility of P minerals in soils is a function of pH and is well described by Lindsay (1979) (Figure 1. 3). In soil systems the solubility of $AlPO_4$ (berlinite) is greater than that of $AlPO_4•2H_2O$ (variscite). Comparing strengite and variscite solubility, if Fe controls Fe^{3+} activity and kaolinite-quartz controls Al^{3+} activity, strengite is more stable. However, if kaolinite-soil-Si controls Al^{3+} activity, then variscite is more soluble. In highly weathered soils when gibbsite controls Al^{3+}, variscite becomes more stable than strengite. So, weathering increases stability of aluminum phosphates and decrease stability of iron phosphates. The solubility of iron phosphates is a function of oxidation state. The solubility of Fe can be controlled by Fe minerals such as strengite (Fe (III) mineral, $FePO_4•2H_2O$) under aerated condition; whereas under moderately reduced or severely reduced conditions, vivianite (Fe (II) mineral, $Fe_3(PO_4)_2•8H_2O$) would control Fe solubility. Vivianite is considered to be more stable than strengite under reduced conditions.

Solubility of P in alkaline soil is controlled by Ca- phosphates and solubility of P in acidic soil is controlled by Fe and Al phosphates (Lindsay, 1979). The availability of P is a function of pH. The best pH range for P availability is 5.5 to 7. Weathering has great impact on distribution of P species in soil. In unweathered soils, apatite, Ca-phosphates are primary P mineral species whereas in areas of intense weathering, with decrease in pH, Al and Fe phases become dominant due to removal of Ca-phosphates by leaching. In soils with high P concentration, soil solution P precipitates in the form of various secondary P solid forms. In acidic soils, Al and Fe phosphates; variscite ($AlPO_4•2H_2O$) and strengite ($FePO_4•2H_2O$) are the secondary P solids to precipitate out depending on Al and Fe solubility. For calcium phosphates, the solubility order is

$CaHPO_4•2H_2O$ ((Brushite, Dicalcium phosphate dihydrate (DCPD))
> $CaHPO_4$ ((Monetite, Dicalcium phosphate (DCP))
> $Ca_4H(PO_4)_3•2.5H_2O$ (Octacalcium phosphate, OCP)
> β-$Ca_3(PO_4)_2$ (β -tricalcium phosphate, β -TCP)
> $Ca_5(PO_4)_3OH$ (Hydroxyapatite)
> $Ca_5(PO_4)_3$(Fluorapatite) (Lindsay, 1979)

1.4.1.2.2 Adsorbed Phosphorus

The fraction of soil P that is bonded to the surface of soil solids where discrete mineral phase is not formed is known as adsorbed P (Foth and Ellis, 1996). Majority of P in soil occurs as inner-sphere complex species (specific adsorption) and partially in the form of either diffuse ion swarm and outer-sphere complex species (non-specific adsorption) (Sposito, 1989). A inner-sphere surface complex is formed when the ligand displaces a water of hydration from the coordination sphere of the metal ion (i.e., surface-bound water) whereas outer-sphere complex is formed when the ligand does not displace surface-bound water, but forms a metal-water-ligand bound complex (Essington, 2004). Inner-sphere complexed P is more stable than the outer-sphere complexed P. Phosphorus is generally found to be adsorbed on the surfaces of clay, amorphous Al or Fe oxides in acid soils, and calcium carbonate in alkaline soils.

Figure 1.3 Solubility of calcium phosphates compared to aluminum and iron phosphates when Ca^{2+} is $10^{-2.5}$ M or fixed by calcite and CO_2 (g) at 0.0003 atm (Modified) Lindsay (1979).

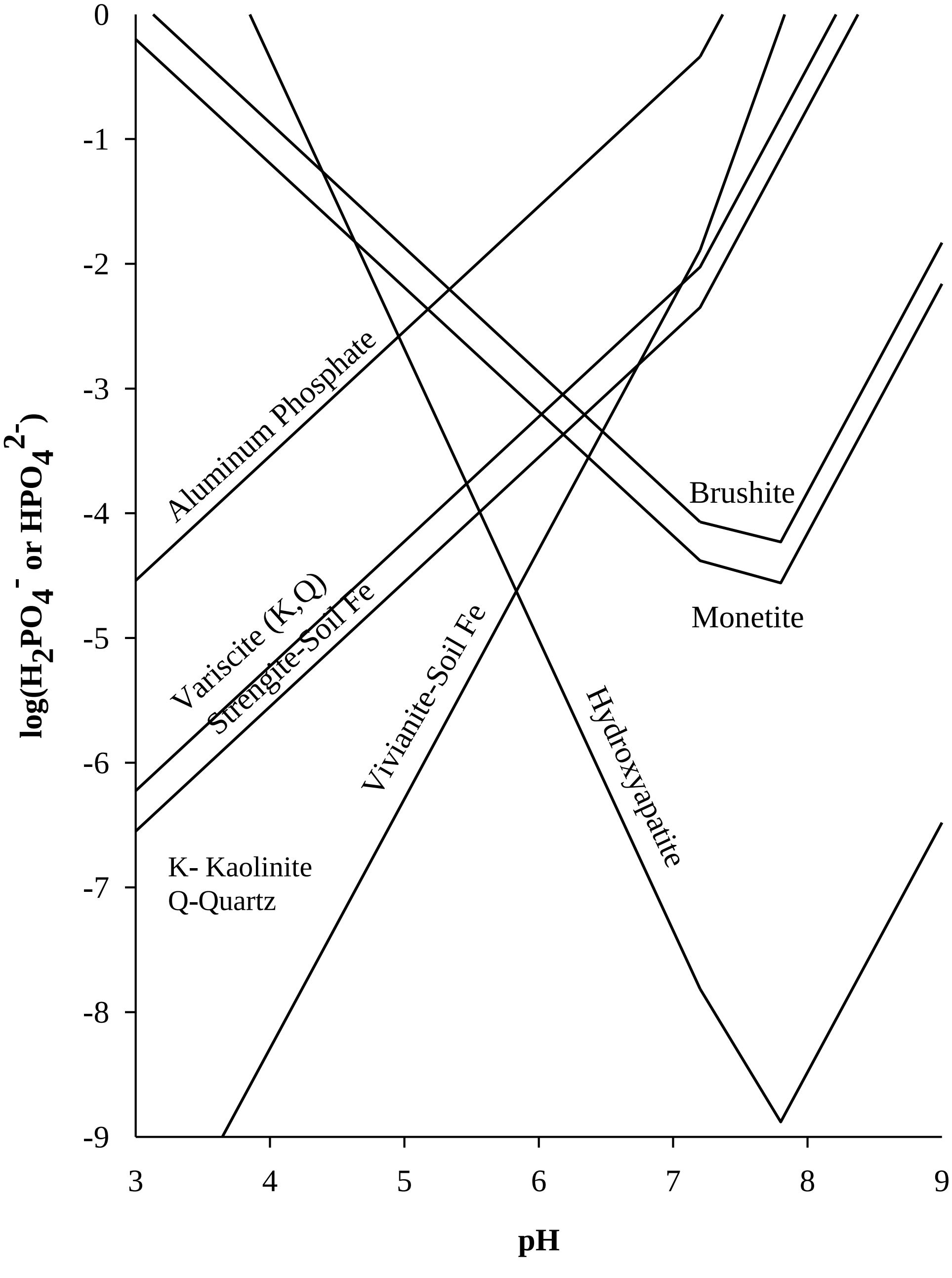


Figure 1.3 shows the solubility of various P minerals as a function of soil pH and P concentration. For development of this figure, for variscite, Al^{3+} activity was considered to be controlled by kaolinite in equilibrium with quartz. For aluminum phosphate, Al^{3+} activity was considered to be controlled by gibbsite. For strengite, Fe^{3+} activity was considered to be in equilibrium with soil-Fe. For vivianite, Fe^{2+} activity was considered to be in equilibrium with soil-Fe at redox level of pe+pH=7.92.

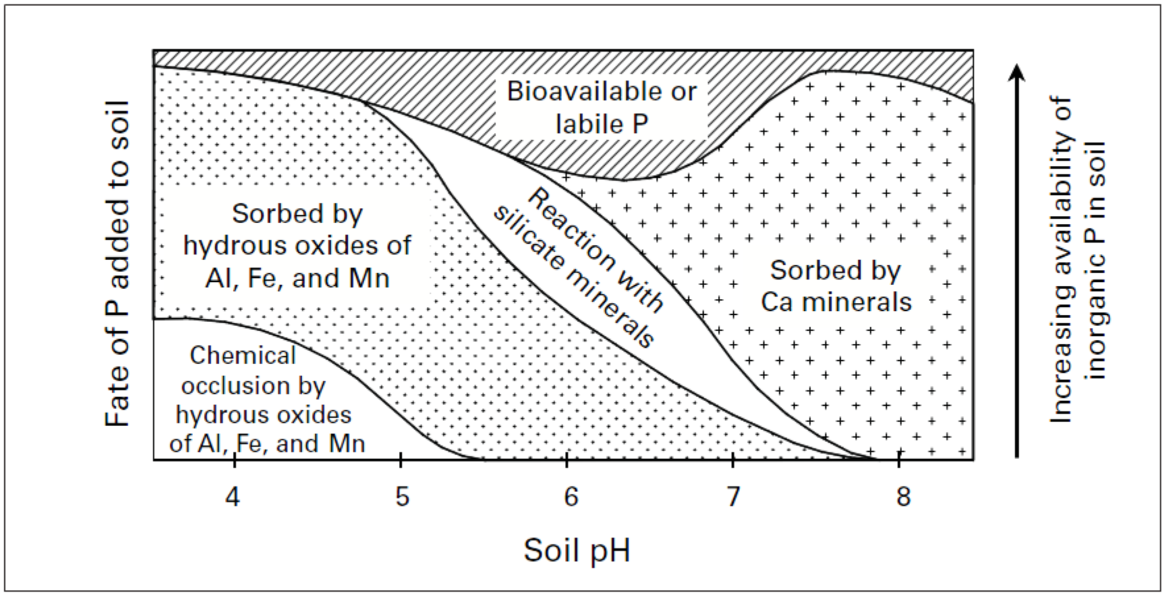
1.5 Fate of Phosphorus in Soils

Phosphorus is an essential nutrient for plant growth. Million of tones of P are applied to the soils annually, however, plant do not have access to all the P that is applied to the soil. Over the time, part of the applied P will be taken up by plants and majority of it reacts with other soil components to from insoluble minerals, sorbed onto mineral or organic surfaces (Hansen et al., 2002). In acidic soils, most of the applied P combines with soil Al and Fe forming minerals like variscite, strengite and vivianite (Lindsay, 1979., Ghosh et al., 1996) whereas in calcareous soil it combines with soil Ca forming minerals like dicalcium phosphate dihydrate, octacalcium phosphate and hydroxyapatite (Lindsay, 1979, Tunesi et al., 1999). When granular P fertilizers are applied to the soil, water from the surrounding soil enters granule through mass flow because of the hygroscopic nature of the P fertilizer granule. Due to dissolution of fertilizer granules, solution is formed which diffuse out of the granule. As it migrates, it will react with the minerals present in the soil (Busman et al., 2009). However, as this mass flow of water occurs in a direction opposite to that of dissolved P diffusion this process hinders the diffusion of P and other elements out of dissolving granules (Lawton and Vomocil, 1954; Hettiarachchi et al., 2006). With water entering the granule via mass flow of water, soluble cations such as Al, Fe and

Ca also enter the granule and precipitate P inside the granule or right adjacent to the granules limiting P diffusion outward (Hettiarachchi et al., 2006; Lombi et al., 2006). Low P concentration would favor adsorption of P, so high P concentration near vicinity of P granules could be conductive to precipitation reactions (Lombi et al., 2006; Tunesi et al., 1999). Ideally, pH 5.5-7 is considered to be the most suitable range of pH for maintaining maximum soluble P in soil (Brady and Well, 2002).

In calcareous soil, the availability of applied phosphate fertilizers is limited largely due to formation of sparingly soluble Ca minerals like dicalcium phosphate, octacalcium phosphate and ultimately into more stable hydroxyapatites (Lindsay, 1979; Freeman and Rowell, 1981). The relative rate of precipitation has been found to differ with granular and liquid P fertilizers in highly calcareous soils. Therefore, liquid forms of phosphate fertilizers have been found to be more effective in providing P for plants as compared to their equivalent granular forms of P in these soils. Holloway et al. (2001) found that application of fluid fertilizers considerably increased (4 to 15 times) the grain yield of wheat on calcareous soil as compared to granular MAP. Similar results were also observed by McBeath et al. (2005). Lombi et al. (2006) found that when granular fertilizers are applied to calcareous soil, P precipitation in the vicinity of granules in the form of octacalcium phosphate or apatite like compounds decreases the availability of P in soil. However, when fluid P fertilizers are applied to soil; more P was in available form due to increased diffusion and solubility. Phosphorus precipitation in the form of apatite or octacalcium phosphate was found to be less prominent in fluid P fertilizers (Lombi et al., 2006). Literature on comparing liquid and granular P fertilizers in acid soils are lacking to our knowledge. The behavior of granular and liquid P fertilizers might be same or different in acidic soils, especially high in Fe and/or Al, with respect to plant uptake or grain yield. Thus, study of reaction products of liquid and granular P in acidic soils would help us to understand the fate of P fertilizers in acidic soils. Further that may help us to design better P formulations and management practices to enhance plant productivity.

Figure 1.4 Approximate representation of the fate of phosphorus added to soil by sorption and occlusion in inorganic forms, as a function of pH (Sharpley et al., 1984).



1.6 Plant Phosphorus

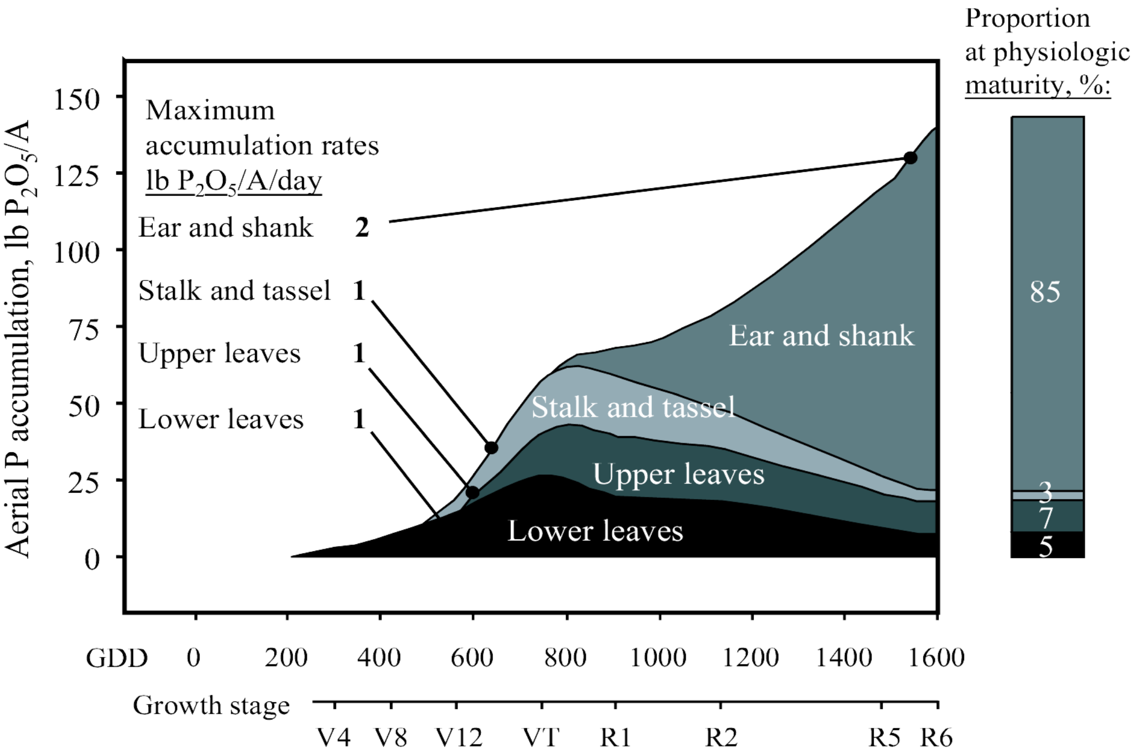
Phosphorus is the second most limiting macronutrient for plant growth after nitrogen (Schatman et al., 1991). Plants take up P only in the form of orthophosphate (HPO_4^{2-} and $H_2PO_4^-$). Phosphorus uptake by plants is calculated by multiplying plant dry biomass (kg/ha) by P concentration in plant (mg/kg). Phosphorus enters the plant through the root hairs. Once it is inside the plant system, P may be stored in the root or transported to upper plant parts. It becomes incorporated into organic compounds like nucleic acids, phosphoproteins, phospholipids, sugar phosphates, enzymes and energy rich compounds like adenosine triphosphate (ATP) through various chemical reactions (PPI, 1991).

Grant et al. (2001) suggested that withholding P during early plant growth will limit crop production and cause a restriction in crop growth from which the plant may not recover. First 5 week of P uptake was found to critical for plant growth. Phosphorus limitation later in the season has a much smaller impact on crop production than P limitations during early growth.

The added P in the soil may not be fully utilized by the plants. Although the total P concentration may be high in soil it may not be able to provide sufficient P for healthy plant growth. Out of total applied P in soil, majority of P becomes immobile and unavailable for plant uptake because of adsorption, precipitation, or conversion to the organic form (Holford, 1997). In such condition, the lower availability of P limits the plant P uptake, hence limiting plant growth. Mackay and Barber (1985) found that soil moisture plays important role in P uptake than the soil P levels and development of root hairs enhance the uptake of P in limited soil P conditions. They explained that with increase in soil moisture, diffusion increases due to direct and shorter pathway for diffusion of P through the soil increasing P uptake. Phosphorus uptake by plants is a common measure to evaluate P sufficiency in plants (Walter and Peck, 1975; Eckert and

Johnson, 1985; Reeves et al., 1986; Mallarino, 1996). Corn increases P uptake after V6 growth stage (i.e. 4 to 6 weeks after planting) and continues till maturity. Karlen et al., 1988(Figure 1.5) showed how corn takes up P during its life cycle. Even though it accumulates the majority of P in later stages of growth, P is critical for plant development in its early stage of life cycle.

Figure 1.5 How a corn plant takes up phosphorus (ISU, 1993)



1.7 Phosphorus Management

Adoption of different tillage systems may affect the fertilization practices. Various tillage systems such as conservation till, no till, reduced till, and conventional till, are practiced throughout the world. Reduced tillage crop production is getting more attention recent days from farmers in many regions of the U.S. and on farms worldwide (Hobbs et al., 2008). Despite various advantages of reduced tillage systems, it has been found that surface broadcast granular P fertilizer applications leads to an accumulation of available P on the surface 0 to 5 cm soil layer and a depletion of available P deeper in the profile (Schwab et al., 2006). Phosphorus stratified at surface soil may support plant root growth under moist condition at initial plant growth stage; however, roots explore deep soil layers for nutrient and moisture as surface soil gets dry during warm summer. Therefore, P management in reduced tillage systems is of a great concern for farmers. Bordoli and Mallarino (1998) suggested that there is decline in nutrient availability due to the accumulation of P at the soil surface in reduced tillage systems, especially if dry conditions persist near the soil surface. Limited soil moisture limits the movement of nutrient and inhibits plant growth. Soil P recommendations based on sampling top 5 cm may sometimes result misleading fertilizer recommendations. Research conducted by Schawb et al. (2006) in southeast Kansas suggested that soil test phosphorus (STP) measured by Bray 1-P method (Bray and Kurtz, 1945) is frequently two to three times higher in the surface 0 to 5 cm layer than in the 5 to 10 cm layer in no till system. Deep banding and starter application of P fertilizers is thought to be beneficial in reduced tillage systems. Starter application of fertilizer has been a common practice to enhance plant nutrient availability in early stages of plant growth. Duiker and Beege (2005) suggested that there may be less need for P starter fertilizer injection in long term no till due to high available P in the surface 5 cm where seed is placed. Bordoli and

Mallarino (1998) recommended that deep placement of nutrients below the first 5 to 10 cm of the soils should be superior to other placements when nutrient stratification was a concern. However, inconsistent results were obtained regarding effects of tillage and granular fertilizer surface and deep band placement on crop growth and yield (Schawb, 2006). Use of liquid P fertilizers in such reduced tillage system is less frequently practiced and may be a suitable alternative to increase P availability. Holloway et al. (2001) reported that fluid monoammonium phosphate was 4 to 5 times as effective as granular monoammonium phosphate in field trials done in calcareous soils of Australia. Similar results were obtained by McBeath et al. (2005). Lombi et al. (2004) suggested that liquid form of P fertilizers are more effective in Australian calcareous soils than their counterpart granular forms, and are thus more available to the crops. Liquid fertilizers showed higher diffusion through soils thereby reducing P precipitation in highly calcareous soil. Use of liquid P fertilizers might be helpful in reducing P precipitation in acidic soils as well, especially for P accumulated surface soils found in no or reduced till system. The use of liquid form of P fertilizers in reduced tillage system is less frequent as compared to the granular P fertilizers. However, deep placement of liquid fertilizers may be a better alternative for no-till systems.

1.8 Methods of P Analysis

There are various methods to obtain total or different fractions of P in soils. Selection of suitable method based on its efficiency, required criteria and availability of resources is the main key for quality data collection. This section will mainly focus on total and available P determination methods used for this thesis study.

1.8.1 Total Phosphorus

Total P content of soil is low averaging up to 1 %. There are several methods used for determination of total P in soil (Bray and Kurtz, 1945; Muir, 1952; Jackson, 1958; Syers et al., 1968; Sommers and Nelson, 1972; Dick and Tabatabai, 1977; Bremner and Mulvaney, 1982; Olsen and Sommers, 1982; Bowman, 1988). Salicylic acid thiosulfate modification of Kjeldhal digestion method suggested by Bremner and Mulvaney(1982) is widely used for total P determination. This method is widely accepted, rapid and gives better results as compared to other acid digestion methods (Amin and Flowers, 2004). In this method, standard amount (0.25g) of soil samples is treated with salicylic-sulfuric acid mixture. Upon digestion at high temperature (380 ^{o}C) acid mixture, P from organic and inorganic components in soils breaks down and gets released into the acid mixture. Sodium thiosulfate is a reducing agent and is added to increases the rate of organic P decomposition. Organic P is extracted by boiling soil with concentrated salicylic sulfuric acid mixture. Potassium sulfate (K_2SO_4) raises the boiling temperature of acid and shortens the time of digestion. Copper sulfate ($CuSO_4$) is used as a catalyst to speed up the reaction (Bremner and Mulvaney, 1982). The digested samples are filtered and measured for total P concentration.

1.8.2 Available Phosphorus

Plant availability of P is a main limiting factor for crop production. The initial level of available P in soil is important to estimate fertilizer required to be applied to meet plant growth needs and maximize profitability. There are various methods used for determination of available P in soil. The conventional method of estimation of available P practiced by most of agronomic stations in the United States is soil test P (STP). However, more sophisticated and robust techniques like resin extractable P (Saggar et al., 1990), isotope dilution (Salcedo et al., 1991), and diffusive gradient thin (DGT) film (Davison and Zhang, 1994) have been developed for estimation of plant available P. These more involved techniques are currently laboratory based and more commonly in use for research purposes only.

1.8.2.1 Soil Test P Methods

The estimated amount of plant available soil P is referred to as soil test P. Representative samples from plow depth (0 to 15 cm) are taken and analyzed using commonly used analytical methods to quantify soil P known as soil test phosphorus (STP) methods. The main purpose of soil P testing is to identify the optimum soil test P concentration required for plant growth to predict the need for additional fertilization or manuring. Sims et al. (1998) stated the other objectives of soil P testing was to: (i) “index” the P supplying capacity of soils, thus estimating the time before fertilization would again be required; (ii) group soils, in terms of the likelihood of an economic response to P, based on their physical and chemical properties; and, (iii) to identify when soils are sufficiently excessive in P to contribute to nonpoint source pollution of surface waters.

The common STP methods used for fertilizer recommendation are listed in table1.1.

Table 1.1 Common soil test phosphorus (P) methods and the associated chemical extractants, pH values, and primary uses (adapted from Sibbesen and Sharpley, 1997).

Soil Test P method	Chemical Extractant	pH	Primary uses	References
Bray -1	$NH_4F + HCl$	3.0	Fertilizer recommendation for acid and neutral soils.	Bray and Kurtz, 1945
Mehlich-1	$HCl + H_2SO_4$	1.2	Multi-element extraction for fertilizer recommendations on acid and neutral soils.	Mehlich, 1953
Mehlich-3	$CH_3COOH + NH_4NO_3 + NH_4F + HNO_3 + EDTA$	2.5	Multi-element extractant for fertilizer recommendations on most soils.	Mehlich, 1984
Olsen	$NaHCO_3$	8.5	Fertilizer recommendations for calcareous soils.	Watanabe and Olsen, 1965

1.8.2.2 Resin Extractable Phosphorus

Conventional methods for determination of soil test P, generally use wide range of chemical reactants and may fail to extract plant available P if used for soil types for which they are not appropriate (Sharpley, 1991). For example, Mehlich-3 method (Mehlich, 1984) is a widely adopted soil test method in the U.S. This method uses chemical extractant; and does underestimate P in soils with higher calcium carbonate (Mallariono and Atia, 2005). Procedures developed to overcome the limitations of chemical extractant include anion resin exchange membrane (Saggar et al., 1990). Unlike conventional soil test P methods resin exchange membrane does not use chemical extractant and it extracts P from soil at its field pH. Anion-exchange resin impregnated membranes has been used for determination of bioavailable P by several researchers (Abrams and Jarrell, 1992; Saggar et al., 1992; Qian et al., 1992; Myers et al., 2005). The soil nutrients are in equilibrium with soil solution and plant roots. Resin P method in laboratory mimics the soil/soil solution/plant root model. Anion exchange resins takes up the nutrients from the soil as plant roots take nutrients and therefore, may be able to mimic the true plant root P acquisition process as compared to the soil test P methods commonly used to determine plant available P. Anion exchange resins saturated with bicarbonate ions have greater affinity for phosphate ions, so phosphate from soil solution is taken by resin exchange membranes. The amount of P adsorbed on resin membrane is proportional to the plant available P. They have advantages over chemical extractants such as those used in Bray1 (Bray and Kurtz, 1945), Mehlich (Mehlich, 1984), and the Olsen procedures (Watanabe and Olsen, 1965). The resin extraction is done in water maintaining natural soil pH and this method is applicable for all kinds of soil regardless of pH. The resin based P extraction is found to be better predictor of soil available P (Sharpley, 1991; Sims et al., 2000; Mallarino and Atia., 2005) but adopting it as a routine soil testing method is still limited. Reports indicates that anion exchange resin have been used as many as 50 to 500 times without losing their extraction efficiency or showing detrimental structural effects (Saggar et al., 1990; Schoenau and Huang , 1991). Silvia and Raji (1999) found that the ion exchange resin method was better correlated with P uptake than the other methods (Olsen, Bray 1, Mehlich 1, Morgan) and it is suitable for all types of soil, both acidic and alkaline. Therefore, anion exchange resin is well suited for routine soil P analysis as it is low cost, simple, and consistent across all soil types. Resin extractable P method is a good alternative for P determination in soils that could improve P fertilizer recommendation and advanced fertilization technologies.

1.8.2.3 Isotope dilution techniques

Isotope dilution technique can be used for estimating plant available P in soil and it is also known as *E*-value. Isotopically exchangeable P (or *E*-value) can be measured by adding ^{32}P or ^{33}P- orthophosphate to a soil suspension, and measuring the decrease of radioactivity over time. The use of radioactive P (^{32}P or ^{33}P) is helpful to evaluate the rates governing phosphate equilibrium between the solution and the solid phases of the soil. It allows measurement of the amount of orthophosphate that can be transferred from the soil solid to the solution in a given time and therefore give information about plant availability (Fardeau, 1993). This method also provides an opportunity to gain an insight into the mechanism of P retention in soil (Lombi et al., 2004) as the E-values allows separation of chemical processes in which P remains exchangeable (such as outer-sphere or diffuse swarm adsorption processes) from the processes where P become “fixed” or non-exchangeable (such as precipitation, intraparticle diffusion, and/or inner-sphere complexed). The primary advantage of this technique is its great sensitivity of measurement for direct assessment of available P in soil. However, short half-life of ^{32}P isotope, safety issues and skilled labor for handling and measurement has limited its widespread use.

1.9 Speciation of Phosphorus

Speciation of an element means determination of the exact chemical form or compound in which an element occurs in a sample (IUPAC, 2000), for example determination of whether P occurs in the form of Ca-, Al-, or Fe-P or as part of an organic molecule, and the quantitative distribution of the different chemical forms of P within a system. The availability, mobility, transport and fate of element is regulated by its chemical form (speciation). Individual metal has its different chemical activity and fate depending upon oxidation state which determines its fate and toxicity in the environment. For example, chromium (III) can be considered as an essential element required for normal glucose metabolism; however, chromium (VI) is genotoxic and carcinogenic. For heavy metals like lead, arsenic, mercury speciation helps to develop effective remedial plans and risk management at contaminated sites where as for elements like P; speciation helps to develop soil and fertilizer management approach ensuring highest bioavailability to crops while protecting the environment. There are different methods for speciation of P in soil. Indirect methods of speciation for P include (i) P fractionation, (i) Scanning electron microscope with energy dispersive x-ray analyzer (SEM- EDXA), and solubility equilibria approach. The direct methods of speciation include (i) X-ray diffraction (XRD), (ii) X-ray absorption spectroscopy (XAS), (iii) Nuclear Magnetic resonance (NMR) spectroscopy, and (iv) Fourier transform infrared resonance (FTIR) spectroscopy.

1.9.1 Indirect Methods

Indirect methods such as solubility equilibria and sequential extraction or fractionation procedures although non-definitive, are used to determine possible solid phase associations of element of interest in soil or sediment. These methods are more easily adopted and accessible as compared to the direct methods. However, for accurate interpretation of the results obtained using indirect methods often need to be combined with complementary direct speciation results.

1.9.1.1 Solubility equilibrium approach

Solubility equilibria approach can be used to predict the activities of the element in the soil solution, and to indirectly estimate the solid/mineral phases present in the soil (Essington, 2004). This approach is based on the major assumption that these solid phases are in equilibrium with ions in soil solution or come to a steady-state (Pierzynski, 1991). McDowell et al. (2003) used solubility equilibrium approach for identification of P forms in equilibrium with calcium chloride solution. Chemical activities were calculated using the MINTEQA2 chemical speciation model. Data from NMR and solubility experiment, they found that soil solution P is controlled by Ca-P, Al-P and Fe-P species. This approach has also been used for speciation of reduced P in the natural environment (sediment, sewage and agricultural processes) (Hanrahan et al., 2004).

