

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

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Phosphorus management in reduced-tillage systems is a great concern for farmers. Conclusive positive results of deep-banding P fertilizers compared with broadcast application and the chemistry of reduced-tillage systems remain unclear. Knowledge of the dominant solid P species present in soil following application of P fertilizers and the resulting potential P availability would help us 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 vs. liquid P), and time on the 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 wk and 6 mo after P application at a rate of 75 kg ha⁻¹ to a soil system that was under long-term reduced tillage. Resin-extractable P was lower for broadcast treatments compared with deep-band treatments for both time periods. Resin-extractable P was greater in the liquid P-treated soils than in the granular P-treated soils. Speciation results showed that granular P fertilizers tended to form Fe-P-like forms, whereas liquid forms remained in adsorbed P-like forms in the soil 5 wk after application; moreover, speciation results showed granular P fertilizers precipitated less when deep-banded. During the 6-mo period following application, reaction products of broadcast granular, broadcast liquid, and deep-band granular fertilizers transformed to Ca-phosphate or mixtures of Ca-, Fe- and adsorbed-phosphate-like forms, whereas deep-band liquid P remained as mainly adsorbed P-like forms. Deep-banding of P would most likely provide a solution that is both agronomically and environmentally efficient for reduced-till farmers.

Abbreviations: LC, linear combination; MAP, monoammonium phosphate; PCA, principal component analysis; XANES, X-ray absorption near edge structure.

Phosphorus is an essential element for all life forms, but it is one of the most difficult nutrients for plants to obtain from the soil, so it often represents a limiting factor to agricultural production. Although P is needed in adequate quantities for optimal crop production, it also has been associated with eutrophication of surface water bodies (Pierzynski et al., 2000). In general, more total P creates more environmental concern. Millions of tonnes of P are applied to soil annually, but plants do not have access to all of it. In time, part of the applied P is taken up by plants, but the majority of P reacts with other soil components, thus altering P availability by forming insoluble secondary P minerals that are precipitated, strongly sorbed onto mineral or organic surfaces (Hansen et al., 2002), or incorporated into soil organic fraction (Fixen and Ludwick, 1982). The fraction of soil P that is bonded to the surface of soil solids where a discrete mineral phase is not formed is known as adsorbed P (Foth and Ellis, 1997). Phosphorus

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is found adsorbed on the surfaces of clay, amorphous Al or Fe oxides in acid soils, and calcium carbonate in alkaline soils. The majority of adsorbed P in soil occurs as inner-sphere complex species (specific adsorption), and some P is adsorbed as either diffuse ion swarm or outer-sphere complex species (nonspecific adsorption) (Sposito, 1989). Inner-sphere complexed P is slower to equilibrate with the soil solution P than outer sphere and diffuse swarm P.

Hedley and McLaughlin (2005) reviewed the reactions that occur when a highly water-soluble fertilizer granule is placed in soil. The first reaction is wetting of the granule, which occurs through capillary flow of water from soil into the porous granule and through water vapor transfer from the soil or atmosphere to the hygroscopic phosphate salt (Lawton and Vomocil, 1954). This movement of water occurs in a direction opposite that of dissolved P diffusion, and hence may slow or restrict the diffusion of P, thus increasing the chances for P fixation due to precipitation reactions. In the case of liquid P fertilizers, this effect is not as great as in the granular P fertilizers due to the amount of water added with liquid P (Hettiarachchi et al., 2006). As P fertilizer granules dissolve, P moves out of the granule and forms two reaction zones in the adjacent soil: a P-saturated zone immediately adjacent to the granule in which the P sorption capacity of the soil is exceeded and precipitates of P form with the metal ions and organic matter released from the soil due to low pH and high salt concentrations, and a P-unsaturated zone in which the P sorption capacity of the soil is not exceeded (Benbi and Gilkes, 1987). These initial reaction products can be fairly soluble, and with time they transform into more stable P forms (Lindsay, 1979). In acidic soils, thermodynamics predicts that the fate of P fertilizers would be the formation of Al and Fe phosphates; variscite, strengite, and vivianite are the secondary P solids that precipitate out, depending on soil conditions such as redox and Al and Fe solubility (Lindsay 1979). Study of six excessively fertilized soils suggested the presence of amorphous analog of variscite in acidic soils (Pierzynski et al., 1990). At higher pH, the initial P reaction products formed are usually the soluble Ca-P forms (such as brushite, monetite, and dicalcium phosphate), and with time they transform into more stable calcium solid P species (analogs of apatite) (Lindsay, 1979).