1.9.2.1 Scanning Electron Microscope-Energy Dispersive X-ray Analysis (SEM- EDXA)

A scanning electron microscope (SEM) is a high magnification microscope and often comes in combination with energy dispersive spectroscopy. Scanning electron microscope is used to study topographic, morphological, compositional and crystallographic information (White, 2008). It can also be used to do chemical quantitative analysis of unknown materials.

Therefore, it is a very useful technique for soil scientists. This technique can be used for identification and morphological studies of soil minerals (White, 2008) and to study surface characteristics of original and incubated fertilizer granules in soils (Lombi et al., 2004; Hettiarachchi et al., 2008). Scanning electron microscope uses primary electron beam generated from an electron source. Primary electron beam is accelerated and demagnified into a smaller beam which then deflected in a raster fashion over the area to be imaged. The interactions between electron beam and sample generates variety of signals. These signals include secondary electrons, backscattered electrons which produce secondary and back scattered images (Susan, 2011). Secondary electron images are useful for morphological and topographical information of samples while backscattered electron images are essentially mapping out the density of the surface of the sample. The backscattered mode is useful in getting elemental contrast information as low-atomic weight areas of the sample will not emit as much backscattered electrons as a high atomic area of a sample. This technique has been widely used by researchers in soil science (Welter et al., 1998; Appel et al., 2003; Cao et al., 2003; Lombi et al., 2004; Hettiarachchi et al., 2008). Usually SEM units are coupled with energy dispersive X-ray spectrometer (EDS) detector or a wavelength dispersive x-ray spectrometer detector (WDS) and they facilitate determination of chemical composition of micro volumes of samples. Scanning electron microscopy coupled with energy or wavelength dispersive spectrometer detectors therefore, can be used to gather information about different solid phases present in soil samples. Because of poor detection limits (about 1000 mg/kg) of these detectors only the major elements in a small sample volume can be detected. This would however suitable for gathering information from dissolving fertilizer granules in soils or soils right adjacent to the granules as they generally have high concentrations of the elements of interest. Pierzynski et al. (1990) used scanning electron microscopy technique for the identification of P solid phases after excessive P application in Plainfield loamy sand and Blount silt loam. Through morphological analysis of < 2.2 Mg m^{-3} density separates of clay sized fractions of soil particles, they suggested that P –rich minerals exist as discrete particles as well as coatings on other particles. Energy dispersive X-ray spectra analysis of particle coating showed variable amounts of Al, Si, P, and Fe. Prochnow et al. (2001) used SEM-EDXA and X-ray diffraction technique for identification of compounds present in single superphosphate produced from Brazilian phosphate rock. They were able to identify various compounds like calcium phosphate monohydrate, triiron potassium octahydrogen hexaphosphate hexahydrate, triiron 15-hydrogen octaphosphate tetrahydrate, triiron potassium 14-hydrogen octaphosphate tetrahydrate and barium sulfate. In summary, this technique gives us general information regarding fertilizer reactions products;however, it is less sensitive to study minerals formed in soils after fertilizer application especially when the concentrations are below 1000 ppm.

1.9.1.2 Phosphorus Fractionation

Knowledge of the dominant solid P species in soils, biosolids and sediments, is useful to understand the fate and transport of the applied P and helps to develop better P management practices. Chemical fractionation technique is a most commonly used method for partitioning of P into different fractions of P such as Fe, Al and Ca-P in soil. The most popular fractionation techniques widely used by researchers are the methods suggested by Chang and Jackson (1957), Hedley et al. (1982) and Tiessen et al. (1984). These fractionation techniques are being used for many years. Identification of P compounds can provide valuable information for P management. Fractionation or sequential extraction procedures utilize the ability of various chemical reagents to selectively solubilize the Al, Fe, or Ca phosphate phases contained in the soil. This technique has been found to be very useful in revealing the controlling phases of soil P dynamics (Beauchemin et al., 2003; Kashem et al., 2004; Ajiboye 2007). The Hedley fractionation assigned P fractions on the basis of their different solubility in extractants of increasing strength; in other words, these P fractions are "operationally defined". In this method, $NaHCO_3$-P was tentatively assigned to inorganic P sorbed on crystalline Al and Fe oxides and easily mineralized organic P, NaOH-P to inorganic P sorbed to amorphous Al and Fe oxides and stable organic P, and HCl-P to Ca-P-compounds (Tiessen et al., 1984). However, a clear confirmation that the above extractants solubilized exclusively the target P fraction is still lacking (Toor et al., 2006). Tiessen et al. (1994) observed that the nature of organic P estimated from fractionation is less well defined as compared to that of the inorganic fractionation. They emphasized that it is unlikely that any extraction procedure can provide an exact separation of different P compounds. For better interpretation of data, the results from chemical fractionation are complementarily coupled with NMR and XANES techniques (Beauchemin et al., 2003; Ajiboye 2007).

1.9.2 Direct Methods

The speciation of P minerals is possible without the use of harsh chemical extractants by use of various direct speciation techniques. Various X-ray based techniques are becoming popular these days for speciation of organic and inorganic forms of P in soil, sediments, biosolids, and agro byproducts. However, these techniques are sophisticated and may not be regularly accessible.

1.9.2.2 X-ray Diffraction (XRD)

X-ray diffraction is a rapid analytical technique that provides detail information about the atomic structure of crystalline substance. It is a powerful tool to identify minerals in rocks and soils (Harris and White, 2008). X-ray diffractometer works on the principle of Bragg's law. The essential criteria for diffraction to occur for wave of any wavelength is that the distance between scattering centers should be the same as the wavelength of the waves being scattered. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. It is done by comparison of d-spacings with standard reference patterns (Moore and Reynolds, 1997).

In soils, minerals may occur in clay fraction or in non clay fraction. Most of the P minerals occur in clay sized fractions. So, particle size separation may be required for identification of those minerals. Samples should be finely ground, homogenous and solid species needs to be sufficiently crystalline for XRD analysis. In some cases, it is required to remove iron oxides, organic materials to get better particle or clay separation and saturation of clay minerals with different cations is needed for differentiating clay minerals (Moore and Reynolds, 1997). It is a powerful tool for identification of minerals. Most of the P minerals in soils are in clay fractions which are too small to apply optical crystallographic methods. So, XRD is an important tool for identification of clay sized minerals in soil (Harris and White, 2008). However, P minerals are no that abundant in soil, so, it may be difficult to identify all P minerals using XRD. Pierzynski et al. (1990) used XRD technique in conjugation with other optical electron microscope technique for isolation and characterization phosphate minerals in clay sized fractions of excessively fertilized soils. However, this technique was not successful in identifying discrete P minerals.

Gungor et al. (2007) used XRD to identify minerals present in dairy manure; however extensive use of XRD for determination of fertilizer reaction products in soil is limited due to lower concentration of those minerals in soil as well as their poor crystallinity. Cao et al. (2003) has used XRD for mineralogical characterization of P applied soil samples in lead contaminated soils. They found that amendment of Pb contaminated soil with P was successful in conversion of lead from non residual to residual form in pyromorphite like form as identified by XRD. However, use of XRD only for identification of reaction products in soil is limited due to relatively lower concentration of those minerals to be detected. Amorphous form of P (or any other) minerals cannot be identified by XRD. For better interpretation of results XRD has been found used complementarily with other direct methods of P speciation.

1.9.2.3 Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Resonance (FTIR) Spectroscopy

Nuclear magnetic resonance (NMR) provides semiquantitative and quantitative information and is useful to analyze both liquid- and solid-state samples. It exploits the property of nuclear spin. The nuclei of element behave like a magnet. In absence of magnetic field, the poles of these nuclei are randomly aligned. However, when magnetic field is applied, certain nuclei align with the field (low energy spin) or against the field (high energy spin) (Essington, 2004).

A typical FTIR spectrometer obtains an infrared spectrum by collecting the interferogram of a sample signal, which contains all the infrared frequencies, applies the fourier transform to the digitized signal, and outputs the spectrum (Griffiths and de Haseth 1986). Pierzynski et al. (1990) used FTIR technique in conjugation with XRD and SEM technique for isolation and characterization phosphate minerals in clay sized fractions of excessively fertilized soils. However, this technique was not successful in identifying discrete P minerals.

These techniques are powerful tool for evaluation of metal speciation and transformation mechanism of P in soil, animal manure and other environmental samples (Zongqui et al. 2007). They used both of these techniques for identification of organic P compounds like phytase. Fourier transform infrared reflectance spectroscopy provided highly specific information about adsorbed species of PO_4 on mineral surface based on unique absorption bands at 1090 and 1150 cm-1 for Al- and Fe-phosphate respectively (He et al,2006). Jingdong et al. (2008) has used both of these techniques to study the influence of animal manure application on the chemical structures of soil organic matter. McBeath et al. (2006) used solid state ^{31}P NMR for identification of hydrolysis product of polyphosphates in soil. They found that NMR technique was able to quantify more of the pyrophosphate added than the extraction method. However, there is less use of these methods for identification of inorganic P minerals due to their lower concentration in soils. Despite their wide application, NMR technique has limitation of determining various inorganic P species (Negassa and Kruse, 2010) in soils. The issues with use of NMR in soil samples is due to presence of magnetic components like Fe(III) and Mn(II, IV) in common environmental matrices which interact with the external magnetic field and detiorate the data quality of solid- state NMR spectra (Kizewski et al., 2010). The main disadvantages of FTIR are the lengthy preparation time required to prepare the pellets and the fact that it is difficult to obtain quantitative results. Also, since only a few mg of soils are used for the preparation of each pellet, the resulting spectrum may not be representative of the bulk soil.

1.9.2.4 X- ray Absorption Fine Structure Spectroscopy (XAFS)

X-ray absorption fine structure spectroscopy (XAFS) technique, also referred as X-ray absorption spectroscopy (XAS), has been applied as a tool for speciation of elements in soils, sediments and biological samples. It is an advanced technique used for direct, *in situ* (no sample preparation) speciation of solid phases (i.e., fertilizer reaction products) regardless of crystallinity or form (i.e., minerals, adsorbed phases). X ray absorption fine structure spectroscopy gives information regarding coordination chemistry, oxidation state of the element of interest and the interatomic distances, coordination number and species of the atoms in the surrounding proximity to the element. This technique works well even at low concentration with minimal sample amount for any element. It is the modulation of the x-ray absorption coefficient at energies near and above an x-ray absorption edge (Newville, 2004). The basic principle behind XAFS is, when X-ray is absorbed by atom, core level of electrons of the atom get ejected leaving an atom in excited state with an empty electronic level. Excess energy form the x-ray is given to the ejected photo-electron. To fulfill this core space, a higher level core electron drops into the core hole, and fluorescent x-ray is emitted.

X-ray absorption spectroscopy can be broken down into two regimes known as (i) X ray absorption near edge structure spectroscopy (XANES) and, (ii) Extended X-ray absorption fine structure (EXAFS) Reviews on principles and theory of XAFS and XANES are found in literature (Durham, 1988; Fendorf et al., 1994; Fendorf and Sparks, 1996) and Matt Newville website (www.xafs.org). This review will only focus on XANES analysis in details.

1.9.2.4.1 X-ray Absorption Near Edge Structure Spectroscopy (XANES)

As stated before for XAS, X-ray absorption near edge structure spectroscopy, is a technique that can be used for heterogeneous soil mixture to identify crystalline or amorphous solid phases in situ. This cannot be achieved by the use of XRD. X-ray absorption near edge structure consists of pre edge region (approximately 20 eV before the edge) and post edge region (approximately 100 eV after the edge) (Kelly et al., 2008). The region beyond 50 eV is generally the focus of EXAFS study. Speciation of P using XANES is possible without using harsh chemical extractants. X-ray absorption near edge structure spectroscopy is not only element specific, also nondestructive technique (Beauchemin et al., 2003) providing information on local molecular bonding environment of the element (Fendorf and Sparks, 1996). Although XANES is a sophisticated technique used for determining the speciation of elements in soils and sediments, travel to synchrotron sources is required for data collection and therefore, still considered as a limitedly used technique.

A XANES spectrum is element specific and sensitive to the local structure and physical state of the element. This technique has then been widely used for speciation of organic and inorganic P in soil, sediments and agricultural byproducts (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003; Lombi et al., 2006; Ajiboye et al., 2008; Kruse and Leinweber, 2008). Major disadvantage of XANES (or XAS) analysis is this techniques is not species specific. Therefore, XANES finger printing methods such as linear combination fitting have been used to recreate or match the sample (unknown) spectrum using known set of standard spectra. Lombi et al. (2006) used XANES for identification of reaction products of granular and fluid P fertilizers in a highly calcareous soil. They found that in this calcareous soil (770 g kg^{-1} of Ca as $CaCO_3$) P is associated with Ca rather than Fe. Precipitation of P in the form of octacalcium phosphate and apatite like compounds was most likely and the dominant mechanism decreasing P isotopic exchangeability of granular fertilizers while P precipitation was found less prominent in case of added fluid fertilizers. Kruse and Leinweber (2008) used XANES to test if P K-

XANES reflected differences in P fractions in fen peat due to sequential extraction and peat degradation. They found that use of sulfuric acid in extraction led to the disappearance of spectral features of Ca and Mg phosphates in peat. So, they proposed a combined sequential fractionation and spectroscopic approach to overcome the limitations of both methods. X-ray absorption near edge structure spectroscopy technology has been used for speciation of P in poultry litter (Peak et al., 2002; Toor et al., 2005), manure and manure amended soil (Sato et al., 2005; Gungor et al., 2007), organic amendments (Ajiboye et al., 2008), and agro byproducts (Kruse et al., 2010).

Sato et al. (2005) assessed forms of Ca-P formed in an originally acidic soil in response to different length of mostly poultry manure applications using XANES spectroscopy. There were not any crystalline Ca-P minerals formed in long term P amended soils. In unamended soils, P was found mainly associated with Fe compounds like strengite whereas in short term manure history, P was found associated with Fe and some soluble Ca-P species. However, in long term manure applied soil, Ca-P forms were the dominant species with transformation from soluble to more stable forms like β-tricalcium phosphate.

Quality of the XANES data is a main key for better speciation results of soil samples. This is especially true for some species due to similarities in their XANES spectra. The overall quality of XANES spectra that affect uncertainties in speciation of P in soils depends upon, (i) the inherent uncertainty in selecting standards to fit, (ii) the lack of distinguishing spectral features for various P species, and (ii) spectral data quality (Kizewski et al., 2010). Therefore for better interpretation of results, XANES technique has been found to be used complementary with fractionation technique (Beauchemin et al., 2003; Lombi et al., 2005; Kruse and Leinweber 2008).

1.10 Summary

Despite various benefits of the reduced tillage system, P management in such systems is still a major concern for the reduced till farmers. Broadcast application of fertilizer P is a major practice used by farmers to supply nutrients to plants. Repeated addition of P fertilizers may satisfy the plant P need; however, over time due to accumulation of P in soil, efficiency of applied P fertilizers might decrease due to increased soil test P levels in the soil. Moreover, higher load of P in surface soil is a major environmental concern as surface runoff of nutrient is a major threat to aquatic ecosystem. Therefore, deep placement or banding of liquid P fertilizers could be a good alternative for no- or reduced-tillage systems. Deep placement of P fertilizer may help enhancing efficiency of P fertilizer and to minimize environmental issues related to high P application by avoiding enrichment of P at the soil surface. It may also be worthwhile to compare the relative effectiveness and the reaction products of granular and liquid P fertilizers in no- or reduced-tillage systems with broadcasted and deep banded P fertilizers. Liquid P may lead to high efficiency or low P "fixation" through enhanced diffusion in soils compared to the granular P. The study of possible reaction products formed after broadcast and deep band application of P fertilizers would help us to understand the fate of the applied fertilizer P, which would help us to better manage P in such systems.

1.11 Objectives

The objective of this thesis research was to study fertilizer placement (broadcast vs. deep placed/banded); and source (granular vs. liquid) effect on (i) reaction products of P, and (ii) plant available P over time (5wk and 6 months), and linking plant available P information to soil P chemistry.

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Chapter 2 - Speciation of Phosphorus in a Fertilized, Reduced Till Soil System: In-Field Treatment Incubation Study

Abstract

Knowledge of the dominant solid phosphorus (P) species present in soil following application of P fertilizers and linking that to potential P availability would help us to understand and efficiently manage P in reduced tillage systems. The objective of this research was to study the influence of placement (broadcast- vs. deep band-P), fertilizer source (granular- versus liquid-P) and time on reaction products of P under field conditions. Changes in soil pH, resin extractable P, total P, and speciation of P were determined at different distances from the point of fertilizer application at 5 weeks and 6 months after P application (at rate 75 kg/ha) to a soil system that was under long-term reduced tillage. Resin extractable P was lower for broadcast treatments as compared to deep band treatments for both the time periods. Resin extractable P was greater for the liquid-P treated soils when compared to the granular-P treated soils. Speciation results showed that granular-P fertilizers tended to form Fe-P like forms whereas liquid forms found to remain in adsorbed-P like forms in soil after 5 weeks of application. Over 6 month time period, reaction products of broadcast-granular and broadcast-liquid and deep band-granular fertilizers transformed to Ca-phosphate- or mixtures of Ca-, Fe-, Al- and adsorbed-phosphate-like forms while deep band-liquid P continued to remain mainly as adsorbed-P like forms.

2.1 Introduction

Phosphorus is an essential element for all life forms. However, it is one of the most difficult nutrients for plants to obtain from the soil and therefore, often represents a limiting factor to agricultural production. While P is needed in adequate quantities for optimal crop production, it has also been associated with eutrophication of surface water bodies. In general more total P creates more environmental concern. Million of tones of P are applied to the soils annually, however, plants do not have access to all the P that is applied to the soil. Over time, part of the applied P will be taken up by plants while majority of P reacts with other soil components to from insoluble minerals, sorbed onto mineral or organic surfaces (Hansen et al., 2002). In acidic soils, most of the applied P combines with soil Al, Fe forming minerals like variscite, strengite and vivianite (Lindsay, 1979., Ghosh et al., 1996) whereas in calcareous soil it combines with soil Ca forming minerals like dicalcium phosphate dihydrate, monocalcium phosphate and hydroxyapatite (Lindsay, 1979, Tunesi et al., 1999). Adoption of various tillage systems might affect the availability and fate of P in soil system. Reduced tillage crop production is getting more attention recent days from farmers in many regions of the U.S. and on farms worldwide (Hobbs et al., 2008). Despite various advantages of reduced tillage systems, it has been found that P applications (granular forms) leads to an accumulation of available P on the surface 0 to 5 cm soil layer and a depletion of available P deeper in the profile (Schwab et al., 2006). Phosphorus stratified at surface soil may support plant root growth under moist condition at initial plant growth stage; however, roots explore deep soil layers for nutrient and moisture as surface soil dry during warm summer. Bordoli and Mallarino (1998) recommended that deep placement of nutrients below the first 5 to 10 cm of the soils should be superior to other placements when nutrient stratification, coupled with topsoil moisture deficit, reduces nutrient uptake from shallow soil layers. Inconsistent results have been obtained from the research conducted to study the effects of tillage and deeper placement of P fertilizers on grain yields of crops grown in Kansas (Schwab et al., 2006). High proportion of applied P is rapidly converted to insoluble phosphates that plants have virtually no access. Due to lack of soil mixing this problem could be particularly pronounced under special management practices such as no-till systems (Schawb et al. 2006). Deposition of crop residues and broadcast application of fertilizers further enhances the stratification of P in soil surface and therefore, P availability in sub surface soil is a main concern in reduced tillage management systems.

Lombi et al. (2004) suggested that liquid forms of P fertilizers are more efficient in highly calcareous Australian soils than their granular form, and are thus more available to the crops. Holloway et al. (2001) reported that fluid monoammonium phosphate was 4 to 5 times as effective as granular monoammonium phosphate in field trials conducted on same type of soils. Similar results were also obtained by McBeath et al. (2005). The superior performance of liquid P was attributed to the greater outward diffusion of P from the point of P placement with liquid compared to granules, reducing the chances of creating micro environments with supersaturated soil solutions with respect to various solid Ca-P species (Lombi et al., 2004; Hettiarachchi et al., 2006). The use of liquid form of P fertilizers in reduced tillage system is less frequent as compared to granular P fertilizers. Thus, surface or deep band placement of fluid fertilizers may be a suitable alternative for reduced tillage systems.

Techniques like fractionation methods have been widely used to reveal controlling phase of soil P samples. Sequential extraction technique as suggested by Hedley et al. (1982) is one of the widely used methods to investigate different P forms in soil (Beauchemin et al., 2003; Kashem et al., 2004; Ajiboye 2007). However, issues with use of harsh chemicals to extract P have been a major concern. Synchrotron based X-ray absorption near edge structure (XANES) offers an advantage for identification of P solid species without any chemical treatment to samples. It is an advanced technique used for direct, *in situ* (no sample preparation) speciation of P in soil and sediments. Hesterberg et al. (1999) have used P-Kedge XANES for speciation of adsorbed and solid state P in agricultural soils. Beauchemin et al. (2003) combined linear combination fitting of XANES with principal component analysis (PCA) to better understand P speciation in mineral and manure P applied slightly acidic and alkaline soils of Canada. The major constraint behind use of this technique is its limited availability. It requires travel to synchrotron sources and proposal based approval for its use. However, this technique has got more attention these days for P speciation in soil, sediments and environmental samples (Arai and Sparks, 2007).

Knowledge of the dominant solid P species present in soil following application of P fertilizers and linking that to potential P availability would help us to better understand and efficiently manage P in reduced tillage systems. Information about dominant P species formed in soil would help us to identify P fertilizers and placement methods that would result higher availability in soil. Additionally, knowledge of solid P species may help us to change solubility of precipitated P forms by altering soil pH conditions to increase availability. This research aims to investigate how different forms of P reacts in reduced tillage soil at the molecular level using synchrotron based X-ray techniques (XANES). The objectives of this study were to: 1) study fertilizer placement (broadcast vs. deep placed/banded); and source (granular vs. liquid) effect on reaction products of P at different time periods (5wk and 6 months), 2) study availability of P at different distances from the point of fertilizer application, and 3) developing relationship between P chemistry and P availability.

2.2 Materials and Methods

2.2.1 Site Description, Soil and Fertilizers

A field based study was conducted at agronomy North farm site located in Manhattan, Kansas. This site has a history of more than 10 years of reduced tillage. The soil at this site is classified as a smolan silt loam (fine, smectitic, mesic Pachic Argiustolls). Granular monoammonium phosphate (MAP) and technical grade monoammonium phosphate (TGMAP) in liquid form were used as P fertilizer sources. Nitrogen (N) was applied at the rate of 200kg/ha and P was applied at the rate of 75 kg/ha. Phosphorus is often applied with N to supply plant nutritional requirements. Nitrogen fertilizers that are applied along with P fertilizers may have potential to influence P chemistry in the soil. Thus urea was applied to all the treatments to supply N by balancing N from MAP for granular and liquid MAP fertilizer treatments. The general properties of soil used for the study are given in Table 2.1. Soil pH was measured in 1:5 soil:water extract (Wateson and Brown, 1998) and cation exchange capacity was determined using summation method as described by Chapman (1965). Mehlich 3 P was determined following procedures described by Frank et al. (1998). Ammonium acetate extractable calcium (Ca) was determined using procedures described by Warncke and Brown (1998). Extractable iron (Fe) and Manganese (Mn) were determined using DTPA extraction technique as described by Whitney (1998).Potassium chloride extractable aluminum (Al) was determined following the procedures described by Mc Lean (1965). Total P and N were determined following the method suggested by Bremner and Mulvaney (1982). Organic matter content was determined following modified Walkley-Black method as described by Combs and Nathan (1998) with “heat of dilution” modification. Particle size distribution was determined using a modification of the pipet method of Kilmer and Alexander (1949) and method 3A1 form the Soil Survey Laboratory Methods Manual (Soil Survey Laboratory Staff, 2004).

2.2.2 Experimental Approach

The treatments structure included;

1. Urea Broadcast (Control),
2. Urea Deepband (Control),
3. MAP Broadcast,
4. MAP Deepband,
5. TGMAP Broadcast, and
6. TGMAP Deepband.

Experimental design was a randomized complete block design with five replications. The plot size was 5’ x 8’ with 3’ alley between the plots. Broadcast treatments were applied on the surface and gently mixed, whereas deep band treatments were applied approximately at 10 cm depth in two rows per plot using tractor driven disc coulter with arrangement for running a twine on deep banded zone for relocating the exact position for later sampling. Soil samples were collected at 5 weeks and 6 months from treatment application time. Sampling was done by extracting 30 cm soil core using probe and separating every 2.5 cm long soil sections for separate analysis. Six representative samples from each plot were taken and mixed depthwise. Soil samples were then air dried and sieved <2mm prior to analysis. For broadcast treatments top three layers i.e. 0-2.5, 2.5-5 and 5-7.5 cm soil samples were analyzed, and for deep band treatments soil samples from 5-7.5, 7.5-10, 10-12.5 and 12.5-15 cm were analyzed.

2.2.3 Wet Chemical Analysis

The wet chemical based analysis included measurement of pH, total P and resin extractable P at different distances from the point of fertilizer application. Soil pH was determined by using 1:5 soil to water ratio (NCRRP, 1998). Total P was determined using modified salicylic sulfuric acid digestion method as described by Bremner and Mulvaney (1982) using inductively coupled plasma optical emission spectroscopy (ICP-OES). Resin extractable P was determined by following the procedure of Myers et al. (2005). A resin membrane BDH product no.55164 S was used for resin P extraction procedure (U.S. distributor: CTL Scientific Supply Corporation, 1016-3 Grand Blvd., Deer Park, NY 11729). The resin membrane comes in pack of six of 12.5 x 12.5 cm sheets. The resin membrane was cut into 5 cm x 2.5 cm saturated with 0.5 M $NaHCO_3$ and two strips were used for 1.0 g of soil used for extraction. Phosphorus was extracted as described by Myers et al., 2005. Basically, 1.0 g of soil was placed in polyethylene container containing 80 ml of water. Two resin strips were added in the container and shaken in orbital shaker for 24 hours. After shaking, the resin stripes were removed from the container, washed with de ionized water to remove any adhering soil particles and transferred to other polyethylene container containing 50 ml of 0.5 M hydrochloric acid (HCl). The resin strips in 0.5 M HCL solution were further shaken for additional 1.5 and filtered using whatman filter paper#2 and analyzed colorimetrically using method of Murphy and Riley (1962).

2.2.4 Statistical Analysis

All data were analyzed by proc mixed procedure using SAS software (SAS 9.1, 2007). Pairwise Bonferroni method was used for pairwise comparisons between treatments at $\alpha = 0.05$ level of significance.

2.2.5 Speciation of Phosphorus

X-ray absorption near edge structure spectroscopy (XANES) was used for speciation of fertilizer reactions products in soils.

2.2.5.1 Phosphorus Standards

The phosphorus standards used in this study were purchased or synthesized. Berlinite ($AlPO_4$), brushite ($CaHPO_4•2H_2O$), hydroxyapatite ($Ca_5 (PO_4)_3(OH)$), monetite ($CaHPO_4$), and rock phosphate were purchased from Sigma Aldrich (St. Louis, MO). Strengite ($FePO_4•2H_2O$) was synthesized following the procedure of Dalas (1991). Strengite with different crystallinities were synthesized by mixing KH_2PO_4 and $Fe (NO_3)_3•9H_2O$ at ambient temperature and heated hydrothermally at 100°C for 24 h and 3 days. Variscite ($AlPO_4•2H_2O$) was synthesized following the procedure of Hsu and Sikora (1993). Vivianite and apatite standards were obtained from University of Adelaide, Australia. Phosphorus pentoxide (P_2O_5) was purchased from Alfa Aesar (Ward Hill, MA). Adsorbed phosphate on goethite and alumina were prepared following the procedure of Oh et al. (1999). Ferrihydrite and gibbsite adsorbed P were prepared following the procedure of Schwertmann and Cornell (1991). The purity of synthesized P standards was verified using XRD. The powdered phosphate standards were spread over double sided carbon tape and mounted on aluminum samples holders for XANES data collection.

2.2.5.2 Data Collection

Phosphorus K-edge XANES data were collected at Sector 9-BM-B, Advanced Photon Source (APS), Argonne National Laboratory, IL. The electron storage ring at the APS is operated at 7 GeV with maximum current of 100 mA. This beamline has energy range of 2.1-23 keV and is equipped with Si (III) monochromator with focused beam size 500µm x 500 µm. The sample compartment was He- purged and data were collected in fluorescence mode using Ge solid stage detector. Phosphorus pentoxide (P_2O_5) standard was used for monochromator calibration. Correction in any energy drifts caused by monochromator drifts were done by collecting spectra of P_2O_5 daily during run time. All samples and standards were calibrated using common energy scale by setting first derivative spectrum of apatite to 2149.25 eV for analysis.

Single replication of soil samples from top 0 to 2.5 cm for broadcast treatments and 7.5 to 10 cm depth for deep banded treatments was used for speciation study. The soil samples were air dried, ground to passed through <150 µm sieve. The samples were further finely grounded with agate mortar and pastel and soil pellets 4 mm in diameter were prepared using KBr quick press kit with 4mm die set (International Crystal Laboratories, Garfield, NJ) to compact samples for better signal. The samples were then mounted on teflon tape and fixed on aluminum sample holders ready for analysis. Four to six scans of samples were taken with scan range from 2110 to 2400 eV. The step size was 2.0 eV on pre edge region (2110 to 2140 eV), 0.125 eV in near edge region (2140 to 2165 eV) and 0.5 in post edge region (2165 to 2400 eV) with reading time of 3 to 6 seconds per point. Four to six scans of collected spectra for particular samples were averaged, the edge energy was calibrated, pre edge was subtracted, and the spectrum was normalized.

2.2.5.3 XANES Analysis

The XANES data were analyzed using Athena software version 0.8.056 (Ravel and Newville, 2005). Speciation was done using linear combination fitting (LCF). The linear combination XANES fitting procedure tried to reconstruct the sample (or experimental) spectra using all combinations of the standard spectra. The weighting factors were forced to sum to one and no energy shifts were permitted in LCF fitting. Out of all possible combinations, the combination with the lowest reduced χ^2 was chosen as the most likely set of components or the best fit. The fitting was done in the first derivative space using quinary (five) combinations of all standards relative to fitting range from -5 to 30 eV of the white line.

2.3 Results and Discussion

2.3.1 Wet Chemical Analysis

Mixed results (lower, higher or no significant difference) were observed for soil pH when comparing differences in soil pH among the urea added control plots and the both urea+ MAP (as granular or liquid) added plots (Figure 2.1). Acidification effects of MAP on soil pH have been reported by many researchers (Hanson and Westfall, 1985; Moody et al., 1995). However, hydrolysis of urea consumes two moles of protons for each mole of urea hydrolyzed, thereby resulting an increase in pH. So combination of these reactions (nitrification of NH_4^+ and hydrolysis of urea) in turn could result mixed effects on overall soil pH. At five weeks, soil pH in both urea and MAP (as granular or liquid) added broadcast and deep banded treatments were significantly lower (by about 0.6 to 1 units) than the original soil pH (5.9). However, soil pH of broadcast P treatments at six months showed that pH of six month samples was restored to initial soil pH. For the deep banded treatments, soil pH was lower (by about 0.2 to 0.6 units) when compared to the soils sampled from the same plots (i.e., that received same soil treatment) at 5 weeks. This could most likely be due to neutralization of treatment effects on soil pH with time and in-field seasonal variation of soil pH.

There was no difference in total P (Figure 2.2) for granular MAP and liquid MAP treatments and no any differences were observed with respect to time. This indicates that we were able to locate the fertilizer bands for sampling. Broadcast control had slightly higher total P concentration (average of 488.09 mg/kg) as compared to that of deep banded (average of 350.33 mg/kg) which may be attributed to the P stratification due to reduced tillage system.

We used resin extractable P to estimate potential available P in soils (Figure 2.3). The P supplying power of soils assessed by anionic exchange resins have been shown to correlate satisfactorily with P uptake and P concentration in the biomass. Therefore, resin extractable P can be considered as a reliable index of available P in soils (Myers et al., 1995). At five weeks, deep banded liquid MAP had highest resin extractable P as compared to other treatments, and the trend was same even after six months time period. Resin extractable P of the liquid MAP treatment was still significantly higher at six months (Figure 2.3). Comparing resin extractable P expressed as a percentage of total P at five weeks, in the urea broadcast (control) and urea deep band (control) plots, % resin extractable P concentrations were 3.4 and 9.2, respectively (Figure 2.4). At six months time, there was no significant difference between broadcast MAP and TGMAP treatments with control when compared as percentage resin extractable P (% of total P) (Figure 2.4). In the deep band P plots both the granular and liquid treatments, had a significantly higher % resin extractable P in comparison to the no P urea broadcast or no P urea deep band treatments. At 6 months, only the deep band liquid treatment, had a significantly higher % resin extractable P in comparison to the both no P urea broadcast or no P urea deep band treatments.

2.3.2 XANES Analyses

X-ray absorption near edge structure (XANES) spectra of standards used for the study are shown in the Figure 2.5. Spectra for Fe-phosphate standards showed a pre-edge feature between -5 and -2 eV relative to the white line which increased with increasing crystallinity. All calcium phosphate minerals have shoulder on the high energy side between +2 and +6 eV relative to the white line. Aluminum phosphate minerals are characterized by weak pre edge inflection at about -1 eV relative to the white line. These spectral features of phosphate bonded with calcium, aluminum and iron have been well documented previously (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003; Khare et al., 2005; Lombi et al., 2006). These spectral features help us to determine the association of phosphate with different elements in soil samples.

The results of linear combination fitting done in the first derivative space using quinary combinations of all standards relative to fitting range from -5 to 30 eV of the white line, is shown in Table 2.2. The XANES analysis suggested that the majority of P (69.2%) in the broadcast granular MAP treatment at 5 wk was vivianite ($Fe(II)_3(PO_4)_2 \bullet 8(H_2O)$)-like P form (Table 2.2). The spectra for broadcast liquid MAP- treated soil suggested two major forms of P in this soil, strengite ($FePO_4 \bullet 2H_2O$)- like (38.9%) and adsorbed P (43.4%). Similarly, for the deep banded granular-MAP-treated soils at 5 wk, the majority of P (64.5%) existed as vivianite-like form while adsorbed P accounted for the rest. The spectra of the deep band liquid MAP-treated soils suggested 46.7% of vivianite-like P and 53.4% as adsorbed-P (Table 2.2). Comparison of resin extractable P data with speciation results indicated that there was positive correlation of adsorbed P species with resin extractable P. For liquid P treatments with higher resin extractable P the dominant P species were in adsorbed P like forms. The linear combination of 5 weeks samples are shown in Figure 2.6.

Speciation results revealed that liquid MAP appeared to be in more “accessible” forms as compared to the granular MAP. It is most likely due to differences in diffusion of P from granular and liquid MAP. Lombi et al. (2006) found liquid MAP remained in potentially plant available form (as measured by isotopically exchangeable P) because of increased diffusion as compared to the granular MAP. The limited diffusion of P from granular MAP is suggested to be because of mass flow of water toward the highly hygroscopic granule moving against the direction of dissolved P diffusion (Lawton and Vomocil, 1954, Hettiarachchi et al., 2006).

2.3.2.1 Time Effect

Over 6 month time period, reaction products of broadcast-granular MAP and liquid-MAP treated soils were transformed to Ca phosphate-, Al phosphate- and Fe phosphate- like forms while the majority of P in the deep banded liquid MAP treated soils continued to remain in adsorbed-P like forms (Table 2.3). The surface soil had relatively lower resin extractable P (25 mg/kg for MAP and 32.65 mg/kg for TGMAP) (Figure 2.3) as compared to deeper (7-15 cm) soil (52.45 mg/kg for MAP-85.38 mg/kg for TGMAP). So, the relative differences in reactions products seen in broadcast and deepband treatments over time might be of a result of resin extractable P levels at given time periods. Soils layer with higher resin extractable P after P application showed relatively more soluble species of P as compared to that of soil layer with low resin extractable P. Lindsay (1979) suggested that the formation of sparingly soluble mixed Al- phosphates and/or Fe-phosphates as a possible mechanism restricting P solubility in acid soils. Calcium phosphates such as apatite are the stable P species formed in alkaline soil over time after P fertilizer applications (Lindsay, 1979). Similarly depending on activity of Ca^{2+} in soil solutions, precipitation of P as Ca-phosphates can also responsible for restricting P solubility in slightly acid, neutral and alkaline soils.

At lower pH, the adsorption capacity of anions in mineral surface of iron and aluminum oxides is high (Hingson et al., 1967, 1968). They suggested that the nature of an oxide-solution interface is determined both by hydrogen ion concentration and the presence of specifically adsorbed anions within the co-ordination shell. However, in soils where there are calcium carbonates, Ca is also responsible for adsorption of P (Wild, 1950; Lehr and Vanwesemael, 1952; Clark and Peech, 1960). In a study conducted by Heylar et al. (1976), using 1 percent suspension of gibbsite at pH 5.5, the increase in Ca content favored increased adsorption of phosphates to gibbsite over time at moderate concentrations of P (0.1 to 1000 µM). However, at lower (0.1 µM) and higher (1000 µM) of phosphate, the effect of Ca was lower. This soil had higher extractable Ca concentration as compared to that of extractable Al and Fe (Table 2.1). Transformation of P overtime to calcium phosphate-like forms in acid soil is not that uncommon, especially when extractable Ca concentrations are relatively higher than Al and Fe (Simard et al.,1995). They related their observations to lime addition and long term application of manure. On the other hand, over time the acidulating effects of MAP might have been neutralized in soil and soil pH tended to come to its initial or original (which was higher) pH and that might have favored formation of Ca-P like forms over a six months time period. In a study conducted by Beauchemin et al. (2003), in mineral P added slightly alkaline soils, Ca-P were the dominant P species while in acidic soils, there was lower percentage of Ca-P species. They also found higher proportion of P adsorbed on Fe or Al-oxide minerals for most of the acidic soils. In this study too majority of adsorbed P species found in our soil were associated with gibbsite and goethite.

2.4 Conclusions

It appears that when liquid MAP is deep banded in no-till soil system, more P remains in resin extractable P forms for six months after fertilizer application. In contrast, broadcasted P, either in granular or in liquid form tended to transform into less extractable P forms after five weeks to six months time period. Speciation results showed that granular-P fertilizers tended to form Fe-P like products whereas liquid forms found to remain in adsorbed-P like forms in soil after 5 weeks of application. Over 6 month time period, reaction products of broadcast-granular and broadcast-liquid and deep band-granular fertilizers transformed to Ca-phosphate- or mixtures of Ca-, Fe-, Al- and adsorbed-phosphate-like forms while deep band-liquid P continued to remain mainly as adsorbed-P like forms. Formation of Fe-, Al-, and/or Ca- P solid species, with different solubilities, may have been the reason for the observed differences in extractability or potential availability of P between broadcasted and deep banded granular and liquid MAP evaluated in this study. Spectroscopic investigations appeared to be in agreement with resin extractable P results and suggest that when liquid P is deep banded, more P remains in comparatively more soluble forms of P in soil while surface applied granular- and liquid P tend to transform into comparatively less soluble P forms over six months time period.

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2.6 Figures and Tables

Figure Captions

Figure 2.1- pH at different distances from the point of fertilizer application over time: (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 2.2- Total P at different distances from the point of fertilizer application over time: (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 2.3- Resin Extractable P at different distances from the point of fertilizer application over time: (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band.

Figure 2.4- Resin extractable P (as % of total P) in soil sections collected at different distances from the point of fertilizer application. The resin extractable P (as a percent of total P) was calculated dividing resin extractable-P values for each section by the corresponding total P concentration. Error bars represent standard errors of five field replicates. (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band treatments. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 2.5- Normalized P K-XANES of standards used for Linear Combination Fitting.

Figure 2.6- Linear combinations fittings of five weeks field samples.

Table 2.1 Basic properties of North farm (NF) soil

Sample Depth	pH	CEC†	M3 P	Extractable				Total N	Total P	OM	Textural Class
				Ca_{ac}	Fe_{dtpa}	Mn_{dtpa}	Al^{3+}_{KCl}				
cm		**meq/100g**	**---**	**---**	**---**	**mg/kg**	**---**	**---**	**---**	**%**	
0-7	5.9	16.1	45.4	2426.0	7.9	58.3	0.0	1598.0	423.0	3.2	SiL
7-15	5.7	20.3	19.6	2540.0	8.2	57.8	0.4	1114.0	329.0	2.3	SiCL
15-30	6.1	18.8	5.9	3174.0	27.8	25.0	0.1	1119.0	278.0	2.2	SiCL

† CEC, cation exchange capacity; M3P, Mehlich III-extractable phosphorus, Ca_{ac} –ammonium acetate extractable calcium; Fe_{dtpa} and Mn_{dtpa} – diethylene triamine pentaaceticacid extractable iron and manganese; Al^{3+}_{KCl} -potassium chloride extractable aluminum; OM, organic matter content; SiL, silty loam; SiCL, silty clay loam.

Table 2.2 Phosphorus K-XANES fitting results for five weeks samples performed in first-derivative space with an energy range between -5 to 30 eV showing the relative proportion of each phosphate standard showing best fit.

	Ca-P minerals			Al-P minerals		Fe-P minerals		Adsorbed P				Red.
Treatment	**1†**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**χ2‡**
Control 0-7	-	9.4	-	-	-	10.2	-	80.4	-	-	-	0.021
Urea Broadcast	-	-		-	-	-	57.9	-	8.5	33.6	-	0.062
MAP Broadcast	-	-	-	11.3	-	-	69.2	19.5	-	-	-	0.003
TGMAP Broadcast	-	17.7	-	-	-	38.9	-	-	-	-	43.4	0.058
Control 7-15	-	-	69.1	-	26.8	-	-	-	-	4.1	-	0.007
Urea Deepband	-	-	47.0	-	40.5	-	-	-	-	12.5	-	0.007
MAP Deepband	-	-	-	-	-	-	64.5	35.5	-	-	-	0.120
TGMAP Deepband	-	-	-	-	-	-	46.7	36.9	-	16.5	-	0.003

†1, Apatite; 2, hydroxyapatite; 3, monetite; 4, aluminum phosphate; 5, variscite; 6, strengite; 7, vivianite; 8, alumina adsorbed P; 9, ferrihydrite adsorbed P; 10, gibbsite adsorbed P; 11, goethite adsorbed P.

‡$\chi 2 = \Sigma(\mathrm{fit} - \mathrm{data})/\varepsilon]^2 / (N_{\mathrm{data}} - N_{\mathrm{components}})$ is the reduced chi-square statistic. Here ε is the estimated uncertainty in the normalized XANES data (taken as 0.01 for all data). The sum is over N_{data} points (185 data points between E=2144 and 2179 eV for all data), and $N_{\mathrm{components}}$ is the number of components in the fit (either 2 or 3 as indicated in the Table). The total percentage was constrained to be 100% in all fits. Typical uncertainties in the percentages listed for each standard component are 5%.

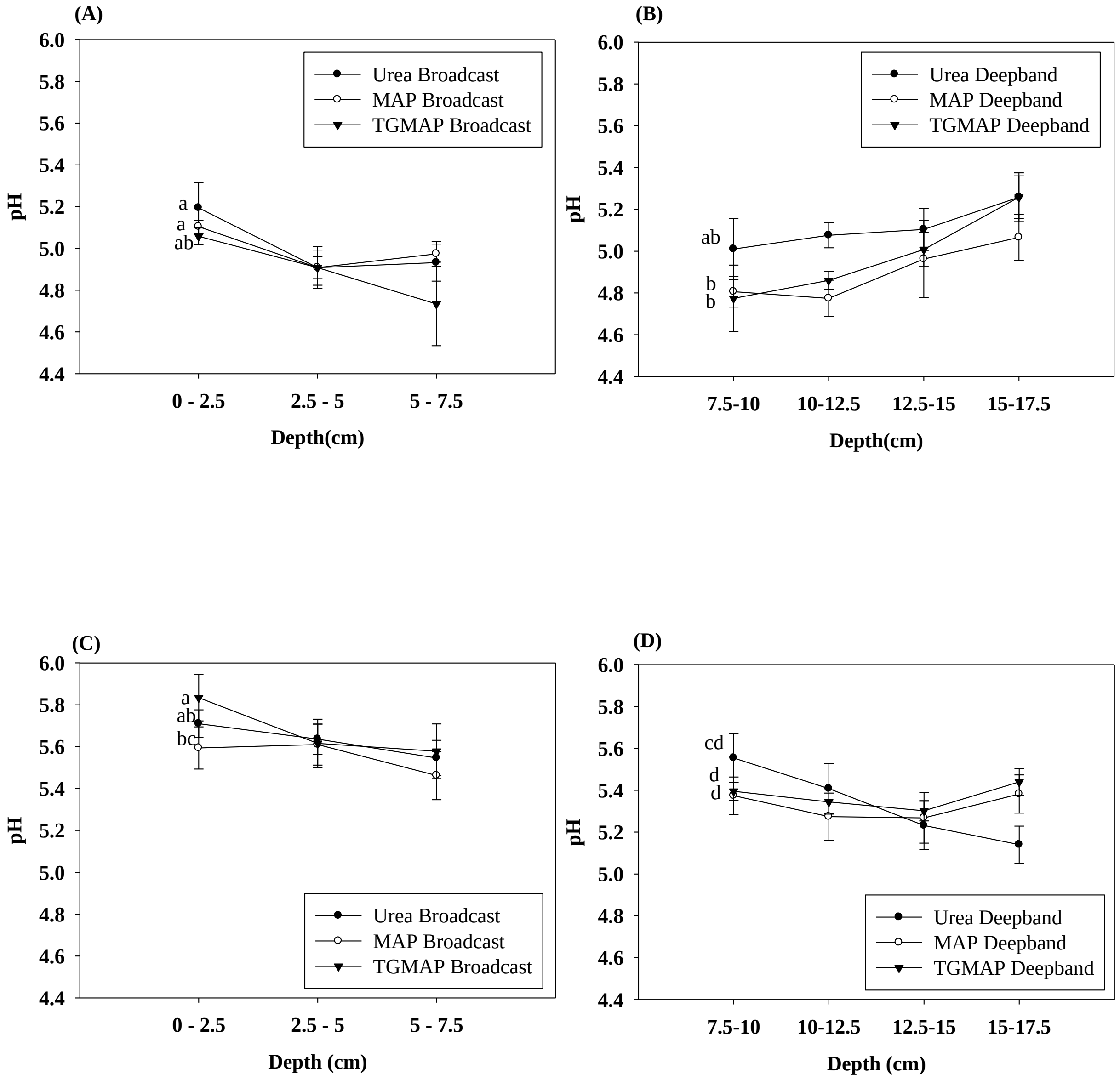
Table 2.3 Phosphorus K-XANES fitting results for six months samples performed in first-derivative space with an energy range between -5 to 30 eV showing the relative proportion of each phosphate standard showing best fit.

	Ca-P minerals			Al-P minerals		Fe-P minerals		Adsorbed P				Red.
Treatment	**1†**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**$\chi 2$‡**
Control 0-7	-	9.4	-	-	-	10.2	-	80.4	-	-	-	0.021
Urea Broadcast	-	-	-	-	60.4	-	39.6	-	-	-	-	0.411
MAP Broadcast	-	-	-	-	46.3	-	-	-	-	7.3	46.3	0.006
TGMAP Broadcast	-	67.9	32.1	-	-	-	-	-	-	-	-	1.130
Control 7-15	-	-	69.1	-	26.8	-	-	-		4.1		0.007
Urea Deepband	53.0	-	-	-	-	-	47.0	-	-	-	-	6.600
MAP Deepband	-	-	1.9	-	49.8	-	-	-	-	37.5	10.9	1.470
TGMAP Deepband	-	-	19.8	-	-	-	-	15.5	-	44.3	20.5	0.010

†1, Apatite; 2, hydroxyapatite; 3, monetite; 4, aluminum phosphate; 5, variscite; 6, strengite; 7, vivianite; 8, alumina adsorbed P; 9, ferrihydrite adsorbed P; 10, gibbsite adsorbed P; 11, goethite adsorbed P.

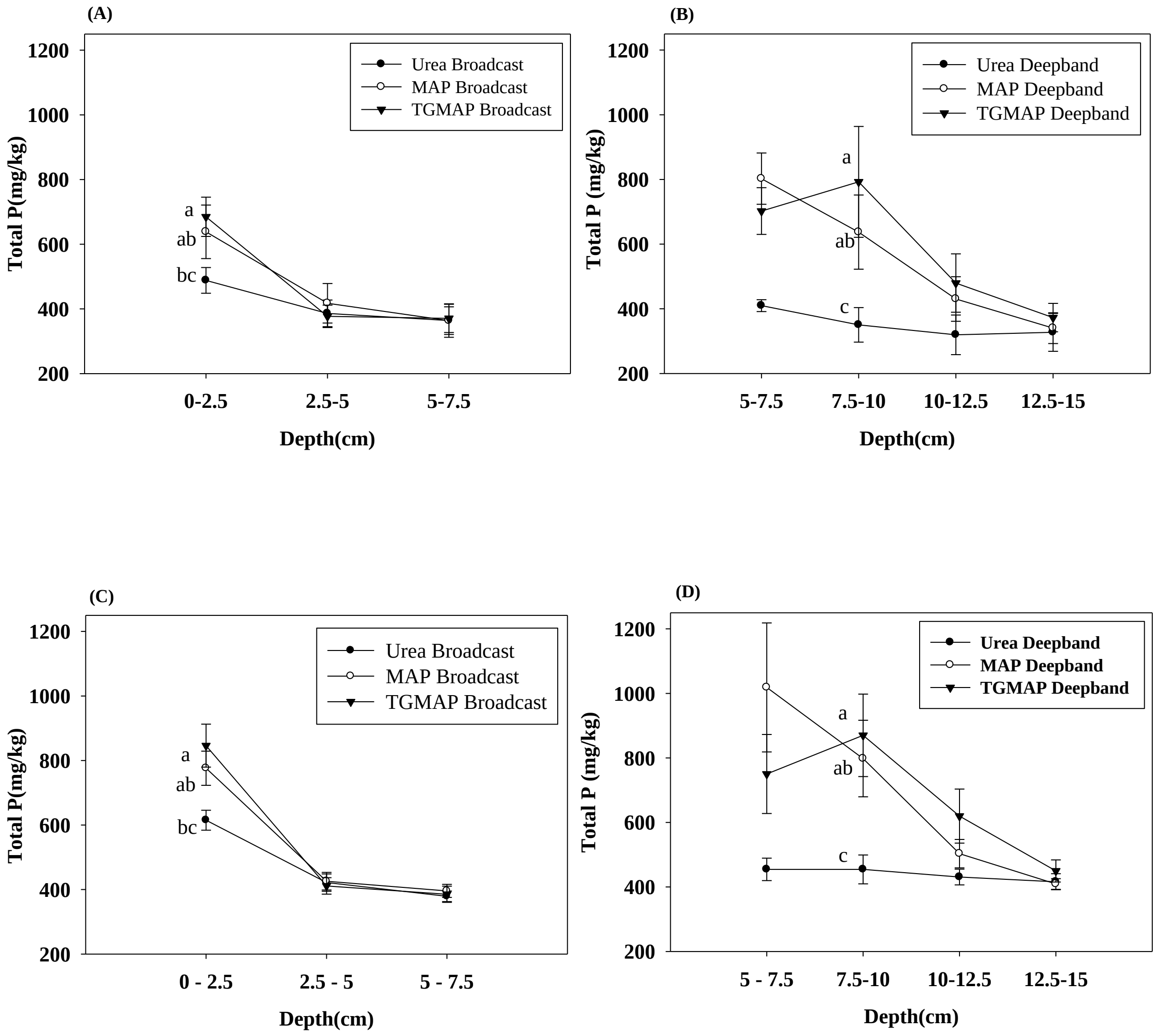
‡$\chi 2 = \Sigma(\text{fit} – \text{data})/\varepsilon]^2$ / $(N_{data} – N_{components})$ is the reduced chi-square statistic. Here ε is the estimated uncertainty in the normalized XANES data (taken as 0.01 for all data). The sum is over N_{data} points (185 data points between E=2144 and 2179 eV for all data), and $N_{components}$ is the number of components in the fit (either 2 or 3 as indicated in the Table). The total percentage was constrained to be 100% in all fits. Typical uncertainties in the percentages listed for each standard component are 5%.

Figure 2.1 pH at different distances from the point of fertilizer application over time: (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band. Granular MAP= MAP; liquid MAP = TGMAP.



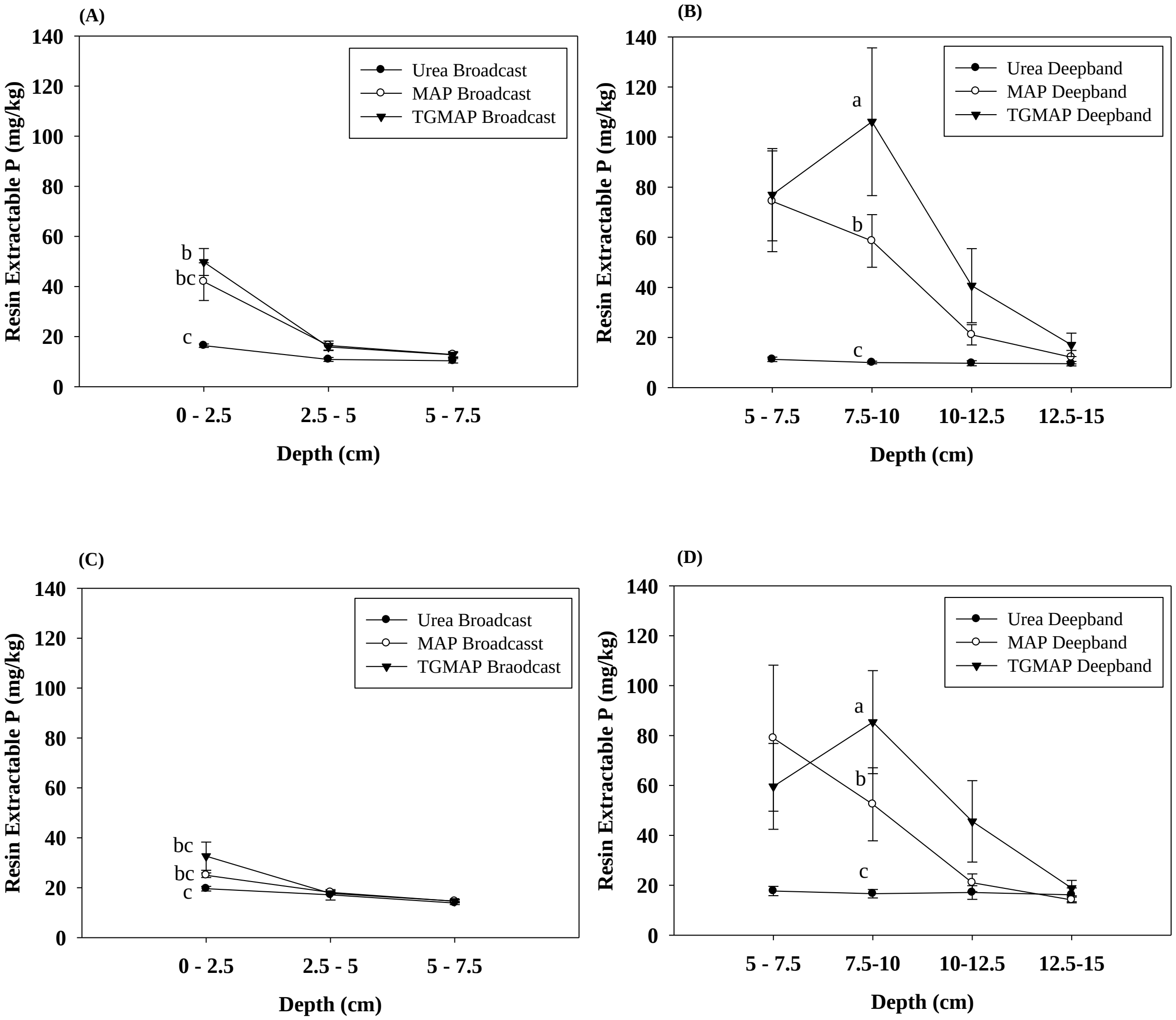
†Letters in figure indicates significance at the 0.05 probability level.

Figure 2.2 Total P at different distances from the point of fertilizer application over time: (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band. Granular MAP= MAP; liquid MAP = TGMAP.



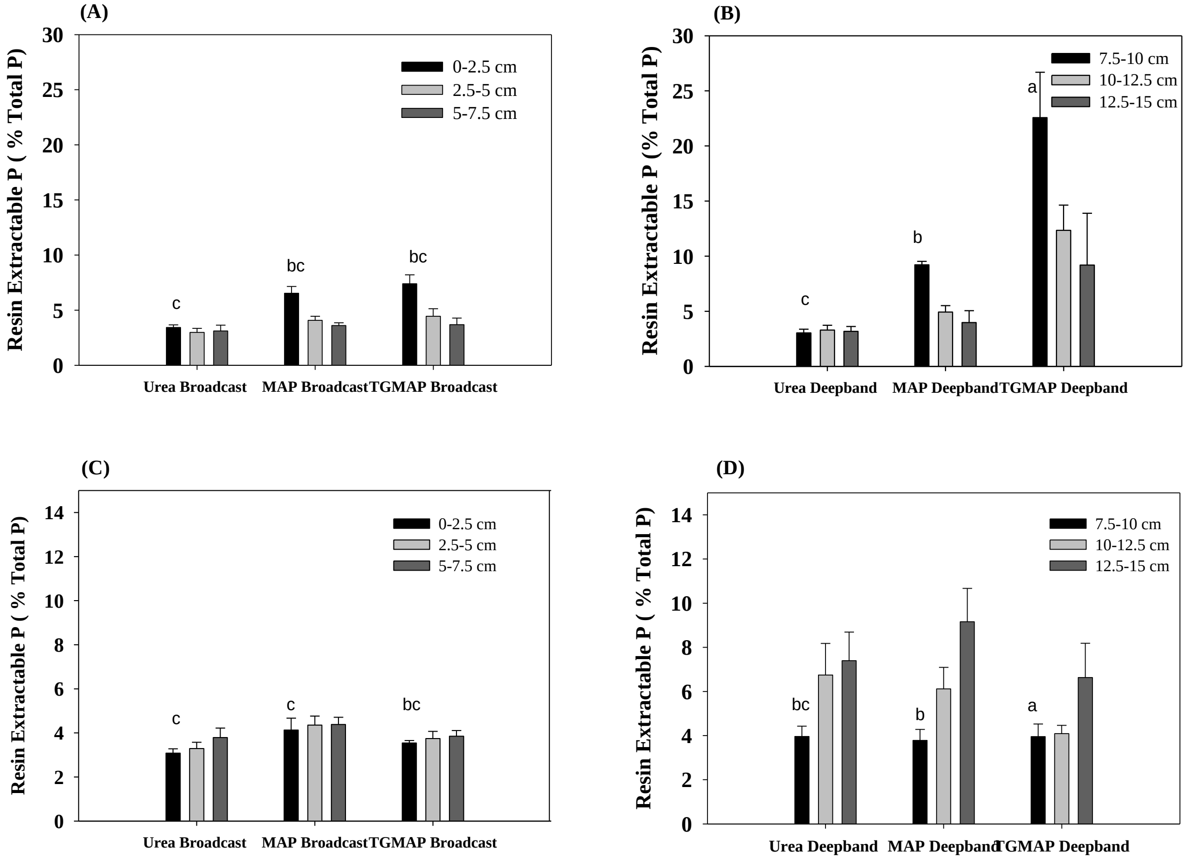
†Letters in figure indicates significance at the 0.05 probability level.

Figure 2.3 Resin Extractable P at different distances from the point of fertilizer application over time: (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band.



†Letters in figure indicates significance at the 0.05 probability level.

Figure 2.4 Resin extractable P (as % of total P) in soil sections collected at different distances from the point of fertilizer application. The resin extractable P (as a percent of total P) was calculated dividing resin extractable-P values for each section by the corresponding total P concentration. Error bars represent standard errors of five field replicates. (A) Five weeks broadcast, (B) Five week deep band, (C) Six months broadcast, and (D) Six months deep band treatments. Granular MAP= MAP; liquid MAP = TGMAP.



†Letters in figure indicates significance at the 0.05 probability level.

Figure 2.5 Normalized P K-XANES of standards used for Linear Combination Fitting.