In many soil systems, a high proportion of applied P is rapidly converted to insoluble phosphates that plants have virtually no ability to access. Adoption of various tillage systems might affect the fate and availability of P in soils. Reduced-tillage crop production is gaining more attention from farmers in many regions of the United States and on farms worldwide (Hobbs et al., 2008). Despite various advantages of reduced-tillage systems, granular P applications have been found to lead to an accumulation of available P on the surface (0–5 cm) soil layer and a depletion of available P deeper in the profile (Schwab et al., 2006), which could be intensified further due to deposition of crop residues. Phosphorus stratified at the soil surface may support plant root growth under moist conditions at initial stages of plant growth; however, roots explore deep soil layers for

nutrients and moisture as surface soil dries in summer, so plants may suffer from low nutrient availability. Bordoli and Mallarino (1998) suggested that deep placement of nutrients (below the first 5–10 cm of the soil) may be superior to other placements such as broadcast when nutrient stratification and topsoil moisture deficits reduce nutrient uptake from shallow soil layers, but inconsistent results have been obtained from research conducted to study the effects of tillage and deeper placement of P fertilizers on grain yields of crops grown in Kansas soil with P stratification (Schwab et al., 2006). We hypothesized that in a reduced-tillage system, P placement—broadcast vs. deep-banding—can have significant influence on P fertilizer reaction products. If P is surface applied (i.e., broadcast), P diffusion from the granules would be slower. So in P-stratified surface soils, P precipitation reactions may be intensified, quickly transforming fertilizer P into more insoluble forms. These effects could be less significant for deep-placed P fertilizers.

Lombi et al. (2004) suggested that liquid forms of P fertilizers are more isotopically exchangeable in highly calcareous Australian soils than granular P forms, and thus are more available to the crops. Holloway et al. (2001) reported that fluid monoammonium phosphate was four to five times more effective than granular monoammonium phosphate in field trials conducted on the same soil types. McBeath et al. (2005) found that wheat biomass was enhanced by P application in 86% of the soils tested. In 62% of the P-responsive soils, wheat dry matter was significantly greater when liquid P fertilizers (phosphoric acid and ammonium polyphosphate) were used compared with the granular form (triple superphosphate), and they related this result to calcium carbonate content of the soils. The superior performance of liquid P was attributed to the greater outward diffusion of liquid P from the point of placement compared with granular P, thus reducing the chances of creating microenvironment soil solutions supersaturated with various solid Ca-P species (Lombi et al., 2004; Hettiarachchi et al., 2006; Lombi et al., 2006). We hypothesized that this enhanced or greater P diffusion would be beneficial for reduced-tillage systems, and that surface or deep-banded liquid P fertilizers may be a suitable alternative for reduced-tillage systems.

Many extractants have been employed for the assessment of available P in soils. Out of those methods, Bray1 (Bray and Kurtz, 1945), Mehlich (Mehlich, 1984), and the Olsen procedures (Watanabe and Olsen, 1965) are the commonly used techniques for the determination of available P (also known as soil test P) in soil. These conventional methods for determination of available P in soils generally use a wide range of chemical reactants and may fail to extract plant-available P if they are used in soil types for which they are not appropriate (Sharpley, 1991). Procedures developed to overcome the limitations of chemical extractants include anion resin exchange membrane (Saggar et al., 1990), the iron-sink method (Menon et al., 1990; Sharpley et al., 1994) and isotopic dilution techniques (Salcedo et al., 1991). Unlike conventional soil test P methods, resin exchange membrane does not use chemical extractant and extracts P from soils at

its inherent pH. Anion exchange resin membrane or iron-sink methods function similarly to plant-root surface by adsorbing available or labile P from the soil labile P pool. Resin-based P extraction has been found to be a better predictor of soil-available P (Sharpley, 1991; Sims et al., 2000; Mallarino and Atia, 2005), but its adoption as a routine soil testing method remains limited.