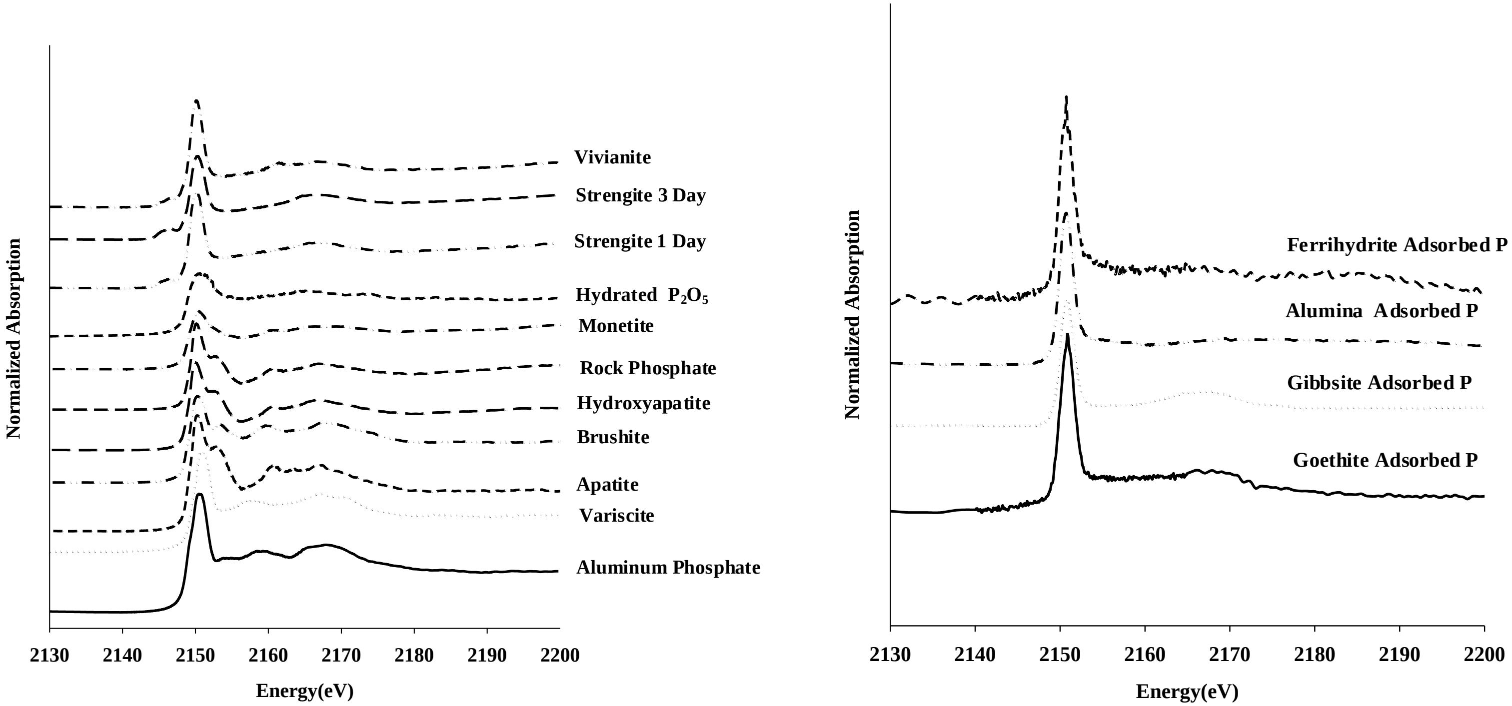
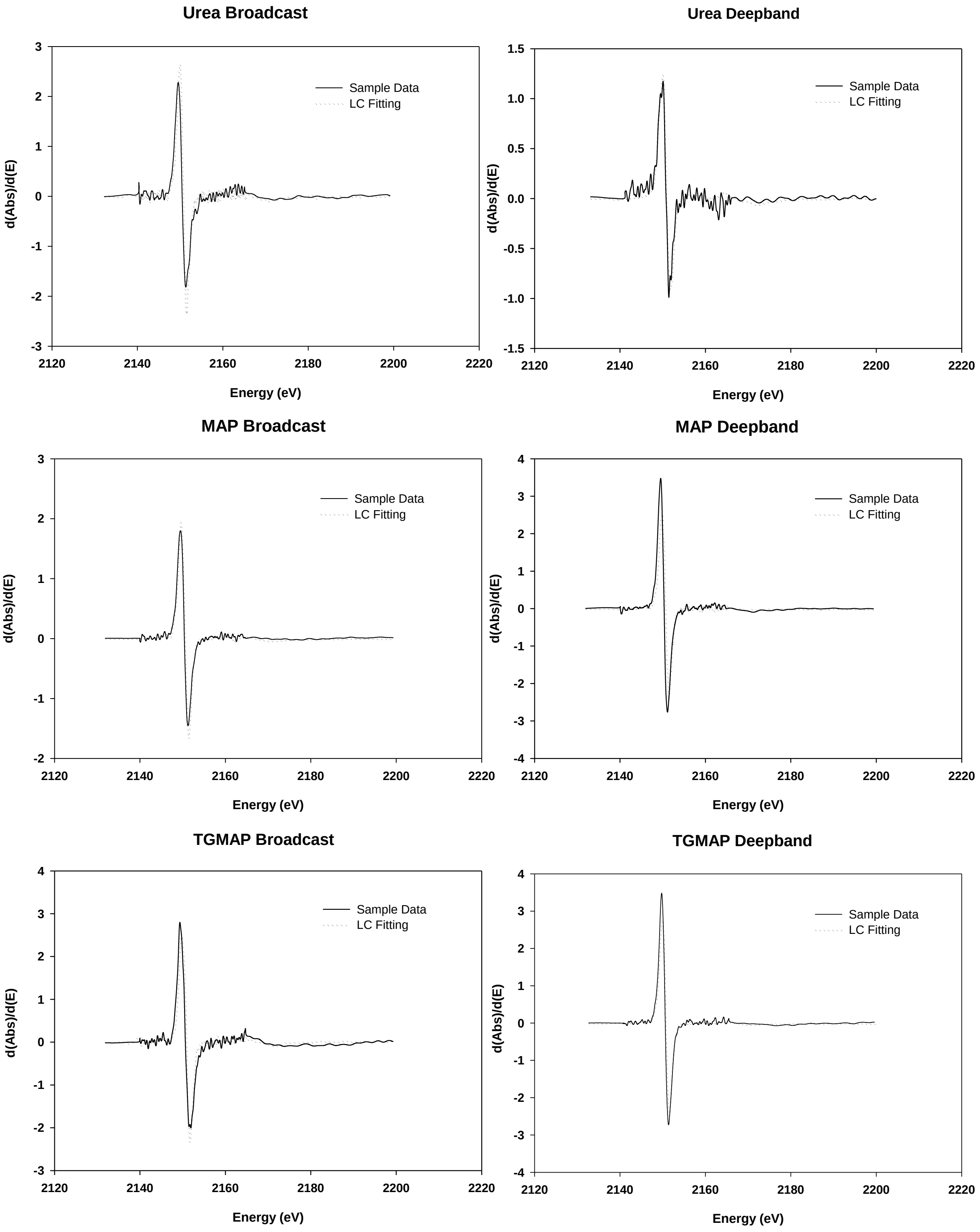


Figure 2.6 Linear combinations fittings of five weeks field samples.



Chapter 3 - Placement and Source Effects of Phosphate Fertilizers on Their Reaction Products in Two Kansas Soils - A Greenhouse Study

Abstract

Crop yields are primarily limited by unavailability of nutrients in agricultural soil. Adoption of reduced and no tillage system leads to stratification of nutrients in surface soil. So, management of phosphorus (P) in these systems is a major issue. The objective of this research was to understand the influence of placement (broadcast- vs. deep placed-P) and fertilizer source (granular- versus liquid-P) on reaction products of P under greenhouse conditions using soil columns with corn ((*Zea mays* L.) plants and without plants. Phosphorus was added at a rate of 75 kg/ha to two soils, an acid soil from Manhattan, KS and a slightly acid to neutral soil from Ottawa, KS. At five weeks after P application plant uptake of P, soil pH, resin extractable P, and speciation of P in soils were determined at different distances from the point of fertilizer application. Scanning electron microscope with energy dispersive X-ray analyzer (SEM-EDXA) and synchrotron based X-ray absorption near edge structure (XANES) spectroscopy were used for P speciation. There were no clear differences in results for P fertilizer sources and placement with respect to resin extractable P in soils and uptake of P by corn for both soils. The XANES speciation revealed that Fe-P like forms were dominating in the acidic soil while Ca-P like forms dominated in the neutral to slightly acidic soil. Furthermore, SEM-EDXA analysis of incubated fertilizer granules extracted from soils in columns without plants at 5-wk, showed enrichment of Al, Fe and Ca in the zones of remaining P in incubated granules indirectly indicating that these cations enter the granules and begin to react with P before granules dissolve completely.

3.1 Introduction

Reduced tillage is becoming popular in the U. S. and worldwide (Hobbs et al., 2008). Despite various advantages of reduced tillage, it has been found that granular P fertilizers applications leads to an accumulation of available P on the surface 0 to 5 cm soil layer and a depletion of available P deeper in the profile (Schwab et al., 2006). Broadcast application of fertilizers is a relatively inexpensive and popular method and is ideal for high-speed operations and high application rates. However, increased adoption of reduced tillage coupled with broadcast fertilization has raised concerns about P management in reduced tillage systems. Concerns related to nutrient stratification include potential impact on nutrient uptake and subsequent crop yield due to inability of the crops to access nutrients (Mallarino and Borges, 2006). Holanda et al. (1998) found P stratification stimulated root growth in conservation systems when compared to the conventional systems. However, Bordoli and Mallarino (1998) suggested that deep placement of nutrients below the first 5 to 10 cm of the soils should be superior to other placements when nutrient stratification was a concern. They did not find response to P placement at any site for corn yield. The general outcome was that the deep placement of P did not increase yield or there was no decrease in yield as compared to the broadcast P treatment, if deep application was done for other agronomic or environmental reasons (minimize ammonia volatilization in moisture deficit conditions and reducing surface runoff of P with water to aquatic systems).

Researches on liquid fertilizers have shown better performance over granular form of P fertilizers in highly calcareous soils. Holloway et al. (2001) reported that fluid monoammonium phosphate was 4 to 5 times as effective as granular monoammonium phosphate in field trial in calcareous soils of South Australia. Lombi et al. (2004) showed that the liquid form of P fertilizers are more isotopically exchangeable in high calcareous soils than their granular forms, and thus considered as more available to the crops. Studies conducted thereafter in similar soils showed liquid fertilizers diffuse further reducing P precipitation in highly calcareous soil

(Hettiarachchi et al., 2006; Lombi et al., 2006). Although the use of liquid P fertilizers in reduced tillage systems is less common as fertilizers are mainly broadcast or stripped applied, it may be a suitable alternative to enhance P availability in reduced tillage systems established on high P fixing soils.

Because of differential plant yield responses observed by the reduced-till researchers and lack of insight into mechanisms responsible for variable responses, there is a need for knowing how different placement of P fertilizers in reduced tillage systems affects P reaction pathways and products in relation to plant growth. Further, studying the dominant solid P species found in soil following application of P fertilizers and linking that to P availability to plants would help us to efficiently manage P in reduced tillage systems. Plant availability of P can be determined directly through plant uptake studies and indirectly through different extractions procedures. One indirect method found to be of superior in performance compared to most soil test P methods (such as Olsen P, Bray 1-P, Mehlich P) is, resin extractable P (Saggar et al., 1990). Resin extractable P method in laboratory mimics the soil/soil solution/plant root model (Bernardo et al., 2009).

Speciation of P reaction products in soils can be achieved by using X-ray absorption near edge structure (XANES) spectroscopy. This technique is advantageous in studying reactions products in soils due to its elemental specificity, superior detection limits, non-sensitivity to crystallinity and the capability to probe the element of interest in situ. Speciation can be done using XANES technique as XANES allows determination of the oxidation state and the local chemical and structural environment of an element (Fendorf and Sparks, 1996). This technique has then been widely used for speciation of organic and inorganic P in soils, sediments and agricultural byproducts (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003;

Lombi et al., 2006; Ajiboye et al., 2008; Kruse and Leinweber, 2008). Beauchemin et al. (2003) used XANES in conjunction with sequential fractionation technique to determine chemical speciation of P in long term fertilized soil differing in pH, clay, and organic matter contents. They found that phosphate adsorbed on Fe-or Al-oxide was present in 5 different soils used for the study, with high proportion in the more acidic soils and with some in slightly alkaline soils. Although XANES is useful to directly identify P species in soils, XANES speciation based on fitting techniques is limited by (i) the data quality, (ii) how well the chosen set of standards actually represents real species in samples (Beauchemin et al., 2002).

Scanning electron microscopy combined with energy dispersive X-ray analyzer (SEM-EDXA) is a technique that can be used to probe enriched samples or enriched zones of samples (at least about 1000 mg/kg) to collect direct information on crystal morphology, size, shape, locations and their associations. Since EDXA provides chemical compositional information SEM combined with EDXA can be used to get indirect information on chemical species present in a sample. Therefore, it can be used to determine morphological and chemical information in enriched soil particles/zones, original and incubated fertilizer granules (Pierzynski et al., 1990; Prochnow et al., 2001; Hettiarachchi et al., 2008) and plant roots (Laperche et al., 1996; 1997). Prochnow et al. (2001) used SEM-EDXA technique for identifying compounds present in single superphosphate produced from Brazilian phosphate rock. They were able to identify various compounds like calcium phosphate monohydrate, triiron potassium octahydrogen hexaphosphate hexahydrate, triiron 15-hydrogen octaphosphate tetrahydrate, triiron potassium 14-hydrogen octaphosphate tetrahydrate and barium sulfate. Identification of solid P species in reduced tillage system following application of P fertilizers will help us to design better P formulations and management practices. The objectives of this greenhouse experiments are to study: 1) fertilizer placement (broadcast vs. deep placed); and source (granular vs. liquid) effect on reaction products of P, 2) availability of P using plant uptake and resin extractable P measured at different distances from the point of fertilizer application, and 3) linking plant uptake of P and resin extractable P to soil P chemistry.

3.2 Methodology

3.2.1 Site Description, Soil and Fertilizers

A greenhouse based study was conducted with soils from agronomy North farm site (Site I) located in Manhattan, KS and Ottawa site, located in East central Kansas experiment field (Site II), Ottawa, KS. The Manhattan site soil is a smolan silt loam (fine, smectitic, mesic Pachic Argiustolls) and the Ottawa site soil is a woodson silt loam (fine, montmorillonitic, thermic, Abruptic Argiaquoll) (Soil Survey Staff, 1992). Manhattan soil had a pH (1:5 soil: H_2O) of 5.9, a clay content of 26.3 %, and an organic matter content of 3.2 % in the surface soil (0 to 15 cm). Total P concentration (digested with salicylic sulfuric acid, Bremner and Mulvaney, 1982) was 423 mg kg^{-1} for surface soil. Ottawa soil had a pH (1: 5 soil: H_2O) of 6.6, a clay content of 18.8 %, and an organic matter content of 5.8% in the surface soil. Total P concentration (digested with salicylic sulfuric acid, Bremner and Mulvaney, 1982) was 774 mg kg^{-1}. The maximum water holding capacity of Manhattan and Ottawa soils was 48.23 % and 57.49 %, respectively and it was determined by using modified method as described by Jenikson and Powlson (1976). The general properties of soil used for the study are given in Table 3.1

Soil pH was measured in 1:5 soil:water extract (Wateson and Brown, 1998) and cation exchange capacity was determined using summation method as described by Chapman (1965). Mehlich 3-P was determined following procedures described by Frank et al. (1998). Ammonium acetate extractable calcium (Ca) was determined using procedures described by Warncke and Brown (1998). Extractable iron (Fe) and manganese (Mn) were determined using DTPA extraction technique as described by Whitney (1998). Potassium chloride extractable aluminum (Al) was determined following the procedures described by Mc Lean (1965). Total P and N were determined following the method suggested by Bremner and Mulvaney (1982). Organic matter content was determined following modified Walkley-Black method as described by Combs and Nathan (1998) with "heat of dilution" modification. Particle size distribution was determined using a modification of the pipet method of Kilmer and Alexander (1949) and method 3A1 form the Soil Survey Laboratory Methods Manual (Soil Survey Laboratory Staff, 2004). Granular monoammonium phosphate (MAP) (11-52-0, N:P_2O_5:K_2O) and technical grade monoammonium phosphate (TGMAP) (12-60-0, N:P_2O_5:K_2O)in liquid form were used as P fertilizer sources. The rate of N and P applied was 200 and 75 kg/ha, respectively. Phosphorus is often applied with N to supply plant nutrient needs. Nitrogen fertilizers that are applied along with P fertilizers may have potential to influence P chemistry in soils. Thus, in this experiment urea was applied together with P to supply and balance nitrogen (N) as per plant nutrient requirements.

3.2.2 Experimental Approach

Soil cores of 30 cm depth were extracted from agronomy North farm (Site I) and East central Kansas experiment field (Site II) using a tractor mounted and driven probe. Extracted soil cores divided into 0-7, 7-15, and 15-30 cm depth and homogenized separately to maintain the nutrient stratification in soil. Depth-wise separated soils were air dried, ground, passed to <2 mm sieve and further homogenized. Then soils were packed in Plexiglas columns of 6.8 cm inner diameter and 35.6 cm long purchased from Busada Manufacturing Corporation (Louisa, VA) by section by section to keep depth-wise differences intact. The treatment structure and rate is same as for the field experiment explained in the Chapter 2. The average P concentration of MAP granules (weighing 42±0.5 mg) used was 9.08 mg P/42 mg of granule. Six granules per column were applied for the 5 columns receiving granular treatment and equivalent amounts of P from (TGMAP) were applied for the columns receiving liquid P treatments. Fertilizers were evenly spread across the surface (0 cm depth) after packing the whole column with soils for the broadcast treatments and at 15 cm depth prior to filling the top soils for the deep placed treatments. The volume of liquid P was maintained at a total of 600 µL by mixing with water. Urea was applied for all treatments at a rate of 200 kg N/ha. The experimental design was randomized complete block design with total of 5 replications. Corn (*Zea mays* L., DKC 64-79 a VT3 hybrid) were planted in each column for 5 weeks. Additional two replicates of column without plants were established in parallel for SEM-EDXA analysis. Greenhouse temperature was maintained at average temperature about 25^{o}C with 14 h photoperiod (6 AM to 8 PM).

The columns were maintained at 80 % of maximum water holding capacity by adding DI water based on weight losses. At 5 weeks time, aerial plant biomass was harvested and soil core was removed from Plexiglas columns. Soils were separated into 2.5 cm slices for wet chemical based analysis and X-ray based studies. Similarly soils in columns without plants were also separated. Further remaining granules in MAP granular added columns without plants were also extracted for SEM-EDXA analysis.

3.2.3 Wet Chemical Analysis of Soils

The wet chemical based analysis included measurement of pH, total P and resin extractable P at different distances from the point of fertilizer application. The ratio of 1:5 soil to water ratio (NCRRP, 1998) was used for the determination of pH. Total P was determined using modified salicylic sulfuric acid digestion method as described by Bremner and Mulvaney (1982) using inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 720-series ICP-OES, Walnut creek, CA). Resin extractable P was determined by following the procedure of Myers et al. (2005). A resin membrane BDH product no.55164 S (U.S. distributor: CTL Scientific Supply Corporation, Deer Park, NY) was used for resin P extraction procedure. The resin membrane comes in pack of six of 12.5 x 12.5 cm sheets. The resin membrane was cut into 5 cm x 2.5 cm saturated with 0.5 M $NaHCO_3$. Two strips were used for 1.0g of soil and P was extracted as described by Myers et al., 2005. Briefly, 1.0 gm of soil was placed in polyethylene bottle containing 80 mL of water. Two resin strips were added to the polyethylene bottle and shaken in an orbital shaker for 24 hours. After shaking, the resin strips were removed from the polyethylene bottle washed with deionized water to remove any adhering soil particles and transferred to other polyethylene 250-mL bottle containing 50 mL of 0.5 M hydrochloric acid (HCl). The resin strips were further shaken with 50 mL of 0.5 M HCl solution for additional 1.5 hours and filtered using whatman filter paper#42 and analyzed colorimetrically using UV/VIS spectrophotometer (Beckman 800, Brea, CA.) following method described by Murphy and Riley (1962).

3.2.4 Plant Analysis

The aboveground plant parts were harvested at 5 weeks were washed with deionized water and blot-dried. Plants were weighed for the fresh weigh and dried in a forced air oven at 60°C for a minimum of 4 days and weighed for biomass calculation. Dried plant materials were ground with a Wiley grinder and digested using a sulfuric acid and hydrogen peroxide method

(Thomas et al., 1967) and analyzed for P using ICP-OES. The biomass weight and P concentration were used to calculate P uptake per column.

3.2.5 Statistical Analysis

All date were analyzed by proc mixed procedure using SAS software (SAS 9.1, 2007). Pairwise Bonferroni method was used for pairwise comparisons between treatments at α= 0.05 level of significance.

3.2.6 Speciation of Phosphorus

3.2.6.1 Scanning Electron Microscopy with Energy Dispersive X-ray Analyzer (SEM-EDXA)

At five weeks, soil applied MAP granules from columns without plants, were extracted and analyzed using scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDXA) together with the original (unexposed to soils) granules. The exposed side of the granules was cross sectioned using stainless steel blade and mounted on aluminum sample holder for SEM-EDXA analysis. The cross sections were sputter coated with 40 % palladium conductive coating of ~4 nm thickness and dried. Palladium coating helps to minimize static electric charge accumulation on the specimen during electron irradiation and increase signal and surface resolution of images. As mentioned before this technique is an indirect, less sensitive technique and therefore, only granules were used for the SEM-EDXA analysis and soil samples were analyzed using X-ray absorption near edge structure spectroscopy (XANES).

3.2.5.2 X-ray Absorption Near Edge Structure Spectroscopy (XANES)

3.2.5.2.1 Data Collection and Analysis

Phosphorus K-edge XANES spectra were collected at Sector 9-BM-B, Advanced Photon Source (APS), Argonne National Laboratory, IL. The electron storage ring at the APS is operated at 7 GeV with maximum current of 100 mA. This beamline has energy range of 2.1 to 23 keV and is equipped with Si (III) monochromator with focused beam size 500µm x 500 µm. The sample compartment was He- purged and data were collected in fluorescence mode using Ge solid stage detector. Phosphorus pentoxide (P_2O_5) standard was used for monochromator calibration. Correction in any energy drifts caused by monochromator drifts were done by collecting spectra of P_2O_5daily during run time. All samples and standards were calibrated using common energy scale by setting first derivative spectrum of apatite to 2149.25 eV for analysis.

The soil samples were air dried and ground to pass through a 150 µm sieve. The samples were further ground to very fine powder with an agate mortar and pestle. Soil pellets with diameter of 4 mm were prepared using KBr quick press kit with 4mm die set (International Crystal Laboratories, Garfield, NJ) to get better signal. The samples were then mounted on a teflon tape and fixed onto aluminum sample holders ready for analysis (see Figure A.7). Four to six scans of samples were collected with a scan range from 2110 to 2400 eV. The step size was 2.0 eV on pre edge region (2110 to 2140 eV), 0.125 eV in near edge region (2140 to 2165 eV) and 0.5 in post edge region (2165 to 2400 eV) with reading time of 3 to 6 seconds per point. Four to six scans of collected spectra were energy calibrated, normalized, merged and smoothed (4 iterations) using IFEFFIT'S three point smoothing algorithm to obtain normalized XANES spectrum. Data reduction was done using Athena software version 0.8.056 (Ravel and Newville, 2005).

The reduced spectra were analyzed using linear combination fitting (LCF) using Athena. The linear combination XANES fitting procedure was used to reconstruct the soil spectra using all combinations of the standard spectra reduced in the same way as described before. The fitting was done in the first derivative space using quinary combinations of all standards relative to fitting range from -5 to 30 eV of white line. The weighting factors were forced to sum to one and no energy shifts were permitted in LCF fitting. The goodness of fit was judged by R factor and χ^2 values. The fit with least χ^2 value was used as the best fit.

3.2.5.2 .2 Standards for Phosphorus K-XANES

The phosphorus standards used in this study were purchased or synthesized. Berlinite ($AlPO_4$), brushite ($CaHPO_4•2H_2O$), hydroxyapatite ($Ca_5 (PO_4)_3(OH)$), monetite ($CaHPO_4$), and rock phosphate were purchased from Sigma Aldrich (St. Louis, MO). Phosphorus pentoxide (P_2O_5) was purchased from Alfa Aesar (Ward Hill, MA). Strengite ($FePO_4•2H_2O$) with different crystallinities were synthesized following the procedure of Dalas (1991) by mixing KH_2PO_4 and $Fe (NO_3)_3•9H_2O$ at ambient temperature and heated hydrothermally at 100°C for 24 h and 3 days. Variscite ($AlPO_4•2H_2O$) was synthesized following the procedure of Hsu and Sikora (1993). Vivianite and apatite standards were obtained from Land and Water, Commonwealth Scientific and Industrial Organization, Adelaide, Australia. Adsorbed phosphate on goethite and alumina were prepared following the procedure of Oh et al. (1999). Ferrihydrite and gibbsite adsorbed P were prepared following the procedure of Schwertmann and Cornell (1991). The purity of synthesized P standards was verified using XRD. The powdered phosphate standards were spread over double sided carbon tape and mounted on aluminum samples holders for XANES data collection.

3.3 Results and Discussion

3.3.1 Wet Chemical Analysis

3.3.1.1 Site I (North Farm, Manhattan)

Surface soil (0 to 7 cm) had initial pH of 5.9 and soil pH was more or less constant throughout the soil depth of 30 cm. Soil texture changed depth-wise and there was a slight increase in the clay content (26.3 to 29.8 %) with increase in depth (Table 3.1). Diethyelene triamine pentaaceticacid (DTPA) extractable -iron (Fe) (48 mg/kg) and -manganese (Mn) (58 mg/kg) concentrations were relatively similar up to 15 cm profile depth; however, at 15-30 cm depth DTPA extractable Fe and Mn concentrations were quite different from the rest (Table 3.1). This soil had very low (>0.4 mg/kg) extractable Al concentration. Ammonium acetate extractable Ca concentrations of the soil were in the range of 2426 to 2540 mg/kg for 0-7 and 7-15 cm depths, respectively and slightly higher (3174 mg/kg) after 15 cm depth. Cation exchange capacity was in the range of 16.1 to 20.3 meq/100g (cmol$_c$/kg) up to 30 cm depth.

There were no significant differences in pH between the treatments (Figure 3.1). However, when compared to the original soil pH addition of urea and phosphate fertilizers reduced the pH of the soil (up to 0.6 units). Acidification effects of MAP on soil pH have been reported by many researchers (Hanson and Westfall, 1985; Moody et al., 1995). In contrast hydrolysis of urea consumes two moles of protons for each mole of urea hydrolyzed, thereby resulting an increase in pH. The decrease in pH for P fertilizer applied soil might be due combination of various reactions (nitrification of NH_4^+, hydrolysis of urea and other reactions such as formation of different reaction products).

Total soil P concentration was found to be different for the surface soil and the deeper layer (7-15 cm). The surface soil had relatively higher initial total P concentration (480 mg/kg) as compared to the deep layer (350 mg/kg). Most probably this caused the total P concentration differences observed between the broadcast and the deep placed P fertilizer treatments (Figure 3.2). For both broadcast and deep placed treatments, granular and liquid fertilizers were spread across the surface. This might have resulted the differences seen between the treatments. For broadcast treatments, granular MAP showed significantly higher resin extractable P followed by the liquid MAP (Figure 3.3). Granular MAP could have released P slowly and this might have helped P to remain in relatively more extractable form longer; on the other hand, liquid P spread across the soil surface or deep layer might have reacted with soil quickly transforming P to unavailable form within short time after application. However, there was no clear differences between liquid and granular fertilizers for deep placed treatments with respect to resin extractable P, and both treatments had significantly lower resin extractable P as compared to the broadcast P treatments. When comparing resin extractable P expressed as % of total P (Figure 3.4), resin extractable P (% of total P) did not show any significant differences between P applied treatments but all P applied treatments had significantly higher resin extractable P (% of total P) compared to the control treatment.

Plant P uptake was calculated by multiplying the plant P concentration (mg/kg) and plant dry biomass (in kg). Plants were P responsive and all P treatments showed significantly higher P uptake than the control treatment. There were no significant differences among P treatments for plant P uptake except between TGMAP broadcast and TGMAP deep placed treatments. Broadcast TGMAP had significantly higher plant P uptake as compared to that of TGMAP deep placed. However, plant P uptake for broadcast TGMAP was not significantly higher than that of MAP broadcast and deep placed treatments (Figure 3.5). Lack of P source or P placement effect might partly be attributed to favorable greenhouse conditions for plant growth and the restricted soil volume that plants were exposed to during this study. Plant P concentration was significantly higher for the TGMAP broadcast treatment (2275 mg/kg) than the TGMAP deep placed treatment (1837.2 mg/kg) followed by the broadcast MAP treatment (1664.4 mg/kg) (Figure 3.6). Except for the MAP deep placed treatments all other treatments had higher plant P concentration than that of the control. However, plant biomass yield was significantly higher for the MAP deep placed followed by the MAP broadcast and the TGMAP treatments (broadcast and deep placed). Biomass yield was significantly higher than the control for all P treatments (Figure 3.6).

3.3.1.2 Site II (Eastern Kansas Experiment Site, Ottawa)

This site had a soil texture of silt loam throughout the soil profile of 30 cm depth. The soil had slightly higher pH (5.9 to 6.6) as compared to that of the site I (5.7 to 6.1) and soil pH decreased with increasing depth. Diethyelene triamine pentaaceticacid (DTPA) extractable Mn concentration was higher in surface soil (55 mg/kg) and decreased with increasing depth (25 mg/kg at 30 cm depth). However, for the DTPA-extractable iron the trend was opposite. Surface soil had relatively lower extractable iron concentration (84 mg/kg) and it increased with increasing depth (116 mg/kg at 30 cm depth). Ammonium acetate extractable Ca concentration of this soil was slightly higher as compared to that of the site I. Further Ca was relatively higher for the surface soil (3732 mg/kg) and decreased with increasing depth. The cation exchange capacity of this soil was relatively higher (53 to 65 meq/100g or $cmol_c$/kg) compared to that of the site I (16 to 20 meq/100g or $cmol_c$/kg). Total P (774 mg/kg for the site II compared to 423 mg/kg for the site I for surface soil) and total N (2395 mg/kg for the site II compared to 1598 for the site I for surface soil) concentrations of this soil was higher than that of the site I soil; however, both P and N decreased with increasing depth (Table 3.1).

There were no significant pH differences between the soils received different P treatments at 5 weeks (Figure 3.7). Total P concentration of P added fertilizer treatment was not significantly different from each other (Figure 3.8). Resin extractable P for both the granular and liquid MAP was significantly higher as compared to deep placed P fertilizer treatment followed by the control (Figure3.9). However, there was no significant difference in resin extractable P between the broadcast or deep placed two P treatments (Figure 3.8). This experiment was conducted during winter time (Nov.-Dec.) in the greenhouse, so environmental stress was seen in some plants and reflected as stunted growth. In some cases this was more severe than the others. Despite all this, plant biomass and P uptake were significantly higher for the broadcast MAP treatment as compared to the deep placed MAP; however, it was not significantly different than the respective liquid P treatments (Figure 3.11 and 3.12). Except for the TGMAP deep placed treatment, for all other treatments plant biomass was significantly higher than that of the control. There were no clear differences between two fertilizer sources or placement methods with respect to plant P concentration (Figure 3.12).

3.3.2 Scanning Electron Microscope with Energy Dispersive X-ray Analyzer (SEM-EDXA)

We were able to extract the remaining MAP granules intact after 5-wk of incubation from the columns without plants from both site I and II soil columns. None of the other columns (columns with plants) had any clearly visible intact granules. The original MAP granules and the incubated MAP granules extracted were analyzed using SEM-EDXA. Energy dispersive X-ray spectroscopy analysis showed that original MAP granules did not contain significant amounts of Al, Ca and Fe as expected (Figure 3.13). However, the incubated granules in soils extracted at 5-wk from both the broadcast and deep placed treatments, showed significant enrichment of Al, Ca and Fe. Further there was still significant amount of P remaining in these incubated granules. These observations are most likely resulted from the precipitation of dissolved P in the granules with soil cations that enter into the granules with the mass flow of water. This enrichment of Al, Fe and Ca in 5-wk incubated granules in soil also indicated that these cations enter the granules and begin to react with P even before granules dissolve completely. Monoammonium phosphate granules are highly hygroscopic and with mass flow of water, cations enter the granules and precipitate P inside the granules (Lombi et al., 2004; Hettiarachchi et al., 2006), thereby making applied P possibly unavailable for plant readily.

3.3.3 Interpretation of XANES Data

X-ray absorption near edge structure spectroscopy (XANES) spectra of standards used for the study is shown in the Figure 2.4 in chapter 2. Spectra for Fe-phosphate standards showed a pre-edge feature between -5 and -2 eV relative to white line. All calcium phosphate minerals had shoulder on the high energy side between 2 and 6 eV relative to white line. Aluminum phosphate minerals are characterized by weak pre edge inflection at about -1 eV relative to white line which can be clearly seen on the first derivative spectra. The adsorbed P species usually had more intense and narrow white line peak. These spectral features of phosphate bonded with Ca, Al and Fe have been observed previously (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003; Khare et al., 2005; Lombi et al., 2006).

3.3.3.1 Site I

The speciation results of soil samples from North farm site are shown in Table 3.1. Speciation of P in original soil showed that adsorbed-P species were the dominant P species in the 0 to 7 cm surface soils while monetite-like form dominated the P speciation in the 7 to 15 cm layer. For P treated soils speciation results showed predominance of Fe-P in all the treatments except for the granular P deep placed treatment. This site had relatively lower pH (5.7 to 5.9) as compared to that of site II, Ottawa site (6.1 to 6.6). At 5-wk time period the soil pH was in the range of 5.2 to 5.3. The predominance of Fe-P like forms may be attributed to the pH level of soil at 5-wk time period which favored the formation of Fe-P like forms (Lindsay, 1979). The adsorbed P species were the second dominating species found in this soil and they were in aluminum oxide-adsorbed P- like forms. Adsorbed P species were relatively in higher proportion in the broadcasted treatments (surface soils) as compared to that of the deep placed treatments. In the MAP deep placed treatment the dominant P species in soil was monetite- like form and there were no any other Ca-P phosphate species identified at this time period. Monetite can be expected as an initial P reaction product formed right after P fertilizer application to soil and is considered more soluble than apatite (Lindsay 1979). For the liquid P treatment the speciation results did not show distinct differences due to P placement. Resin extractable P at this site was relatively lower for both broadcast and deep placed treatments as compared to the Ottawa site. Moreover for this soil resin extractable P was relatively higher for the broadcast granular P treatment followed by the broadcast liquid P and the deep placed-granular and -liquid treatments. However resin extractable P calculated as a percentage of total P was not different for fertilizer source or placement methods. Both speciation and resin extractable P results indicated that there was no distinguishable difference between the broadcasted and deep placed liquid fertilizer treatments for this soil.

3.3.3.2 Site II

The speciation results for the Ottawa site soil are shown in Table 3.2. For P treated soils, speciation results showed that the major reaction products formed in this soil at 5-wk after P fertilizer application were Ca-P like forms. However, significant amount of P species were found in adsorbed forms as well. For broadcast P fertilizer treatments, the reaction products were found to be in relatively more adsorbed forms as compared to that of the deep placed treatments. Aluminum and Fe-P phosphate were seen sporadically in some granular P applied treatments however not in significant amounts.

Originally this soil had relatively higher pH (6.1 to 6.6) compared to the site I, North farm soil. At 5-wk time period the pH of the soil was significantly higher (6.6 to 6.7) as compared to that of the site I (5.2 to 5.3). Ammonium oxalate extractable Ca concentration was also relatively higher (3136 to 3732 mg/kg) for this soil as compared to the North farm soil (2426 to 2550 mg/kg). The dominance of Ca-P minerals found in this soil may be attributed to the relatively higher soil pH, which favored formation of Ca- P like forms (Lindsay 1979), and to the high levels of extractable Ca in soil. For the liquid (TGMAP) deepband treatment, 74.5 % of P was in monetite-like P while remaining P was in hydroxyapatite-like. Monetite-like P forms are initial P reaction products formed at high pH and are more soluble than apatite-like forms (Lindsay 1979). The occurrence of Ca-P in slightly acidic soil has been reported by other researchers (Simard et al. 1995; Beauchemin et al.2003). In a study conducted by Beauchemin et al. (2003), in mineral P added slightly alkaline soils, Ca-P was the dominant P species. However, in acidic soil there was a lower percentage of Ca-P species. Resin extractable P was relatively higher as compared to that of the site I, North farm soil and ranged from 40 to 45 mg/kg for the broadcast P treatments and 28-35 mg/kg for the deep placed P treatments. The higher proportion of adsorbed species in this soil as compared to the soil from site I might be the reasoning for observing higher amounts of resin extractable in this soil. In general, weakly adsorbed P species (via outer-sphere complexation and diffuse-swarm) could be considered as relatively more extractable than most P minerals seen in soils. Moreover, higher resin extractable P levels can also be explained by relatively high, near neutral pH of this soil. In general near neutral soils have relatively high P availability as precipitation of P as Fe-, Al- and Ca- P would be reduced. Majority of adsorbed P species were found to be in associated with alumina and ferrihydrite for this site. Beauchemin et al. (2003) also found higher proportion of P adsorbed on Fe or Al-oxide minerals for most of the acidic soils. Relatively lower percentage of P reactions products were found be in association with Fe and Al for the granular broadcast and the granular- and liquid-deep placed treatments as compared to the liquid-broadcast P treatment.

3.4 Conclusions

Although plants were P responsive no clear differences in plant P uptake with respect to P source or P placement method were observed in the site I study. This may be partly attributed to the restricted soil volume that plants had been exposed to during this greenhouse column study conducted during summer/fall months. There were differences in plant P uptake between the no P control and some P treatments and between different P treatments in the site II study. These differences might partly be attributed to the greenhouse conditions existed during winter months. This observation might be an indication that P source or P placement methods could matter particularly when plants are under stress conditions. Reaction products formed after application of P in two different soils at 5-wk was highly correlated with soil pH. Speciation results for the soils from site I with relatively lower pH at 5 -wk time showed that the reaction products of P fertilizers dominated by Fe-P like forms. However, speciation results of soil from site II with neutral to slightly acid pH (6.6-6.7) at 5-wk time showed that the reaction products of P fertilizers dominated by Ca-phosphate like forms. There were no clear trends in reaction products with respect to P source or the P placement. Broadcast granular MAP showed higher resin extractable P at both the sites compared to the other treatments; however, when resin extractable P concentrations expressed as a percentage of total P those differences disappeared. It is therefore, hard to rule out the possibility that reasoning for observed differences in the resin extractable-P were not due the differences in total P concentration in soil. Results from scanning electron microscope combined with energy dispersive X-ray analysis of incubated fertilizer granules extracted from soils at 5-wk showed enrichment of Al, Fe and Ca in granules indirectly indicating that these cations enter the granules and begin to react with P even before granules dissolve completely.

3.5 References

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3.6 Figures and Tables

Figure Captions

Figure 3.1- pH at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.2- Total P at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.3- Resin extractable P at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.4- Resin Extractable P (as % of Total P) at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.5- Plant P Uptake (mg P/column) for different treatments (Site I).

Figure 3.6- Total plant P concentration (A) and plant dry biomass (B) at five weeks time (Site I).

Figure 3.7- pH at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.8- Total P at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.9- Resin extractable P at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.10- Resin extractable P (as % of total P) at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed. Granular MAP= MAP; liquid MAP = TGMAP.

Figure 3.11- Plant P Uptake (mg P/column) for different treatments (Site II).

Figure 3.12- Total plant P concentration (A) and plant dry biomass (B) at five weeks time (Site II).

Figure 3.13- Scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA) comparison of original and soil applied MAP granules.

Table 3.1 Basic properties of soil used for the study (A) Site I, and (B) Site II.

(A)

Sample Depth	**pH**	**CEC†**	**Extractable** **M3 P**	**Extractable** **Ca$_{ac}$**	**Extractable** **Fe$_{dtpa}$**	**Extractable** **Mn$_{dtpa}$**	**Extractable** **Al$^{3+}_{KCl}$**	**Total N**	**Total P**	**OM**	**Textural Class**
cm		**meq/100g**	**-----------------------------------mg/kg----------------------------------**							**%**	
0-7	5.9	16.1	45.4	2426.0	7.9	58.3	0.0	1598.0	423.0	3.2	SiL
7-15	5.7	20.3	19.6	2540.0	8.2	57.8	0.4	1114.0	329.0	2.3	SiCL
15-30	6.1	18.8	5.9	3174.0	27.8	25.0	0.1	1119.0	278.0	2.2	SiCL

(B)

Sample Depth	**pH**	**CEC†**	**Extractable** **M3 P**	**Extractable** **Ca$_{ac}$**	**Extractable** **Fe$_{dtpa}$**	**Extractable** **Mn$_{dtpa}$**	**Extractable** **Al$^{3+}_{KCl}$**	**Total N**	**Total P**	**OM**	**Textural Class**
cm		**meq/100g**	**-----------------------------------mg/kg-------------------------------**							**%**	
0-7	6.6	65.5	48.0	3732.0	84.0	55.0	0.1	2395.0	774.0	5.8	SiL
7-15	6.1	63.0	49.8	3136.0	112.0	50.0	0.1	1588.0	559.0	3.7	SiL
15-30	5.9	53.7	38.6	3202.0	116.0	25.0	0.2	1194.0	396.0	3.0	SiL

† CEC, cation exchange capacity; M3P, Mehlich III-extractable phosphorus, Ca$_{ac}$ –ammonium acetate extractable calcium; Fe$_{dtpa}$ and Mn$_{dtpa}$ – diethylene triamine pentaaceticacid extractable iron and manganese; Al$^{3+}_{KCl}$ -potassium chloride extractable aluminum; OM, organic matter content; SiL, silty loam; SiCL, silty clay loam.

Table 3.2 Fitting results for the final fit performed in first-derivative space with an energy range between -5 to 30 eV (Site I): Five weeks samples with plants.

	Ca-P minerals				**Al-P minerals**		**Fe-P minerals**		**Adsorbed P**				**Red.**
Treatment	**1†**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**χ2‡**
Control 0-7	-	9.4	-	-	-	-	10.2	-	80.4	-	-	-	0.021
Urea Broadcast	-	-	-	-	-	-	75.2	-	-	-	-	24.8	0.074
MAP Broadcast	-	-	-	-	-	-	-	69.7	30.3	-	-	-	0.009
TGMAP Broadcast	-	-	2.8	-	-	-	-	72.6	24.6	-	-	-	0.006
Control 7-15	-	-	-	69.1	-	26.8	-	-	-	-	4.1	-	0.007
MAP Deep placed	-	-	-	50.2	-	-	-	38.4	10.7	-	-	-	0.005
TGMAP Deep placed	-	-	-		-	-	-	77.5	17.6	4.9	-	-	0.009

† 1, Apatite, 2, hydroxyapatite; 3, rock phosphate; 4, monetite; 5,aluminum phosphate; 6, variscite; 7, strengite; 8, vivianite; 9, alumina adsorbed P; 10, ferrihydrite adsorbed P; 11, gibbsite adsorbed P; 12, goethite adsorbed P.

‡$\chi 2 = \Sigma(\mathrm{fit} - \mathrm{data})/\varepsilon]^2$ / $(N_{data} - N_{components})$ is the reduced chi-square statistic. Here ε is the estimated uncertainty in the normalized XANES data (taken as 0.01 for all data). The sum is over N_{data} points (185 data points between E=2144 and 2179 eV for all data), and $N_{components}$ is the number of components in the fit (either 2 or 3 as indicated in the Table). The total percentage was constrained to be 100% in all fits. Typical uncertainties in the percentages listed for each standard component are 5%.

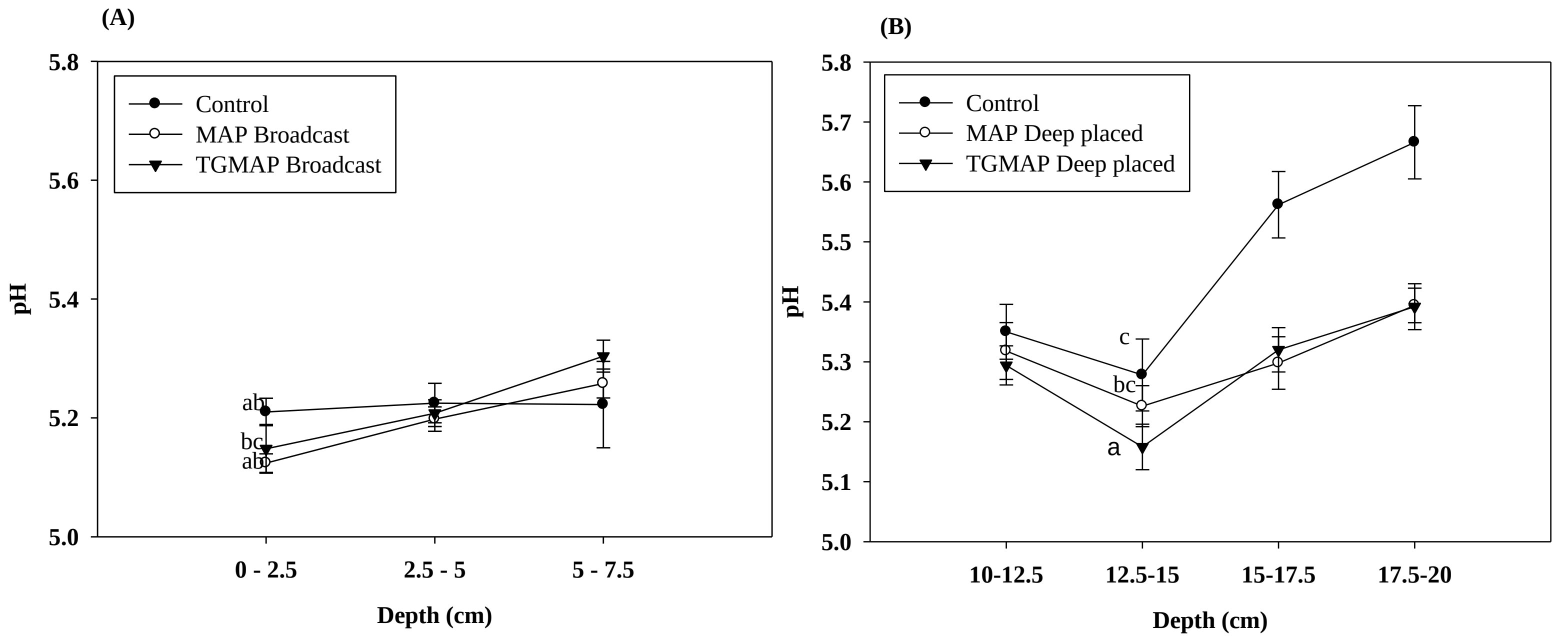
Table 3.3 Fitting results for the final fit performed in first-derivative space with an energy range between -5 to 30 eV (Site II): Five weeks samples with plants.

	Ca-P minerals				**Al-P minerals**		**Fe-P minerals**		**Adsorbed P**				**Red.**
Treatment	**1†**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**$\chi2$‡**
Control 0-7	-	25.7	-	-	-	11.2	-	29.0	34.2	-	-	-	0.006
Urea Broadcast	-	-	-	-	-	-	7.1	-	-	92.9	-	-	0.131
MAP Broadcast	28.5	-	-	-	-	-	-	6.7	64.8	-	-	-	0.007
TGMAP Broadcast	10.9	-	-	-	-	-	-	-	49.8	39.3	-	-	0.022
Control 7-15	-	-	-	68.9	-	11.8	6.2	-	13.0	-	-	-	0.007
Urea Deep placed	-	33.4	-	-	-	18.8	-	-	47.8	-	-	-	0.003
MAP Deep placed	-	37.5	-	-	-	10.7	-	-	9.0	6.5	36.3	-	0.002
TGMAP Deep placed	-	25.5	-	74.5	-	-	-	-	-	-	-	-	1.362

† 1, Apatite, 2, hydroxyapatite; 3, rock phosphate; 4, monetite; 5,aluminum phosphate; 6, variscite; 7, strengite; 8, vivianite; 9, alumina adsorbed P; 10, ferrihydrite adsorbed P; 11, gibbsite adsorbed P; 12, goethite adsorbed P.

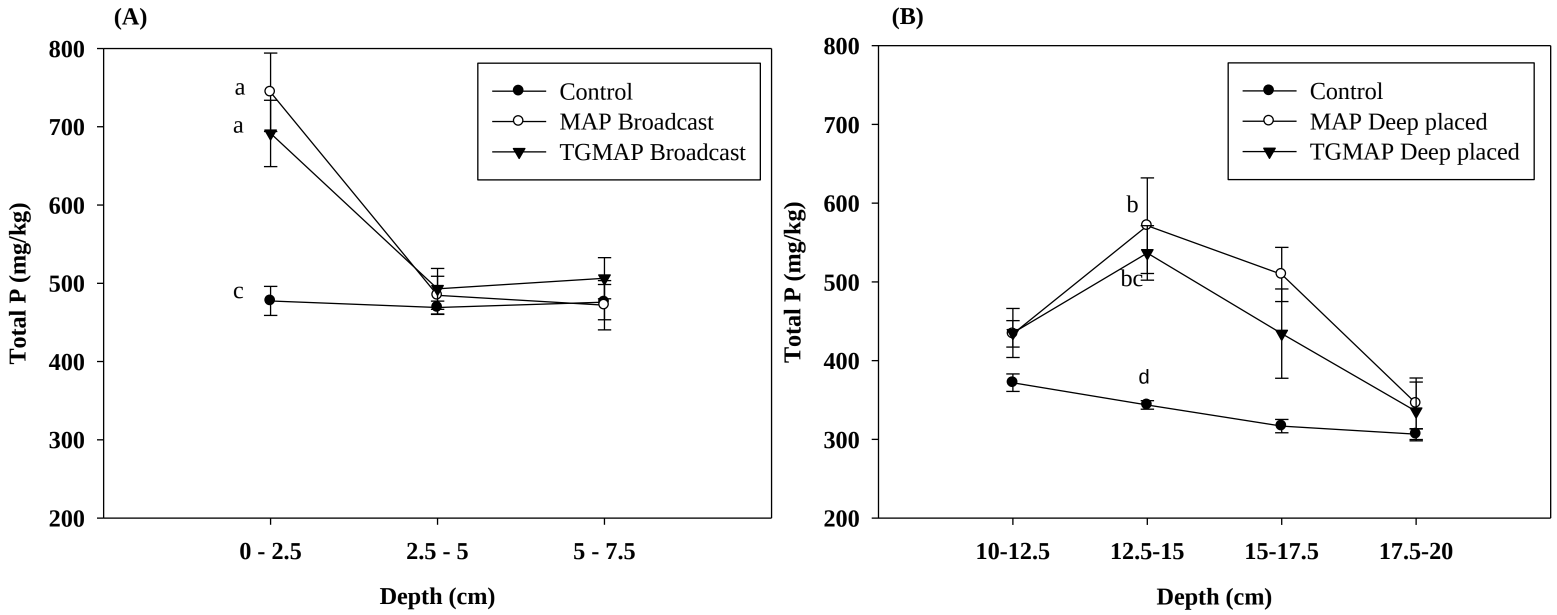
‡$\chi2 = \Sigma(\text{fit} - \text{data})/\varepsilon]^2$ / $(N_{data} - N_{components})$ is the reduced chi-square statistic. Here ε is the estimated uncertainty in the normalized XANES data (taken as 0.01 for all data). The sum is over N_{data} points (185 data points between E=2144 and 2179 eV for all data), and $N_{components}$ is the number of components in the fit (either 2 or 3 as indicated in the Table). The total percentage was constrained to be 100% in all fits. Typical uncertainties in the percentages listed for each standard component are 5%.

Figure 3.1 pH at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed.



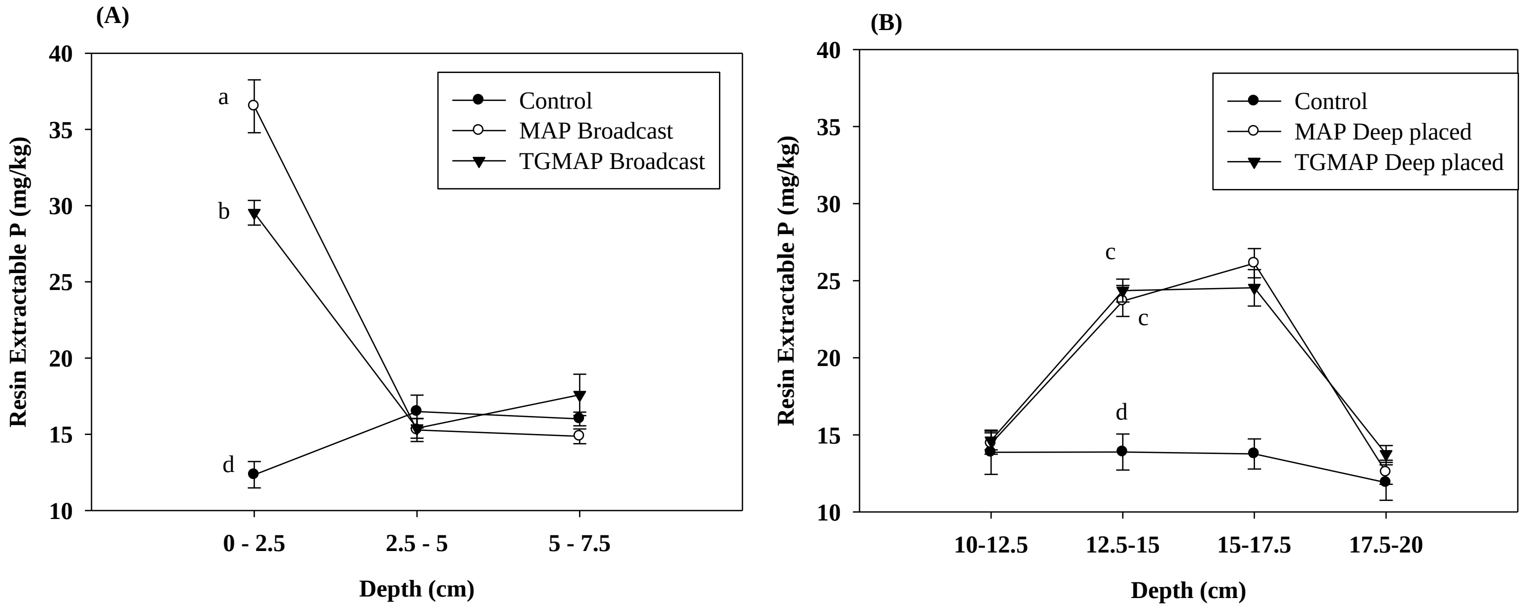
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.2 Total P at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed.



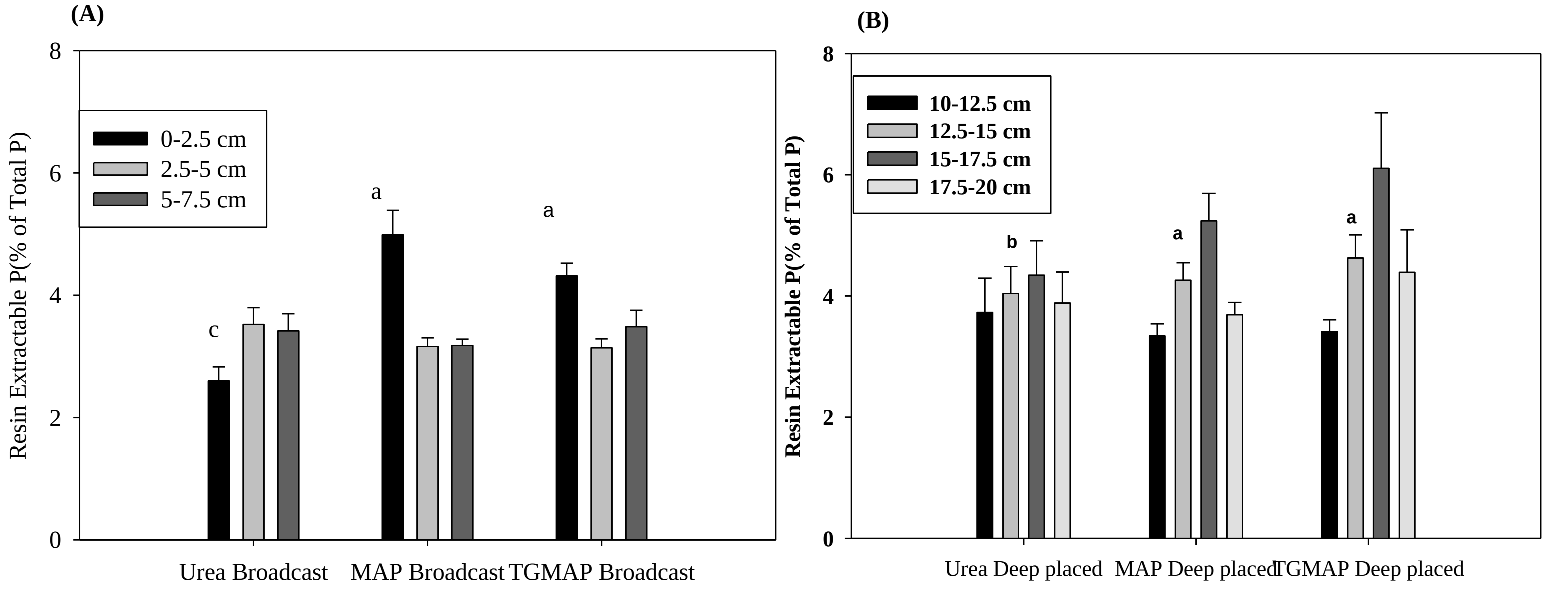
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.3 Resin extractable P at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed.



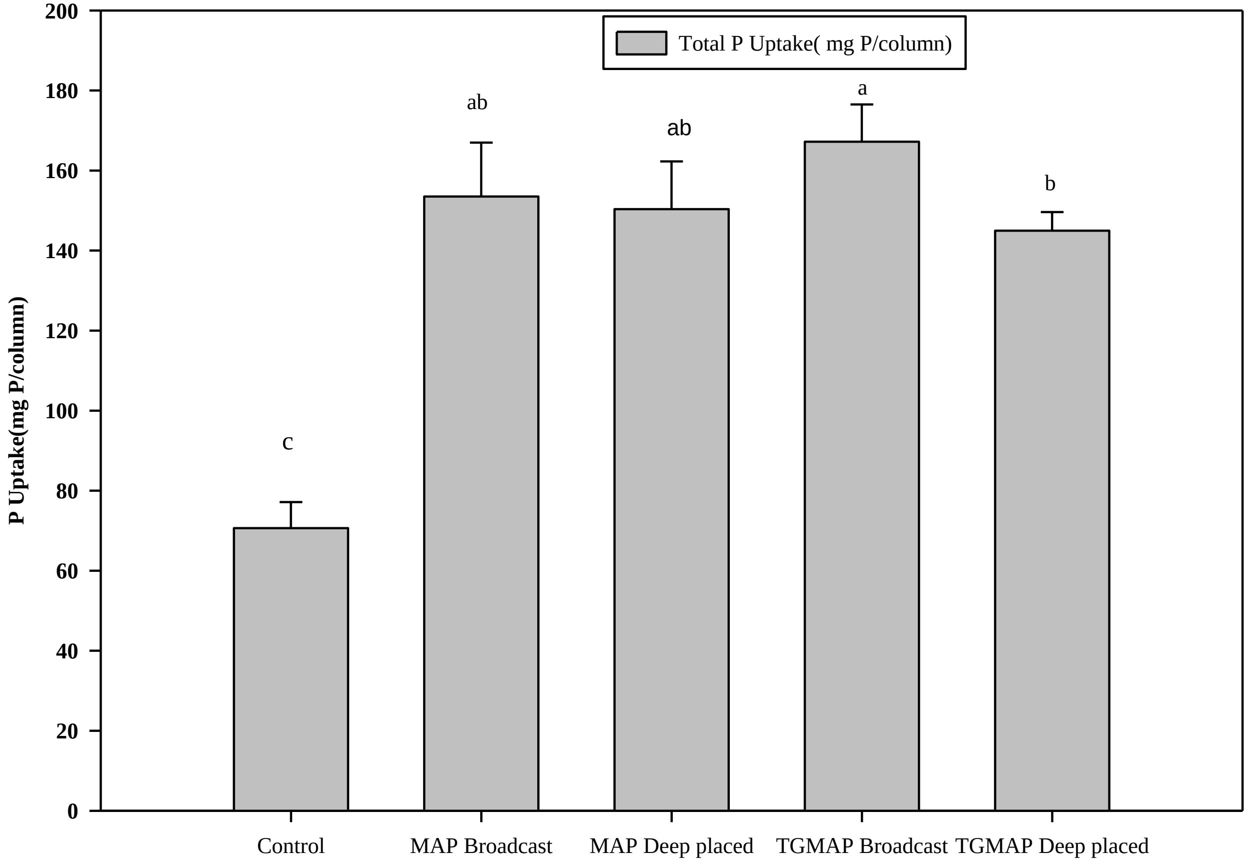
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.4 Resin extractable P (% of Total P) at different distances from the point of fertilizer application (Site I): (A) Five weeks broadcast, and (B) Five weeks deep placed.



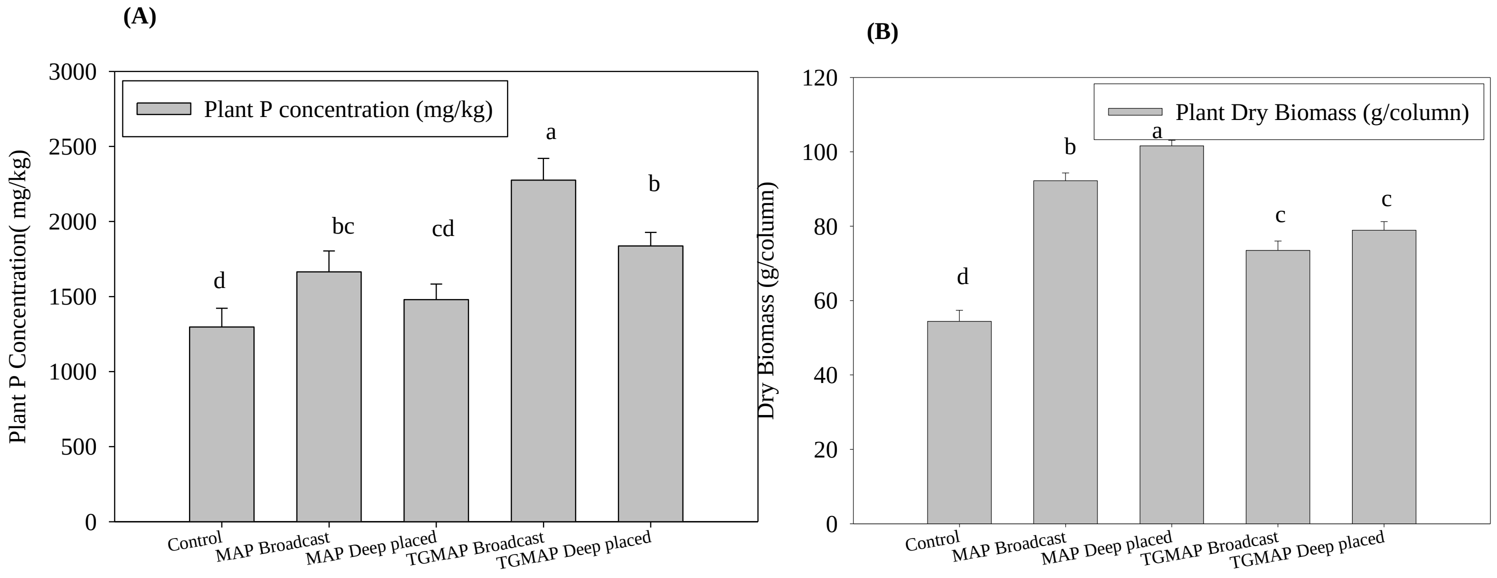
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.5 Plant P Uptake (mg P/column) for different treatments (Site I).



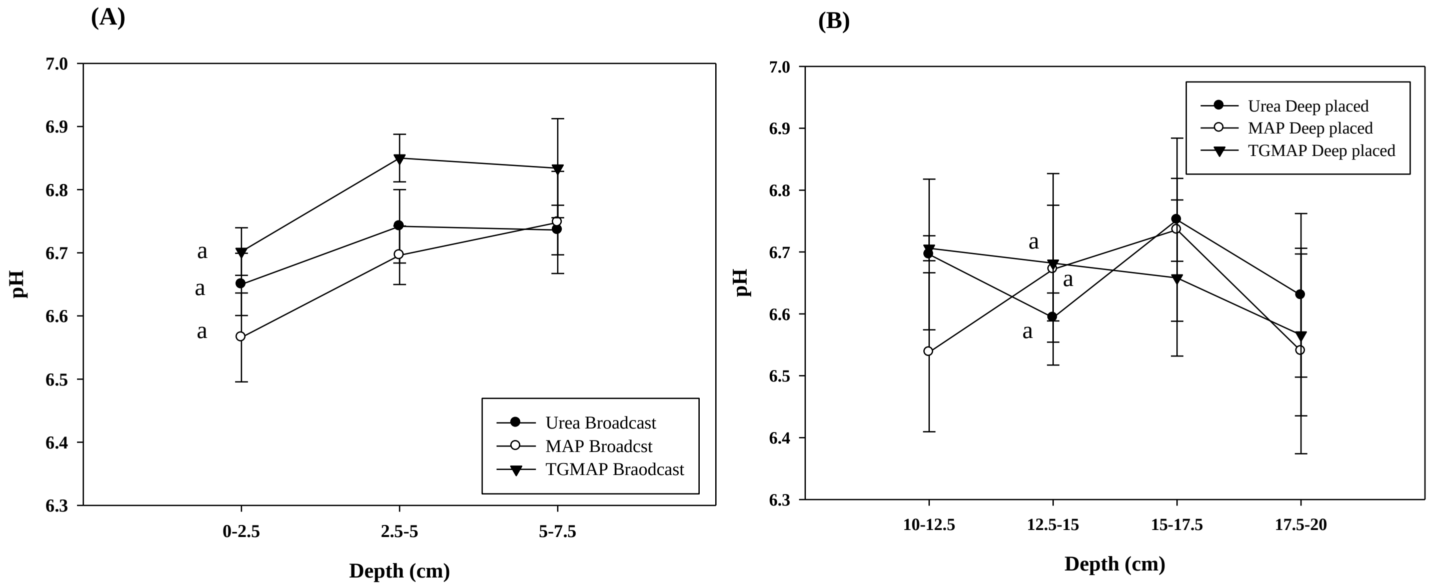
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.6 Total plant P concentration (A) and plant dry biomass (B) at five weeks time (Site I).



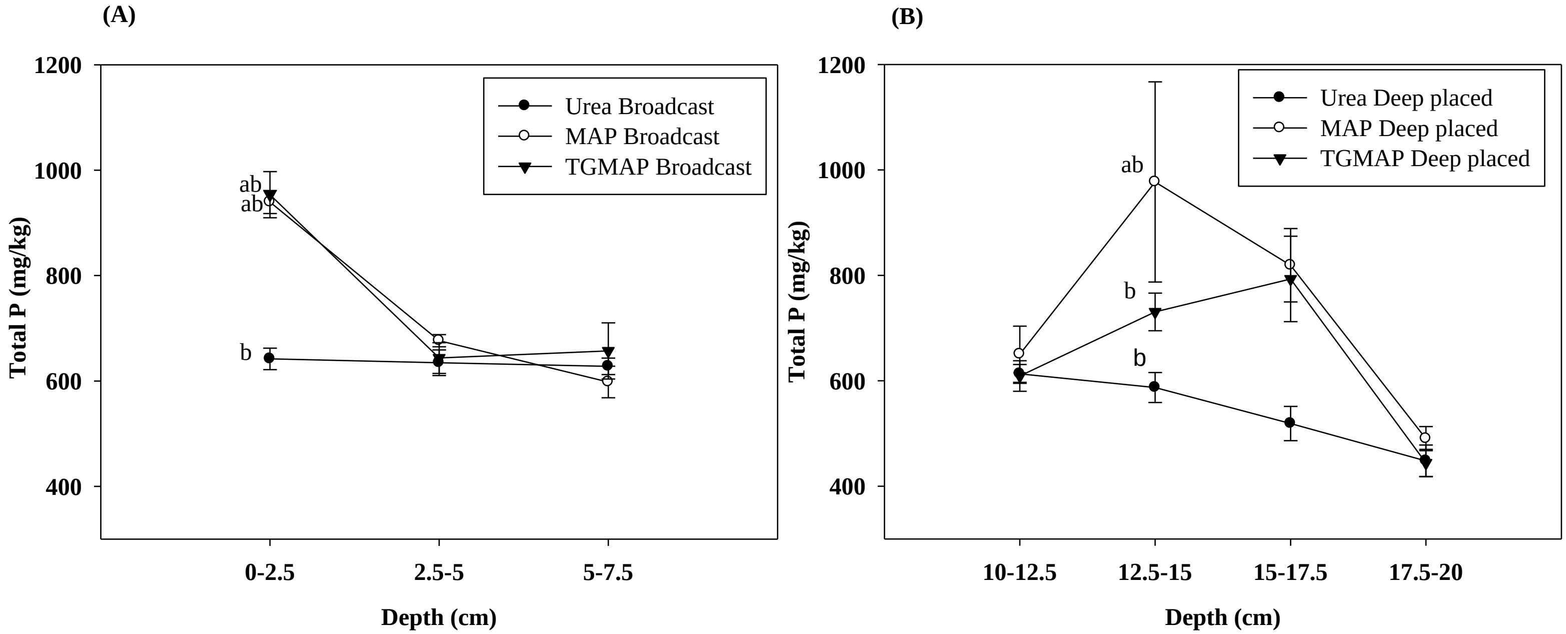
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.7 pH at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed.



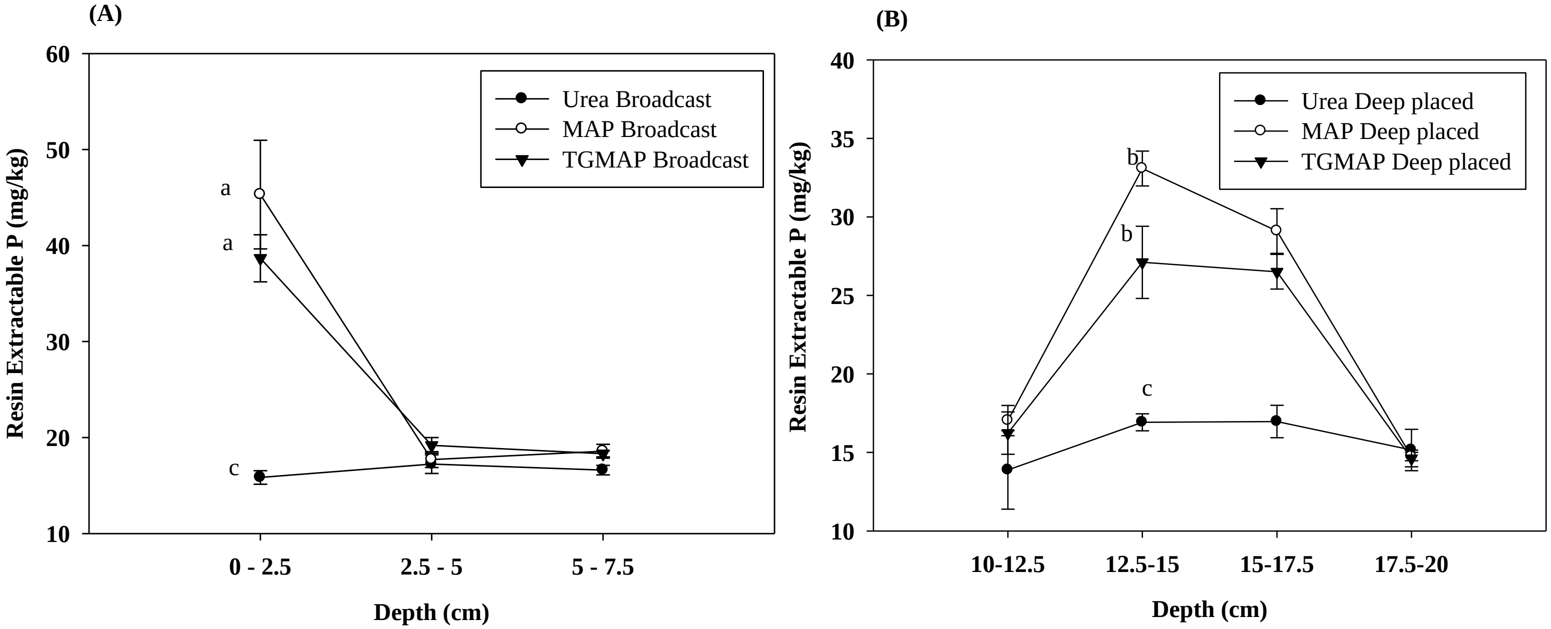
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.8 Total P at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed.



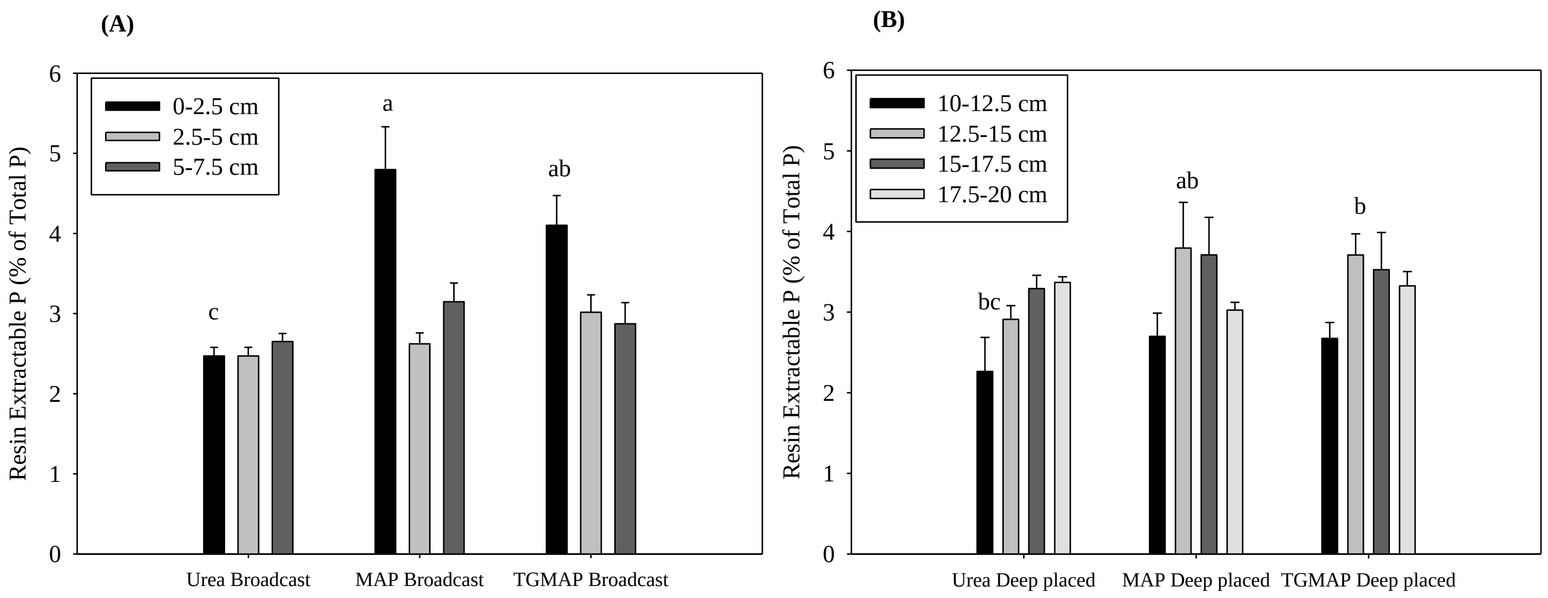
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.9 Resin extractable P at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed.



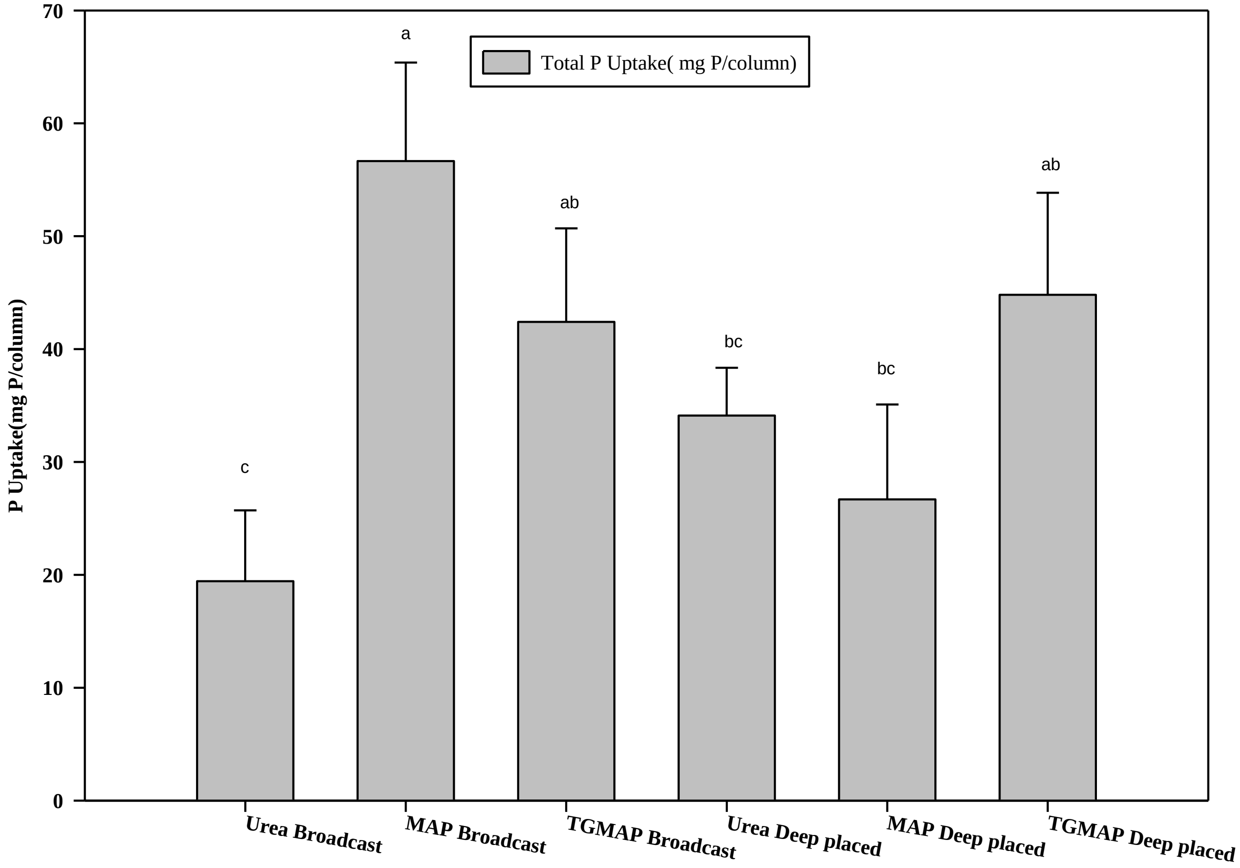
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.10 Resin extractable P (% of Total P) at different distances from the point of fertilizer application (Site II): (A) Five weeks broadcast, and (B) Five weeks deep placed.



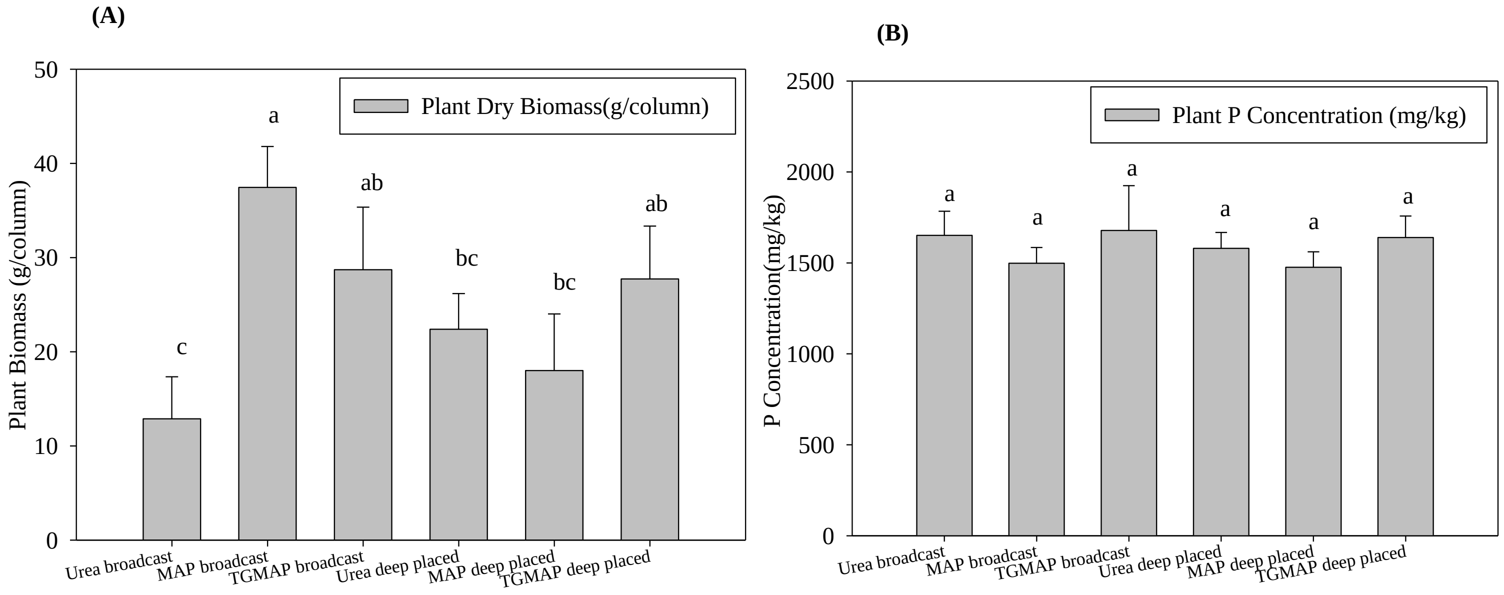
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.11 Plant P uptake (mg P/column) for different treatments (Site II).



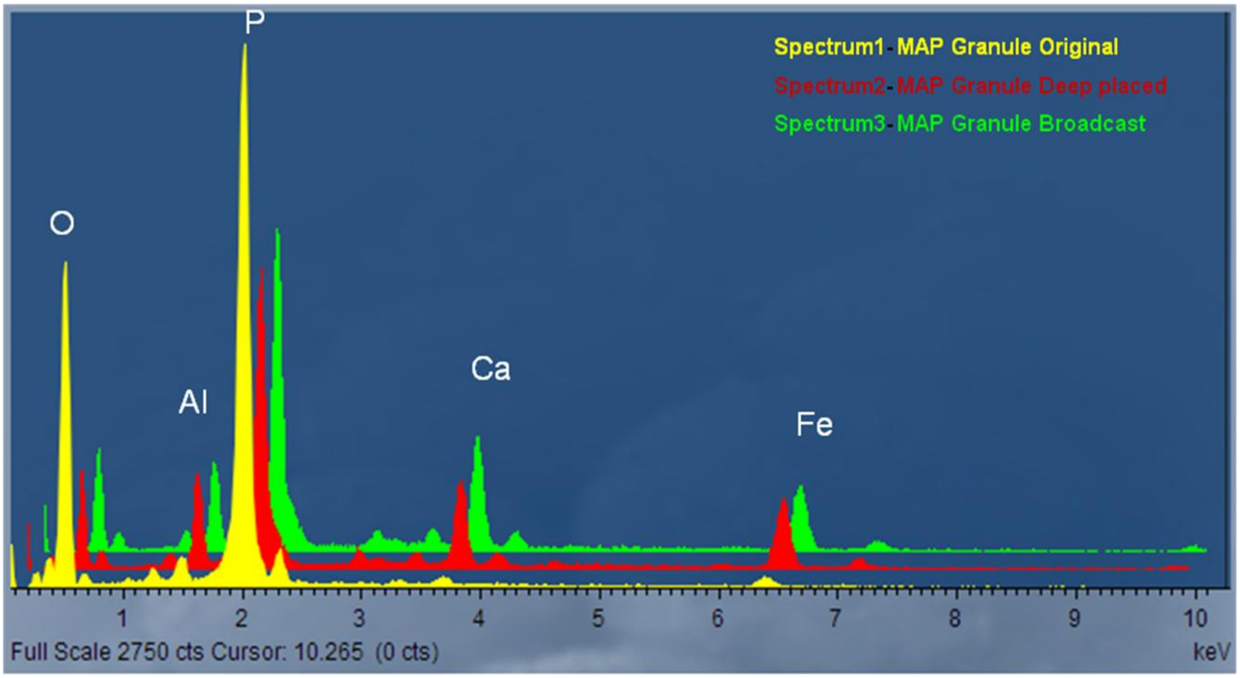
†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.12 Plant biomass (A) and total plant P concentration (B) and at five weeks time (Site II).



†Letters in figure indicates significance at the 0.05 probability level.

Figure 3.13 Scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA) comparison of original and soil applied MAP granules.



Chapter 4 - Conclusions

Results from the field and greenhouse experiments indicated that the nature of reaction products formed after application of P fertilizers in soils is mainly dependent on pH conditions of the soil. Acidic pH (pH < 5.8) tended to favor formation of Fe-P and Al-P like forms whereas slightly acidic near neutral pH favored formation of Ca-P like forms. Further, P placement and source appeared have significant effects on reaction pathways of P fertilizers. The availability of applied P fertilizers was found to be enhanced as a result of deep banding compared to the surface broadcasting or the deep placed/deep broadcasting methods. Field experiment showed that in deep banded liquid MAP fertilizer added system, P continued to remain in relatively more resin extractable forms, and more adsorbed P-like forms even after 6 months of fertilizer application. Our results indicate that deep banding of liquid P fertilizers would most likely to provide agronomically and environmentally efficient P management strategy at least for this acid soil under long-term no-till practice. We believe this finding warrants further investigations.

Appendix A - Speciation Study

Figure A.1 North farm field study plot map.

501	502	503	504	505	506
401	402	403	404	405	406
301	302	303	304	305	306
201	202	203	204	205	206
101	102	103	104	105	106

^ East

Plot dimensions are 5’ by 8’ with a 3’ alley

Treatments were applied 7/10/09

Treatments:

1. Broadcast Urea
2. Deep Band Urea
3. Broadcast MAP
4. Deep Band MAP
5. Broadcast TG MAP
6. Deep Band TG MAP

Figure A.2 X-ray diffraction of (XRD) pattern of ferrihydrite.

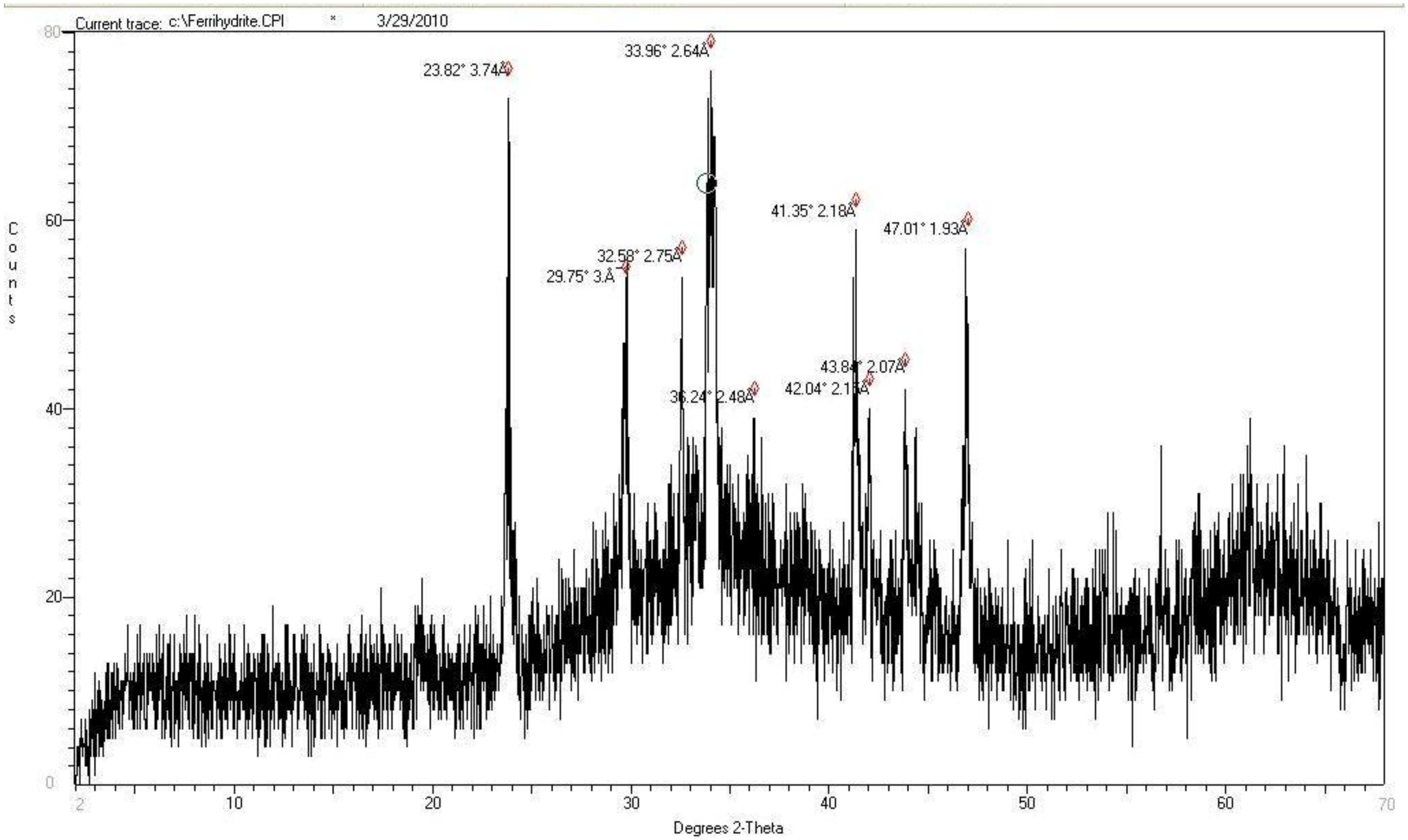


Figure A.3 X-ray diffraction of (XRD) pattern of goethite.

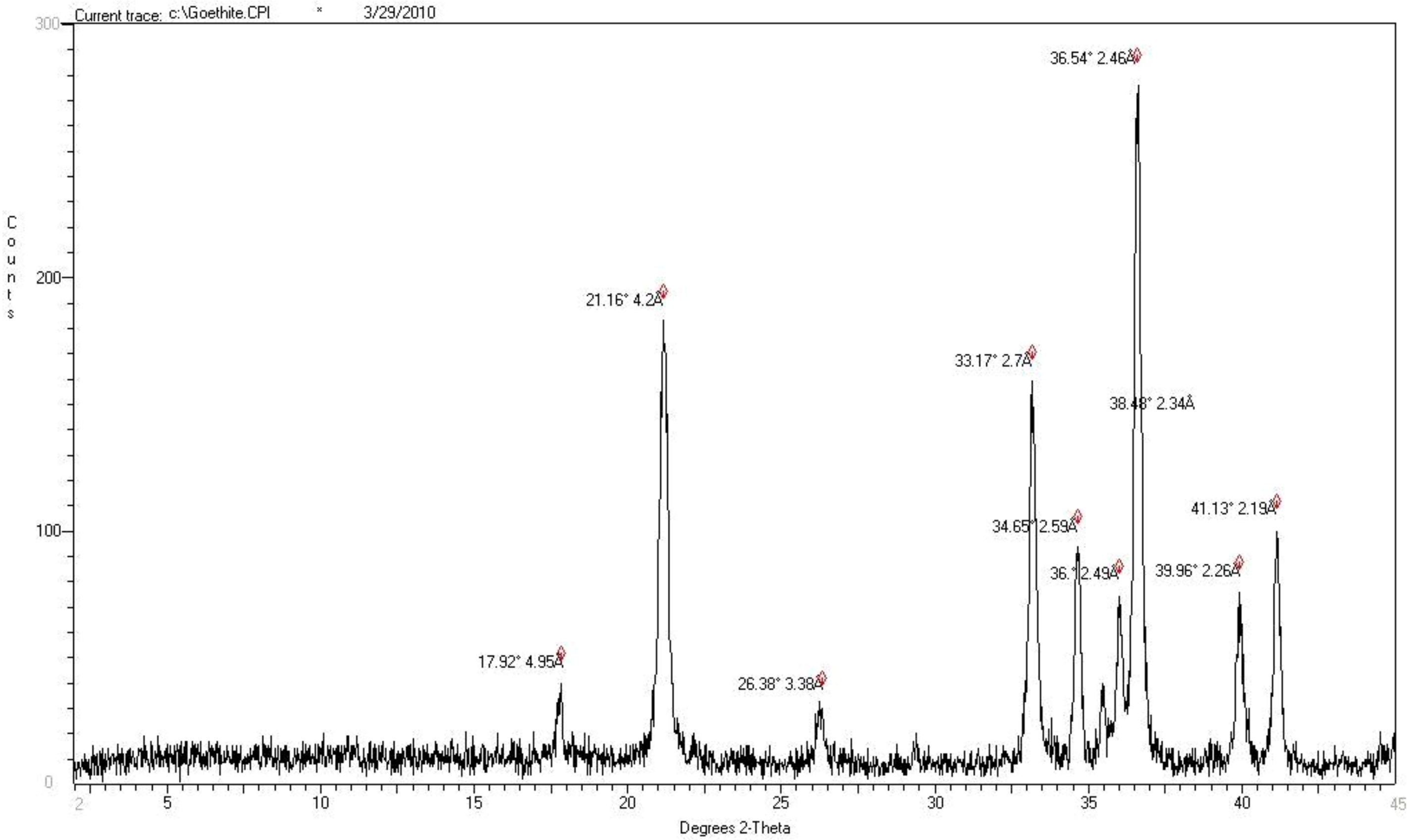


Figure A.4 X-ray diffraction of (XRD) pattern of strengite (I).

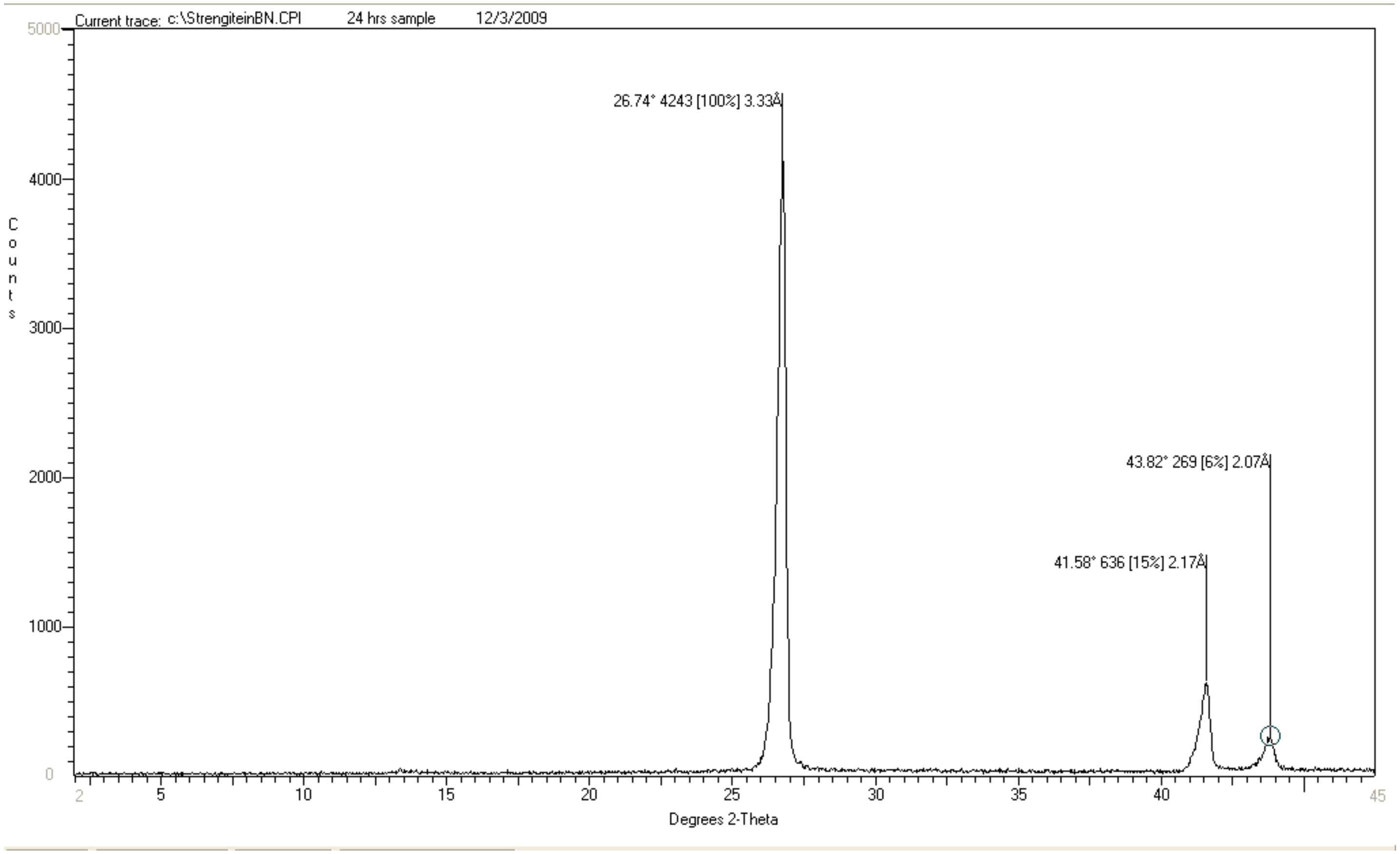


Figure A.5 X-ray diffraction of (XRD) pattern of strengite (II).

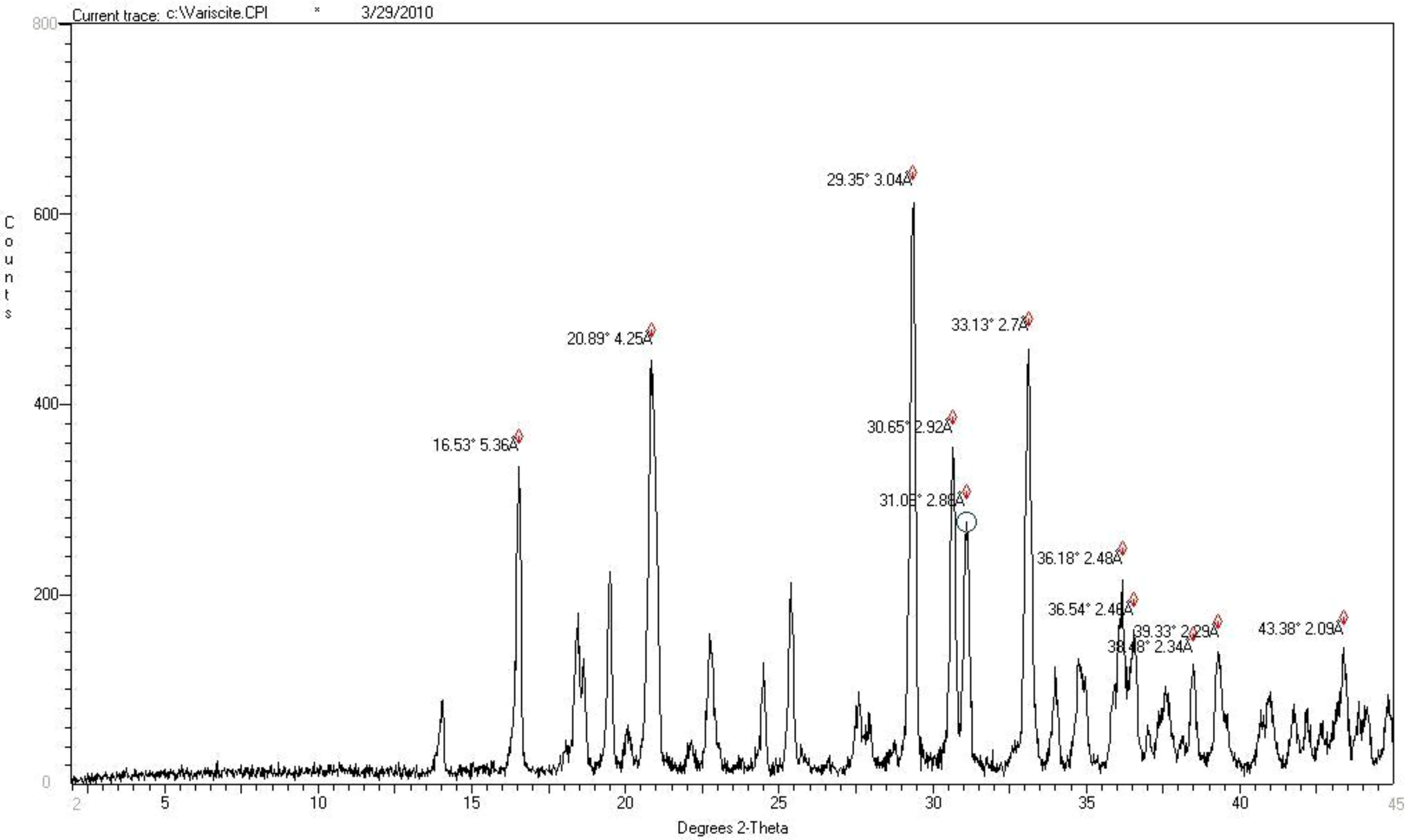


Figure A.6 Scanning electron microscope image of incubated granule.

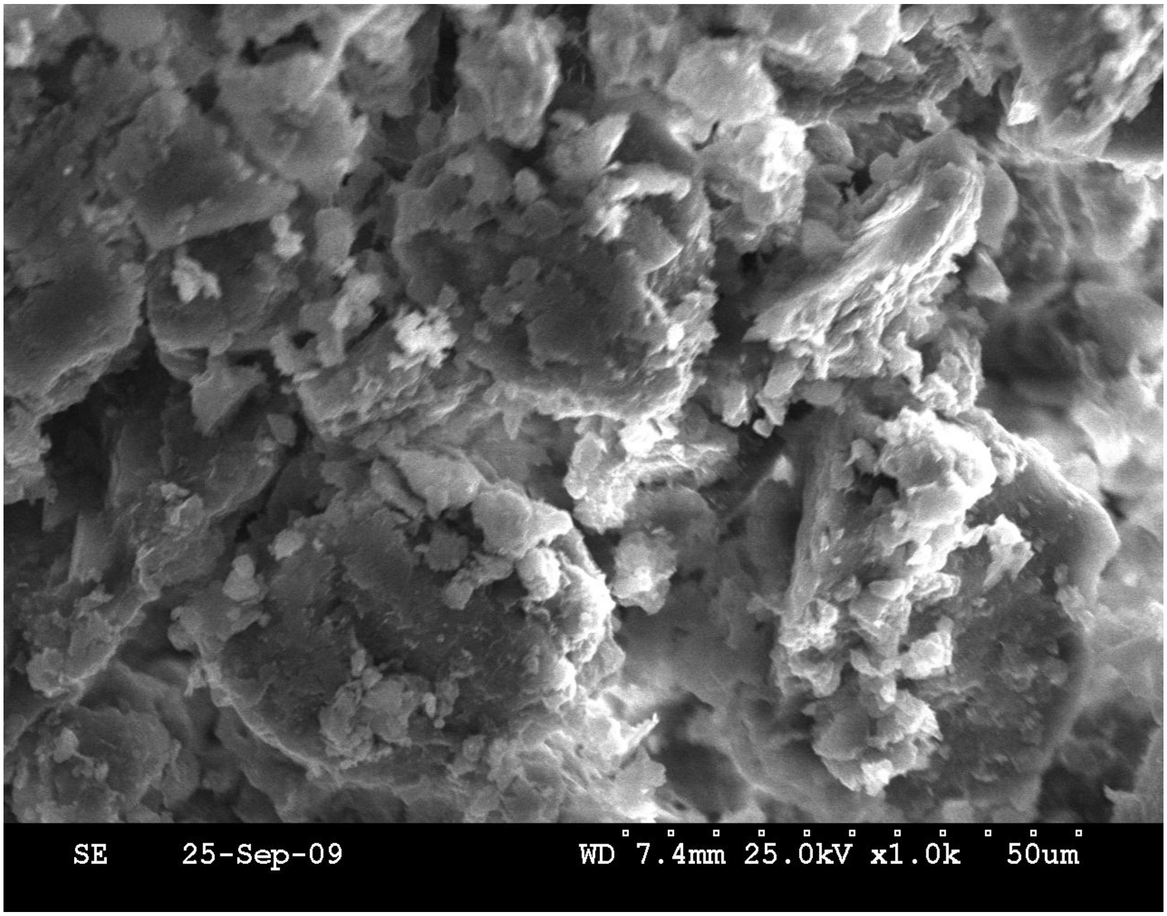
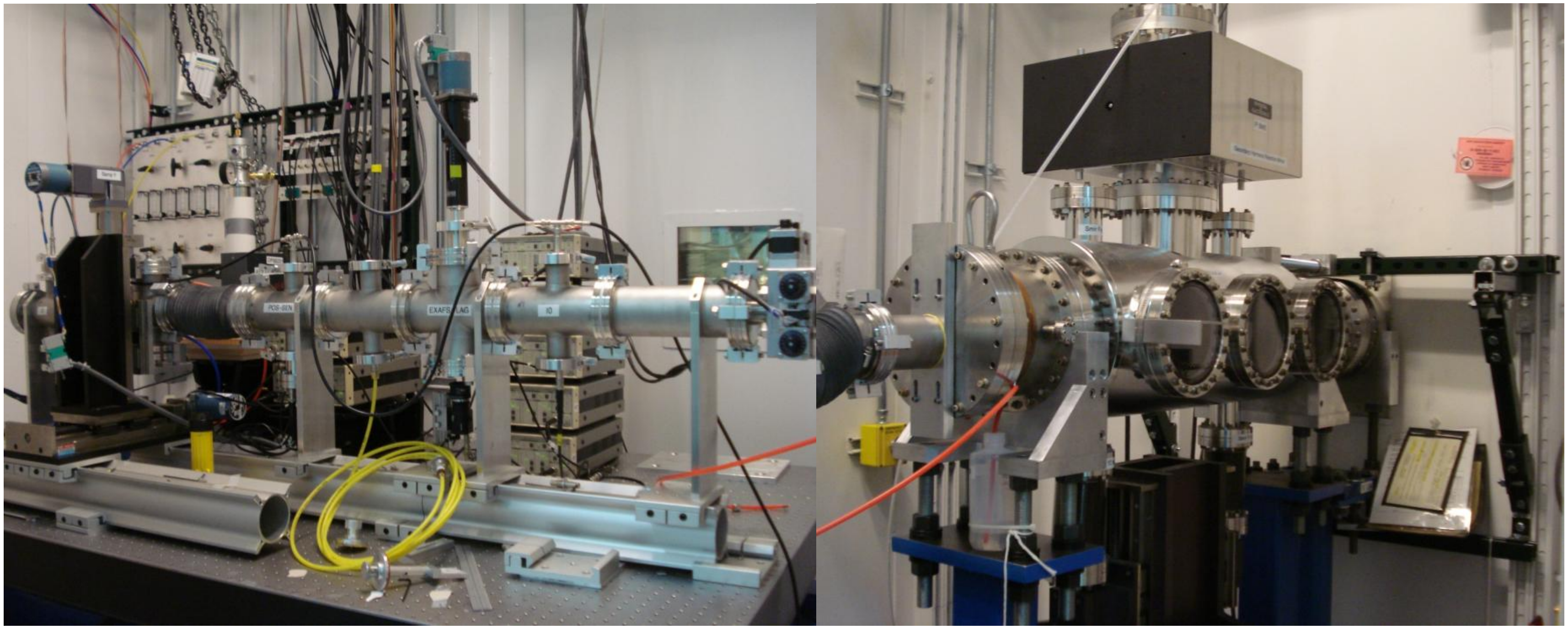


Figure A.7 Sample setup for XANES analysis.

Figure A.8 Beamline Setup, Sector 9 BM-B (Picture I).

Figure A.9 Beamline Setup, Sector 9 BM-B (Picture II).



Appendix B - Laboratory Data

Table B.1Phosphorus content analysis of selected MAP granules.

Sample ID	P 178.222 (mg/L)	MAP (g)	Dilution (ml)	P 178.222 (mg/kg)	P(mg/42mg)	Average P(mg/42 mgMAP)	Standard Error
Sample 1	80.690	0.039	100.000	209585.195	8.803	9.088	0.231
Sample 2	73.010	0.034	100.000	212237.890	8.914		
Sample 3	79.312	0.036	100.000	223415.257	9.383		
Sample 4	106.009	0.048	100.000	219026.298	9.199		
Sample 5	82.248	0.038	100.000	217587.284	9.139		

Table B.2 pH at different distance from point of fertilizer application data from North farm 5 weeks field samples.

Sample ID	pH	Sample ID	pH	Sample ID	pH	Sample ID	pH	Sample ID	pH	Average pH	Standard Error
104 0-2.5	5.63	201 0-2.5	5.26	302 0-2.5	5.01	405 0-2.5	5.13	504 0-2.5	4.94	5.19	0.12
104 2.5-5	5.28	201 2.5-5	4.78	302 2.5-5	4.96	405 2.5-5	4.75	504 2.5-5	4.77	4.91	0.10
104 5-7.5	5.20	201 5-7.5	4.97	302 5-7.5	4.97	405 5-7.5	4.65	504 5-7.5	4.87	4.93	0.09
106 7.5-10	4.69	202 7.5-10	4.98	306 7.5-10	5.44	402 7.5-10	5.23	501 7.5-10	4.71	5.01	0.15
106 10-12.5	4.91	202 10-12.5	5.20	306 10-12.5	5.19	402 10-12.5	5.12	501 10-12.5	4.96	5.08	0.06
106 12.5-15	5.16	202 12.5-15	5.42	306 12.5-15	5.04	402 12.5-15	4.80	501 12.5-15	5.10	5.10	0.10
106 15-17.5	5.31	202 15-17.5	5.48	306 15-17.5	5.12	402 15-17.5	4.88	501 15-17.5	5.50	5.26	0.12
106 17.5-20	5.44	202 17.5-20	5.59	306 17.5-20	5.24	402 17.5-20	4.89	501 17.5-20	5.23	5.28	0.12
105 0-2.5	5.11	206 0-2.5	5.22	305 0-2.5	5.06	401 0-2.5	5.04	505 0-2.5	5.09	5.10	0.03
105 2.5-5	4.76	206 2.5-5	5.16	305 2.5-5	4.90	401 2.5-5	5.02	505 2.5-5	4.70	4.91	0.08
105 5-7.5	5.02	206 5-7.5	5.00	305 5-7.5	4.97	401 5-7.5	5.12	505 5-7.5	4.76	4.97	0.06
103 7.5-10	5.04	204 7.5-10	4.77	301 7.5-10	4.80	404 7.5-10	4.84	506 7.5-10	4.58	4.81	0.07
103 10-12.5	5.02	204 10-12.5	4.75	301 10-12.5	4.84	404 10-12.5	4.78	506 10-12.5	4.48	4.77	0.09
103 12.5-15	5.31	204 12.5-15	5.00	301 12.5-15	5.32	404 12.5-15	4.87	506 12.5-15	4.31	4.96	0.18
103 15-17.5	5.15	204 15-17.5	5.24	301 15-17.5	5.31	404 15-17.5	4.71	506 15-17.5	4.92	5.07	0.11
103 17.5-20	5.25	204 17.5-20	5.32	301 17.5-20	5.33	404 17.5-20	5.07	506 17.5-20	5.16	5.23	0.05
101 0-2.5	5.18	203 0-2.5	5.01	303 0-2.5	4.94	406 0-2.5	5.07	502 0-2.5	5.09	5.06	0.04
101 2.5-5	5.08	203 2.5-5	4.98	303 2.5-5	4.85	406 2.5-5	4.83	502 2.5-5	4.80	4.91	0.05
101 5-7.5	5.13	203 7.5-10	4.96	303 5-7.5	5.03	406 5-7.5	4.07	502 5-7.5	4.48	4.73	0.20
102 7.5-10	5.23	205 7.5-10	4.64	304 7.5-10	5.05	403 7.5-10	4.59	503 7.5-10	4.36	4.77	0.16
102 10-12.5	4.94	205 10-12.5	4.97	304 10-12.5	4.85	403 10-12.5	4.80	503 10-12.5	4.74	4.86	0.04
102 12.5-15	5.02	205 12.5-15	5.27	304 12.5-15	4.76	403 12.5-15	4.95	503 12.5-15	5.04	5.01	0.08
102 15-17.5	5.25	205 15-17.5	5.57	304 15-17.5	4.95	403 15-17.5	5.17	503 15-17.5	5.35	5.26	0.10
102 17.5-20	5.13	205 17.5-20	5.61	304 17.5-20	5.30	403 17.5-20	5.37	503 17.5-20	5.51	5.38	0.8

Table B.3 Total P at different distance from point of fertilizer application data from North farm 5 weeks field samples.

Sample ID	†P 178.222 mg/kg	Sample ID	P 178.223 mg/kg	Sample ID	P 178.223 mg/kg	Sample ID	P 178.223 mg/kg	Sample ID	P 178.223 mg/kg	Average P mg/kg	Standard Error
104 0-2.5	408.20	201 0-2.5	378.39	302 0-2.5	540.04	405 0-2.5	534.20	504 0-2.5	579.62	488.09	39.76
104 2.5-5	349.17	201 2.5-5	264.85	302 2.5-5	407.27	405 2.5-5	392.27	504 2.5-5	517.56	386.22	41.13
104 5-7.5	314.00	201 5-7.5	202.59	302 5-7.5	376.50	405 5-7.5	414.34	504 5-7.5	512.80	364.05	51.67
106 5-7.5	353.20	202 5-7.5	410.63	306 5-7.5	459.52	402 5-7.5	436.16	501 5-7.5	389.79	409.86	18.40
106 7.5-10	264.56	202 7.5-10	292.12	306 7.5-10	250.87	402 7.5-10	414.70	501 7.5-10	529.43	350.33	53.32
106 10-12.5	207.02	202 10-12.5	191.68	306 10-12.5	269.08	402 10-12.5	441.00	501 10-12.5	489.18	319.59	61.27
106 12.5-15	260.42	202 12.5-15	213.72	306 12.5-15	224.09	402 12.5-15	457.98	501 12.5-15	479.99	327.24	58.49
106 15-17.5	227.91	202 15-17.5	244.26	306 15-17.5	233.30	402 15-17.5	454.43	501 15-17.5	406.41	313.26	48.50
106 17.5-20	239.82	202 17.5-20	230.63	306 17.5-20	232.14	402 17.5-20	334.45	501 17.5-20	372.39	281.89	29.85
105 0-2.5	445.51	206 0-2.5	453.03	305 0-2.5	654.28	401 0-2.5	814.82	505 0-2.5	824.19	638.37	82.90
105 2.5-5	342.70	206 2.5-5	315.95	305 2.5-5	306.00	401 2.5-5	610.55	505 2.5-5	511.93	417.42	61.04
105 5-7.5	325.32	206 5-7.5	292.98	305 5-7.5	272.95	401 5-7.5	432.74	505 5-7.5	494.66	363.73	42.79
103 5-7.5	547.59	204 5-7.5	992.61	301 5-7.5	766.79	404 5-7.5	756.27	506 5-7.5	948.46	802.34	79.32
103 7.5-10	499.40	204 7.5-10	469.76	301 7.5-10	542.33	404 7.5-10	585.29	506 7.5-10	1088.79	637.11	114.60
103 10-12.5	465.48	204 10-12.5	247.70	301 10-12.5	400.62	404 10-12.5	371.14	506 10-12.5	666.91	430.37	68.90
103 12.5-15	295.86	204 12.5-15	186.89	301 12.5-15	339.49	404 12.5-15	434.77	506 12.5-15	444.46	340.29	47.58
103 15-17.5	243.33	204 15-17.5	212.35	301 15-17.5	301.13	404 15-17.5	334.17	506 15-17.5	390.84	296.36	31.82
103 17.5-20	245.95	204 17.5-20	291.98	301 17.5-20	324.44	404 17.5-20	378.05	506 17.5-20	384.29	324.94	26.14
101 0-2.5	707.99	203 0-2.5	536.70	303 0-2.5	632.06	406 0-2.5	645.12	502 0-2.5	901.75	684.72	60.79
101 2.5-5	321.35	203 2.5-5	302.21	303 2.5-5	400.30	406 2.5-5	362.88	502 2.5-5	498.61	377.07	34.80
101 5-7.5	432.39	203 7.5-10	209.71	303 5-7.5	376.07	406 5-7.5	372.58	502 5-7.5	462.52	370.65	43.70
102 5-7.5	423.79	205 5-7.5	780.83	304 5-7.5	706.24	403 5-7.5	822.77	503 5-7.5	777.86	702.30	72.10
102 7.5-10	247.89	205 7.5-10	565.17	304 7.5-10	1146.35	403 7.5-10	1117.31	503 7.5-10	885.69	792.48	171.42
102 10-12.5	278.96	205 10-12.5	252.12	304 10-12.5	703.88	403 10-12.5	572.15	503 10-12.5	591.05	479.63	90.36
102 12.5-15	393.59	205 12.5-15	210.17	304 12.5-15	462.44	403 12.5-15	431.21	503 12.5-15	366.92	372.87	43.80
102 15-17.5	228.86	205 15-17.5	205.50	304 15-17.5	333.59	403 15-17.5	380.88	503 15-17.5	311.99	292.16	32.79
102 17.5-20	366.97	205 17.5-20	257.02	304 17.5-20	222.18	403 17.5-20	354.58	503 17.5-20	360.45	312.24	30.23

†P 178.22- phosphorus concentration measured at 178.22 nm wavelength

Table B.4 Resin extractable P at different distance from point of fertilizer application data from North farm 5 weeks field samples.

Sample ID	P Conc. mg/kg	Sample ID	P Conc. mg/kg	Sample ID	P Conc. mg/kg	Sample ID	P Conc. mg/kg	Sample ID	P Conc. mg/kg	Average P mg/kg	Standard Error
104 0-2.5	16.03	201 0-2.5	14.71	302 0-2.5	17.29	405 0-2.5	18.53	504 0-2.5	15.37	16.38	0.68
104 2.5-5	12.09	201 2.5-5	10.12	302 2.5-5	12.80	405 2.5-5	11.09	504 2.5-5	8.32	10.88	0.79
104 5-7.5	11.28	201 5-7.5	9.44	302 5-7.5	12.90	405 5-7.5	7.63	504 5-7.5	10.38	10.33	0.88
106 5-7.5	12.70	202 5-7.5	10.49	306 5-7.5	11.94	402 5-7.5	13.02	501 5-7.5	8.21	11.27	0.88
106 7.5-10	9.15	202 7.5-10	8.66	306 7.5-10	9.87	402 7.5-10	11.84	501 7.5-10	10.45	9.99	0.55
106 10-12.5	9.96	202 10-12.5	5.93	306 10-12.5	9.77	402 10-12.5	10.98	501 10-12.5	11.94	9.72	1.02
106 12.5-15	9.43	202 12.5-15	7.21	306 12.5-15	9.91	402 12.5-15	8.60	501 12.5-15	12.54	9.54	0.88
105 0-2.5	33.79	206 0-2.5	26.72	305 0-2.5	31.34	401 0-2.5	67.37	505 0-2.5	50.47	41.94	7.52
105 2.5-5	17.62	206 2.5-5	11.99	305 2.5-5	14.28	401 2.5-5	22.61	505 2.5-5	15.63	16.43	1.80
105 5-7.5	14.32	206 5-7.5	9.25	305 5-7.5	10.93	401 5-7.5	14.46	505 5-7.5	15.33	12.86	1.17
103 5-7.5	30.03	204 5-7.5	85.40	301 5-7.5	41.52	404 5-7.5	70.63	506 5-7.5	144.35	74.38	20.10
103 7.5-10	47.33	204 7.5-10	45.54	301 7.5-10	43.55	404 7.5-10	56.81	506 7.5-10	99.55	58.56	10.50
103 10-12.5	32.90	204 10-12.5	13.11	301 10-12.5	15.84	404 10-12.5	14.94	506 10-12.5	28.56	21.07	4.03
103 12.5-15	22.79	204 12.5-15	9.57	301 12.5-15	8.85	404 12.5-15	8.90	506 12.5-15	10.61	12.14	2.68
101 0-2.5	68.85	203 0-2.5	48.13	303 0-2.5	38.37	406 0-2.5	41.25	502 0-2.5	52.30	49.78	5.36
101 2.5-5	20.46	203 2.5-5	16.42	303 2.5-5	15.71	406 2.5-5	15.10	502 2.5-5	11.59	15.86	1.42
101 5-7.5	15.98	203 7.5-10	12.48	303 5-7.5	11.33	406 5-7.5	11.85	502 5-7.5	12.06	12.74	0.83
102 5-7.5	13.85	205 5-7.5	68.46	304 5-7.5	81.67	403 5-7.5	125.58	503 5-7.5	95.58	76.15	19.18
102 7.5-10	9.45	205 7.5-10	86.20	304 7.5-10	189.08	403 7.5-10	132.97	503 7.5-10	113.00	107.00	28.79
102 10-12.5	13.77	205 10-12.5	17.11	304 10-12.5	95.28	403 10-12.5	45.88	503 10-12.5	31.42	43.44	13.76
102 12.5-15	27.50	205 12.5-15	7.58	304 12.5-15	29.18	403 12.5-15	12.38	503 12.5-15	8.65	14.33	3.89

Table B.5 pH at different distance from point of fertilizer application data from North farm 6 months field samples.

Sample ID	pH	Sample ID	pH	Sample ID	pH	Sample ID	pH	Sample ID	pH	Average pH	Standard Error
1002 5-7.5	5.27	2005 5-7.5	5.46	3004 5-7.5	5.42	4003 5-7.5	5.43	5003 5-7.5	5.50	5.40	0.04
1002 7.5-10	5.37	2005 7.5-10	5.42	3004 7.5-10	5.25	4003 7.5-10	5.18	5003 7.5-10	5.36	5.34	0.06
1002 10-12.5	5.28	2005 10-12.5	5.14	3004 10-12.5	5.30	4003 10-12.5	5.43	5003 10-12.5	5.63	5.30	0.05
1002 12.5-15	5.54	2005 12.5-15	5.36	3004 12.5-15	5.39	4003 12.5-15	5.28	5003 12.5-15	5.61	5.44	0.06
1003 5-7.5	5.54	2004 5-7.5	5.23	3001 5-7.5	5.14	4004 5-7.5	5.35	5006 5-7.5	5.06	5.37	0.09
1003 7.5-10	5.46	2004 7.5-10	5.28	3001 7.5-10	5.02	4004 7.5-10	5.58	5006 7.5-10	5.03	5.27	0.11
1003 10-12.5	5.51	2004 10-12.5	5.43	3001 10-12.5	5.01	4004 10-12.5	5.45	5006 10-12.5	4.94	5.27	0.12
1003 12.5-15	5.54	2004 12.5-15	5.49	3001 12.5-15	5.07	4004 12.5-15	5.53	5006 12.5-15	5.28	5.38	0.09
1006 5-7.5	5.62	2002 5-7.5	5.63	3006 5-7.5	5.12	4002 5-7.5	5.57	5001 5-7.5	5.83	5.55	0.12
10067.5-10	5.57	2002 7.5-10	5.48	3006 7.5-10	4.95	4002 7.5-10	5.62	5001 7.5-10	5.42	5.41	0.12
1006 10-12.5	5.52	200210-12.5	5.33	3006 10-12.5	4.92	4002 10-12.5	5.00	5001 10-12.5	5.39	5.23	0.12
1006 12.5-15	5.47	2002 12.5-15	5.10	3006 12.5-15	4.96	4002 12.5-15	5.15	5001 12.5-15	5.02	5.14	0.09
1001 0-2.5	6.09	2003 0-2.5	5.53	3003 0-2.5	5.61	4006 0-2.5	5.99	5002 0-2.5	5.95	5.83	0.11
1001 2.5-5	5.34	2003 2.5-5	5.63	30032.5-5	5.3	4006 2.5-5	5.93	5002 2.5-5	5.80	5.62	0.12
1001 5-7.5	5.22	2003 5-7.5	5.72	3003 5-7.5	5.38	4006 5-7.5	5.97	5002 5-7.5	5.60	5.58	0.13
1004 0-2.5	5.90	2001 0-2.5	5.76	3002 0-2.5	5.65	4005 2.5-5	5.74	5004 0-2.5	5.50	5.71	0.07
1004 2.5-5	5.91	2001 2.5-5	5.57	3002 2.5-5	5.60	4005 2.5-5	5.62	5004 2.5-5	5.48	5.64	0.07
1004 5-7.5	5.88	2001 5-7.5	5.51	3002 5-7.5	5.45	4005 5-7.5	5.45	5004 5-7.5	5.44	5.55	0.08
1005 0-2.5	5.90	2006 0-2.5	5.68	3005 0-2.5	5.42	4001 0-2.5	5.64	5005 0-2.5	5.33	5.59	0.10
1005 2.5-5	5.72	2006 2.5-5	5.45	3005 2.5-5	5.75	4001 2.5-5	5.82	5005 2.5-5	5.31	5.61	0.10
1005 5-7.5	5.69	2006 5-7.5	5.38	3005 5-7.5	5.51	4001 5-7.5	5.67	5005 5-7.5	5.06	5.46	0.12

Table B.6 Total P at different distance from point of fertilizer application data from North farm 6 months field samples.

Sample ID	†P 178.22	Sample ID	P 178.22	Sample ID	P 178.22	Sample ID	P 178.22	Sample ID	P 178.22	Average P	Standard Error
	mg/kg		**mg/kg**		**mg/kg**		**mg/kg**		**mg/kg**	**mg/kg**	
1002 5-7.5	695.75	2005 5-7.5	475.73	3004 5-7.5	760.90	4003 5-7.5	1068.992	5003 5-7.5	750.34	750.34	122.49
1002 7.5-10	702.18	2005 7.5-10	505.14	3004 7.5-10	833.21	4003 7.5-10	1186.286	5003 7.5-10	1123.51	870.07	127.86
1002 10-12.5	512.96	2005 10-12.5	419.77	3004 10-12.5	858.84	4003 10-12.5	774.525	5003 10-12.5	532.30	619.68	83.72
1002 12.5-15	406.46	2005 12.5-15	370.46	3004 12.5-15	561.80	4003 12.5-15	491.215	5003 12.5-15	418.69	449.72	34.21
1003 5-7.5	625.18	2004 5-7.5	1368.39	3001 5-7.5	700.17	4004 5-7.5	778.463	5006 5-7.5	1620.63	1018.57	199.83
1003 7.5-10	458.39	2004 7.5-10	963.79	3001 7.5-10	622.22	4004 7.5-10	1125.331	5006 7.5-10	820.57	798.06	118.61
1003 10-12.5	502.80	2004 10-12.5	440.47	3001 10-12.5	413.67	4004 10-12.5	666.374	5006 10-12.5	492.94	503.25	43.98
1003 12.5-15	401.64	2004 12.5-15	365.07	3001 12.5-15	396.77	4004 12.5-15	466.587	5006 12.5-15	416.45	409.30	16.59
1006 5-7.5	370.59	2002 5-7.5	395.25	3006 5-7.5	545.97	4002 5-7.5	436.690	5001 5-7.5	524.28	454.56	34.72
1006 7.5-10	367.83	2002 7.5-10	367.64	3006 7.5-10	507.35	4002 7.5-10	429.072	5001 7.5-10	600.77	454.53	44.66
1006 10-12.5	360.73	2002 10-12.5	398.57	3006 10-12.5	436.15	4002 10-12.5	454.839	5001 10-12.5	503.55	430.77	24.34
1006 12.5-15	360.62	2002 12.5-15	365.54	3006 12.5-15	468.64	4002 12.5-15	407.358	5001 12.5-15	478.79	416.19	24.90
1001 0-2.5	709.14	2003 0-2.5	668.29	3003 0-2.5	953.43	4006 0-2.5	897.492	5002 0-2.5	1002.27	846.12	66.68
1001 2.5-5	329.03	2003 2.5-5	419.23	3003 2.5-5	425.67	4006 2.5-5	486.787	5002 2.5-5	395.05	411.16	25.49
1001 5-7.5	321.72	2003 5-7.5	332.89	3003 5-7.5	400.06	4006 5-7.5	449.854	5002 5-7.5	422.09	385.32	25.03
1004 0-2.5	654.01	2001 0-2.5	624.97	3002 0-2.5	656.11	4005 2.5-5	524.449	5004 0-2.5	614.89	614.88	30.97
1004 2.5-5	352.51	2001 2.5-5	424.34	3002 2.5-5	429.16	4005 2.5-5	388.730	5004 2.5-5	513.79	421.71	26.85
1004 5-7.5	407.16	2001 5-7.5	401.81	3002 5-7.5	352.43	4005 5-7.5	405.865	5004 5-7.5	327.54	378.96	16.41
1005 0-2.5	848.99	2006 0-2.5	738.36	3005 0-2.5	584.41	4001 0-2.5	851.992	5005 0-2.5	856.70	776.09	52.79
1005 2.5-5	318.38	2006 2.5-5	468.75	3005 2.5-5	446.49	4001 2.5-5	448.780	5005 2.5-5	447.22	425.92	27.20
1005 5-7.5	416.953	2006 5-7.5	324.387	3005 5-7.5	440.62	4001 5-7.5	417.033	5005 5-7.5	380.34	395.87	20.31

†P 178.22- phosphorus concentration measured at 178.22 nm wavelength

Table B.7 Resin extractable P at different distance from point of fertilizer application data from North farm 6 months field samples.

Sample ID	P Conc.	Sample ID	P Conc.	Sample ID	P Conc.	Sample ID	P Conc.	Sample ID	P Conc.	Average P	Standard Error
	mg/kg		mg/kg		mg/kg		mg/kg		mg/kg	mg/kg	
1004 0-2.5	19.95	2001 0-2.5	17.03	3002 0-2.5	19.05	4005 0-2.5	19.10	5004 0-2.5	22.88	19.60	0.95
1004 2.5-5	16.82	2001 2.5-5	14.66	3002 2.5-5	25.30	4005 2.5-5	14.30	5004 2.5-5	14.68	17.15	2.09
1004 5-7.5	15.50	2001 5-7.5	13.22	3002 5-7.5	12.71	4005 5-7.5	14.04	5004 5-7.5	13.87	13.87	0.53
1006 5-7.5	15.74	2002 5-7.5	13.72	3006 5-7.5	17.10	4002 5-7.5	24.70	5001 5-7.5	17.26	17.70	1.86
1006 7.5-10	16.15	2002 7.5-10	12.86	3006 7.5-10	17.05	4002 7.5-10	22.73	5001 7.5-10	14.25	16.61	1.69
1006 10-12.5	11.35	2002 10-12.5	12.90	3006 10-12.5	24.25	4002 10-12.5	23.16	5001 10-12.5	13.85	17.10	2.73
1006 12.5-15	11.04	2002 12.5-15	11.60	3006 12.5-15	23.96	4002 12.5-15	21.77	5001 12.5-15	12.52	16.18	2.76
1005 0-2.5	24.90	2006 0-2.5	22.53	3005 0-2.5	25.67	4001 0-2.5	23.88	5005 0-2.5	28.07	25.01	0.93
1005 2.5-5	18.90	2006 2.5-5	19.81	3005 2.5-5	15.67	4001 2.5-5	17.92	5005 2.5-5	18.31	18.12	0.69
1005 5-7.5	16.52	2006 5-7.5	15.66	3005 5-7.5	12.98	4001 5-7.5	13.73	5005 5-7.5	14.07	14.59	0.65
1003 5-7.5	31.31	2004 5-7.5	151.60	3001 5-7.5	28.71	4004 5-7.5	33.52	5006 5-7.5	149.63	78.95	29.27
1003 7.5-10	19.05	2004 7.5-10	85.64	3001 7.5-10	33.24	4004 7.5-10	89.64	5006 7.5-10	34.71	52.45	14.63
1003 10-12.5	22.78	2004 10-12.5	19.55	3001 10-12.5	13.91	4004 10-12.5	33.64	5006 10-12.5	15.19	21.01	3.53
1003 12.5-15	12.81	2004 12.5-15	14.75	3001 12.5-15	11.81	4004 12.5-15	18.43	5006 12.5-15	12.85	14.13	1.18
1001 0-2.5	19.56	2003 0-2.5	26.88	3003 0-2.5	39.31	4006 0-2.5	26.25	5002 0-2.5	51.27	32.65	5.64
1001 2.5-5	17.53	2003 2.5-5	19.58	3003 2.5-5	16.09	4006 2.5-5	17.25	5002 2.5-5	18.13	17.72	0.57
1001 5-7.5	15.39	2003 5-7.5	13.45	3003 5-7.5	13.73	4006 5-7.5	16.18	5002 5-7.5	14.33	14.61	0.51
1002 5-7.5	51.98	2005 5-7.5	17.62	3004 5-7.5	68.71	4003 5-7.5	100.20	4003 5-7.5	59.63	59.63	17.20
1002 7.5-10	64.69	2005 7.5-10	17.66	3004 7.5-10	98.53	4003 7.5-10	139.00	5003 7.5-10	107.02	85.38	20.65
1002 10-12.5	32.20	2005 10-12.5	17.37	3004 10-12.5	104.20	4003 10-12.5	56.61	5003 10-12.5	17.65	45.61	16.30
1002 12.5-15	16.73	200512.5-15	14.03	3004 12.5-15	29.96	4003 12.5-15	20.82	5003 12.5-15	12.75	18.86	3.10

Table B.8 pH at different distance from point of fertilizer application data from North farm greenhouse study.

	Replication						
Treatment	I	II	III	IV	V	Average	Standard Error
	-------------------------------pH-----------------------------						
T1 0-2.5	5.20	5.21	5.17	5.26	5.30	5.21	0.02
T1 2.5-5	5.31	5.14	5.21	5.24	5.32	5.23	0.03
T1 5-7.5	5.37	5.24	5.29	4.99	5.40	5.22	0.07
T2 0-2.5	5.13	5.09	5.12	5.10	5.18	5.12	0.02
T2 2.5-5	5.24	5.24	5.18	5.13	5.20	5.20	0.02
T2 5-7.5	5.25	5.21	5.21	5.28	5.34	5.26	0.02
T4 0-2.5	5.19	5.07	5.10	5.09	5.29	5.15	0.04
T4 2.5-5	5.14	5.20	5.22	5.20	5.28	5.21	0.02
T4 5-7.5	5.29	5.28	5.26	5.28	5.41	5.30	0.03
T1 10-12.5	5.25	5.45	5.28	5.30	5.47	5.35	0.05
T1 12.5-15	5.07	5.38	5.28	5.25	5.41	5.28	0.06
T1 15-17.5	5.37	5.63	5.51	5.62	5.68	5.56	0.06
T1 17.5-20	5.45	5.83	5.68	5.68	5.69	5.67	0.06
T3 10-12.5	5.27	5.23	5.24	5.48	5.37	5.32	0.05
T3 12.5-15	5.15	5.15	5.25	5.25	5.33	5.23	0.03
T3 15-17.5	5.30	5.19	5.24	5.45	5.31	5.30	0.04
T3 17.5-20	5.35	5.34	5.36	5.49	5.43	5.39	0.03
T5 10-12.5	5.28	5.22	5.31	5.25	5.41	5.29	0.03
T5 12.5-15	5.10	5.13	5.19	5.08	5.29	5.16	0.04
T5 15-17.5	5.29	5.30	5.31	5.24	5.46	5.32	0.04
T5 17.5-20	5.42	5.33	5.41	5.29	5.51	5.39	0.04

Table B.9 Total P at different distance from point of fertilizer application data from North farm greenhouse study.

	Replication						
Treatment	I	II	III	IV	V	Average P	Standard Error
	------------------------------mg/kg-------------------------------						
T1 0-2.5	467.02	457.52	500.46	427.34	534.92	477.45	18.51
T1 2.5-5	462.02	442.43	491.51	471.30	478.01	469.05	8.21
T1 5-7.5	492.46	398.02	523.58	509.91	455.69	475.93	22.56
T2 0-2.5	623.59	633.65	806.99	775.72	880.46	744.08	50.14
T2 2.5-5	422.89	449.54	528.67	553.24	468.55	484.58	24.44
T2 5-7.5	378.44	457.56	450.94	569.38	503.38	471.94	31.52
T4 0-2.5	631.77	558.80	732.30	795.58	738.85	691.46	42.38
T4 2.5-5	444.13	418.97	510.88	550.67	539.37	492.80	26.14
T4 5-7.5	470.09	426.53	514.09	571.35	550.06	506.42	26.35
T1 10-12.5	355.40	395.12	361.56	345.77	401.60	371.89	11.14
T1 12.5-15	346.74	324.78	358.32	343.46	344.73	343.61	5.40
T1 15-17.5	321.06	299.31	324.88	341.84	296.97	316.81	8.40
T1 17.5-20	301.07	317.33	293.02	327.99	293.47	306.58	6.93
T3 10-12.5	395.57	397.57	451.08	483.94	441.45	433.92	16.80
T3 12.5-15	409.34	484.92	564.20	759.58	638.27	571.26	60.69
T3 15-17.5	433.66	469.96	599.04	585.83	458.40	509.38	34.47
T3 17.5-20	250.60	296.25	376.17	435.08	369.50	345.52	32.38
T5 10-12.5	371.55	352.40	460.64	478.31	512.46	435.07	31.13
T5 12.5-15	447.06	516.47	500.82	652.03	567.03	536.68	34.61
T5 15-17.5	366.17	421.32	552.87	565.19	265.67	434.24	56.76
T5 17.5-20	328.73	325.57	403.23	414.54	205.17	335.45	37.39

Table B.10 Resin extractable P at different distance from point of fertilizer application data from North farm greenhouse study.

	Replication						
Treatment	I	II	III	IV	V	Average P	Standard Error
	---------------------------------------mg/kg------------------------------------						
T1 0-2.5	8.52	12.94	13.20	13.74	13.32	12.34	0.86
T1 2.5-5	16.28	16.16	14.62	21.08	14.29	16.49	1.09
T1 5-7.5	16.36	17.58	15.06	14.79	16.23	16.00	0.45
T2 0-2.5	31.88	40.96	38.00	31.95	39.83	36.52	1.74
T2 2.5-5	12.59	14.19	16.16	16.09	17.36	15.28	0.75
T2 5-7.5	13.06	14.67	15.03	16.43	15.14	14.87	0.48
T3 10-12.5	11.98	16.02	13.29	15.23	15.65	14.43	0.69
T3 12.5-15	21.42	21.64	23.93	27.68	23.76	23.68	1.01
T3 15-17.5	26.12	23.63	24.80	26.17	29.95	26.13	0.95
T3 17.5-20	11.07	9.93	13.62	14.31	13.94	12.57	0.78
T4 0-2.5	26.84	28.46	31.52	31.51	29.32	29.53	0.81
T4 2.5-5	12.82	15.50	15.17	16.42	17.04	15.39	0.65
T4 5-7.5	18.85	14.83	14.86	16.51	22.88	17.58	1.35
T5 10-12.5	12.53	14.24	16.74	14.67	15.00	14.63	0.61
T5 12.5-15	26.35	22.80	23.33	22.90	26.42	24.36	0.74
T5 15-17.5	23.36	28.77	20.83	25.85	23.88	24.54	1.19
T5 17.5-20	11.53	14.91	13.40	14.48	14.46	13.76	0.55
T1 10-12.5	10.93	13.86	12.39	17.52	14.63	13.87	1.44
T1 12.5-15	10.61	13.88	15.97	13.96	15.00	13.88	1.17
T1 15-17.5	10.95	13.75	15.45	14.11	14.53	13.76	0.98
T1 17.5-20	10.09	11.90	9.74	13.93	13.86	11.90	1.15

Table B.11 pH at different distance from point of fertilizer application data from Ottawa greenhouse study.

Treatment	Replication I	II	III	IV	V	Average	Standard Error
	---pH------------------------------						
S1 0-2.5	6.65	6.77	6.63	6.72	6.48	6.65	0.05
S1 2.5-5	6.89	6.72	6.68	6.85	6.57	6.74	0.06
S1 5-7.5	6.73	6.72	6.71	6.88	6.64	6.74	0.04
S2 10-12.5	6.68	6.43	6.48	7.11	6.78	6.70	0.12
S2 12.5-15	6.51	6.54	6.54	6.68	6.70	6.59	0.04
S2 15-17.5	6.88	6.67	6.87	6.81	6.53	6.75	0.07
S2 17.5-20	6.27	6.48	7.03	6.81	6.56	6.63	0.13
S3 0-2.5	6.40	6.46	6.77	6.69	6.51	6.57	0.07
S3 2.5-5	6.63	6.66	6.88	6.65	6.66	6.70	0.05
S3 5-7.5	6.62	6.59	7.03	6.82	6.68	6.75	0.08
S4 10-12.5	6.44	6.14	6.93	6.55	6.63	6.54	0.13
S4 12.5-15	6.28	6.44	7.16	6.85	6.63	6.67	0.15
S4 15-17.5	6.32	6.52	7.14	6.97	6.73	6.74	0.15
S4 17.5-20	6.53	5.92	6.66	6.90	6.69	6.54	0.17
S5 0-2.5	6.76	6.56	6.77	6.72	6.70	6.70	0.04
S5 2.5-5	6.98	6.86	6.86	6.78	6.77	6.85	0.04
S5 5-7.5	6.99	7.01	6.79	6.58	6.80	6.83	0.08
S6 10-12.5	6.65	6.72	6.71	6.68	6.77	6.71	0.02
S6 12.5-15	6.45	6.71	6.99	6.53	6.73	6.68	0.09
S6 15-17.5	6.32	6.66	7.03	6.46	6.82	6.66	0.13
S6 17.5-20	6.11	6.69	6.91	6.54	6.58	6.57	0.13

Table B.12 Total P at different distance from point of fertilizer application data from Ottawa greenhouse study.

Sample ID	P 178.22†	Sample ID	P 178.22	Sample ID	P 178.22	Sample ID	P 178.22	Sample ID	P 178.22	Average P	Standard Error
	mg/kg		mg/kg		mg/kg		mg/kg		mg/kg	mg/kg	
S1R1 0-2.5	593.59	S1R2 0-2.5	688.72	S1R3 0-2.5	664.83	S1R4 0-2.5	592.68	S1R5 0-2.5	669.54	641.87	20.30
S1R1 2.5-5	643.78	S1R2 2.5-5	603.81	S1R3 2.5-5	641.45	S1R4 2.5-5	569.02	S1R5 2.5-5	714.63	634.54	24.28
S1R1 5-7.5	603.34	S1R2 5-7.5	636.04	S1R3 5-7.5	619.80	S1R4 5-7.5	595.90	S1R5 5-7.5	683.97	627.81	15.66
S2R1 10-12.5	585.15	S2R2 10-12.5	672.02	S2R3 10-12.5	591.70	S2R4 10-12.5	579.45	S2R5 10-12.5	637.16	613.10	17.92
S2R1 12.5-15	572.12	S2R2 12.5-15	607.23	S2R3 12.5-15	563.31	S2R4 12.5-15	510.32	S2R5 12.5-15	682.51	587.10	28.45
S2R1 15-17.5	561.30	S2R2 15-17.5	498.12	S2R3 15-17.5	500.61	S2R4 15-17.5	420.81	S2R5 15-17.5	613.52	518.87	32.51
S2R1 17.5-20	374.63	S2R2 17.5-20	431.51	S2R3 17.5-20	414.54	S4R3 17.5-20	552.55	S2R5 17.5-20	467.04	448.05	30.06
S3R1 0-2.5	882.87	S3R2 0-2.5	911.88	S3R3 0-2.5	921.41	S3R4 0-2.5	997.05	S3R5 0-2.5	983.84	939.41	21.88
S3R1 2.5-5	686.10	S3R2 2.5-5	688.14	S3R3 2.5-5	670.31	S3R4 2.5-5	635.53	S3R5 2.5-5	702.07	676.43	11.40
S3R1 5-7.5	660.78	S3R2 5-7.5	637.29	S3R3 5-7.5	505.38	S3R4 5-7.5	636.85	S3R5 5-7.5	549.95	598.05	29.90
S4R1 10-12.5	636.42	S4R2 10-12.5	604.99	S4R3 10-12.5	560.37	S4R4 10-12.5	857.66	S4R5 10-12.5	592.18	650.32	53.25
S4R1 12.5-15	1725.57	S4R2 12.5-15	863.35	S4R3 12.5-15	691.11	S4R4 12.5-15	852.99	S4R5 12.5-15	752.66	977.14	189.83
S4R1 15-17.5	1021.10	S4R2 15-17.5	874.82	S4R3 15-17.5	650.37	S4R4 15-17.5	673.22	S4R5 15-17.5	875.97	819.09	69.60
S4R1 17.5-20	506.30	S4R2 17.5-20	493.20	S2R4 17.5-20	423.80	S4R4 17.5-20	465.79	S4R5 17.5-20	562.09	490.23	22.85
S5R1 0-2.5	929.19	S5R2 0-2.5	798.06	S5R3 0-2.5	978.33	S5R4 0-2.5	1051.87	S5R5 0-2.5	1010.09	953.51	43.73
S5R1 2.5-5	610.33	S5R2 2.5-5	593.12	S5R3 2.5-5	646.26	S5R4 2.5-5	755.08	S5R5 2.5-5	612.93	643.54	29.18
S5R1 5-7.5	748.74	S5R2 5-7.5	527.53	S5R3 5-7.5	593.80	S5R4 5-7.5	814.06	S5R5 5-7.5	600.71	656.97	53.39
S6R1 10-12.5	597.26	S6R2 10-12.5	505.72	S6R3 10-12.5	643.48	S6R4 10-12.5	677.24	S6R5 10-12.5	621.68	609.08	28.99
S6R1 12.5-15	709.37	S6R2 12.5-15	654.82	S6R3 12.5-15	726.67	S6R4 12.5-15	865.05	S6R5 12.5-15	697.07	730.59	35.64
S6R1 15-17.5	1009.63	S6R2 15-17.5	813.48	S6R3 15-17.5	506.66	S6R4 15-17.5	837.89	S6R5 15-17.5	797.98	793.13	81.05
S6R1 17.5-20	468.58	S6R2 17.5-20	414.81	S6R3 17.5-20	360.79	S6R4 17.5-20	509.24	S6R5 17.5-20	468.18	444.32	25.71

†P 178.22- phosphorus concentration measured at 178.22 nm wavelength

Table B.13 Resin extractable P at different distance from point of fertilizer application data from Ottawa greenhouse study.

Sample ID	P Conc.	Sample ID	P Conc.	Sample ID	P Conc.	Sample ID	P Conc.	Sample ID	P Conc.	Average P	Standard Error
	mg/kg		mg/kg		mg/kg		mg/kg		mg/kg	mg/kg	
S1R1 0-2.5	13.07	S1R2 0-2.5	16.05	S1R3 0-2.5	16.67	S1R4 0-2.5	16.85	S1R5 0-2.5	16.55	15.84	0.70
S1R1 2.5-5	15.13	S1R2 2.5-5	18.43	S1R3 2.5-5	15.21	S1R4 2.5-5	20.20	S1R5 2.5-5	17.20	17.24	0.97
S1R1 5-7.5	15.73	S1R2 5-7.5	15.48	S1R3 5-7.5	16.33	S1R4 5-7.5	18.04	S1R5 5-7.5	17.47	16.61	0.50
S2R1 10-12.5	4.25	S2R2 10-12.5	14.62	S2R3 10-12.5	15.93	S2R4 10-12.5	18.73	S2R5 10-12.5	15.91	13.89	2.50
S2R1 12.5-15	18.91	S2R2 12.5-15	16.53	S2R3 12.5-15	17.16	S2R4 12.5-15	15.96	S2R5 12.5-15	16.04	16.92	0.54
S2R1 15-17.5	16.25	S2R2 15-17.5	15.34	S2R3 15-17.5	15.99	S2R4 15-17.5	16.22	S2R5 15-17.5	21.04	16.97	1.03
S2R1 17.5-20	12.54	S2R2 17.5-20	13.78	S2R3 17.5-20	13.70	S2R4 17.5-20	20.00	S2R5 17.5-20	15.77	15.16	1.32
S3R1 0-2.5	40.96	S3R2 0-2.5	26.87	S3R3 0-2.5	50.60	S3R4 0-2.5	61.13	S3R5 0-2.5	46.99	45.31	5.66
S3R1 2.5-5	15.29	S3R2 2.5-5	16.23	S3R3 2.5-5	18.98	S3R4 2.5-5	18.46	S3R5 2.5-5	19.56	17.70	0.83
S3R1 5-7.5	16.36	S3R2 5-7.5	17.73	S3R3 5-7.5	19.18	S3R4 5-7.5	20.64	S3R5 5-7.5	18.94	18.57	0.72
S4R1 10-12.5	14.28	S4R2 10-12.5	16.93	S4R3 10-12.5	18.07	S4R4 10-12.5	15.91	S4R5 10-12.5	19.97	17.03	0.96
S4R1 12.5-15	31.95	S4R2 12.5-15	29.50	S4R3 12.5-15	36.03	S4R4 12.5-15	34.38	S4R5 12.5-15	33.54	33.08	1.11
S4R1 15-17.5	24.00	S4R2 15-17.5	30.48	S4R3 15-17.5	30.91	S4R4 15-17.5	31.97	S4R5 15-17.5	28.14	29.10	1.42
S4R1 17.5-20	15.23	S4R2 17.5-20	15.15	S2R4 17.5-20	13.93	S4R4 17.5-20	14.29	S4R5 17.5-20	15.10	14.74	0.26
S5R1 0-2.5	30.42	S5R2 0-2.5	42.73	S5R3 0-2.5	43.77	S5R4 0-2.5	40.42	S5R5 0-2.5	36.00	38.67	2.46
S5R1 2.5-5	17.35	S5R2 2.5-5	20.58	S5R3 2.5-5	20.32	S5R4 2.5-5	17.03	S5R5 2.5-5	20.63	19.18	0.82
S5R1 5-7.5	17.28	S5R2 5-7.5	18.95	S5R3 5-7.5	18.17	S5R4 5-7.5	18.04	S5R5 5-7.5	19.15	18.32	0.34
S6R1 10-12.5	15.39	S6R2 10-12.5	13.82	S6R3 10-12.5	21.09	S6R4 10-12.5	13.87	S6R5 10-12.5	16.98	16.23	1.35
S6R1 12.5-15	26.72	S6R2 12.5-15	19.72	S6R3 12.5-15	33.57	S6R4 12.5-15	29.77	S6R5 12.5-15	25.77	27.11	2.30
S6R1 15-17.5	24.58	S6R2 15-17.5	27.09	S6R3 15-17.5	26.00	S6R4 15-17.5	24.40	S6R5 15-17.5	30.46	26.50	1.10
S6R1 17.5-20	13.39	S6R2 17.5-20	14.23	S6R3 17.5-20	13.86	S6R4 17.5-20	15.27	S6R5 17.5-20	16.35	14.62	0.53