Synchrotron-based X-ray absorption near edge structure (XANES) spectroscopy has emerged as an advanced technique for identification of solid and adsorbed forms of P in soils (Hesterberg et al., 1999). Samples can be analyzed in the presence of water, making P K-edge XANES a direct in situ method for understanding P speciation without pretreatment or extraction from soils (Toor et al., 2006). XANES “fingerprinting” methods such as linear combination fitting in conjunction with principal component analysis (PCA) have been used to recreate or match the sample (unknown) spectrum using a known set of standard spectra. Sato et al. (2005) reported P associations with Fe minerals in an acidic forest soil using linear combination fitting of P K-edge XANES spectra. Beauchemin et al. (2003) combined linear combination fitting of P K-edge XANES with PCA on P-enriched agricultural soils to show that P was bound in adsorbed forms with Fe- and Al-oxide minerals, with a higher proportion of adsorbed P identified in more acidic soils. They also reported Ca–P mineral forms in all of the soil samples whose pH values ranged from 5.5 to 7.6.

Information on both resin-extractable P and dominant P species formed in reduced-tillage soil systems after different P treatments and placement methods would help us explore whether certain P fertilizers and placement methods result in superior (i.e., maintaining high P availability) short- and long-term performance in soil and understand reasons or possible mechanisms that explain their superior performance. The objectives of this study were to: (i) study the effects of fertilizer placement (broadcast vs. deep-placed/banded) and source (granular vs. liquid) on reaction products of P and availability of P at two different time periods (5 wk and 6 mo), (ii) study the availability of P at different distances from the point of fertilizer application, and (iii) develop the relationship between P chemistry and P availability. We used XANES to determine P reaction products in soils and a resin membrane technique for determining potential plant-available P.

MATERIALS AND METHODS

Site Description, Soil, and Fertilizers

A field-based study was conducted at the Department of Agronomy North Farm site in Manhattan, KS. This site has a history of more than 10 yr 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 was applied at a rate of 200 kg ha⁻¹, and P was applied at a rate of 75 kg ha⁻¹. These application rates are based on the total nutrient content of the fertilizers. Phosphorus is often applied with N to supply plant nutritional requirements. Nitrogen fertilizers that are applied along with P fertilizers may have the 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. Before initiating the study, soil samples were extracted to study the general properties of the soil (Table 1). Soil pH was measured in 1:5 soil/water extract (Wateson and Brown, 1998), and cation exchange capacity was determined using the summation method described by Chapman (1965). Mehlich-3 P was determined following the procedures described by Frank et al. (1998). Ammonium acetate-extractable Ca was determined using the procedures described by Warncke and Brown (1998). Extractable Fe and Mn were determined using the DTPA extraction technique described by Whitney (1998), and potassium chloride-extractable Al was determined following the procedures described by McLean (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 a “heat of dilution” modification. Particle size distribution was determined using a modification of the pipette method of Kilmer and Alexander (1949) and method 3A1 from the Soil Survey Laboratory Methods Manual (Soil Survey Laboratory Staff, 2004).

Experimental Approach

The treatment structure included: (i) urea broadcast (+N control), (ii) urea deep-band (+N control), (iii) MAP broadcast, (iv) MAP deep-band, (v) TGMAP broadcast, and (vi) TGMAP deep-band. In addition, control broadcast and control deep-band samples representing the soil’s background P levels were obtained before P treatment application. Experimental design was a randomized complete block with five replications. The plot size was 1.52 by 2.44 m with a 0.91-m alley between the plots. Broadcast treatments were applied on the surface and gently mixed by hand with the surface 1 cm of soil, and deep-band treatments were applied approximately at a 10-cm depth in two rows per plot using a tractor-driven disc coultter with an

Table 1. Basic properties of North Farm soil.

Sample depth cm	pH	CEC† cmol _c kg ⁻¹	Extractable					Total N	Total P	OM %	Textural class
			M3P	Ca _{ac}	Fe _{dtpa}	Mn _{dtpa}	Al _{KCl} ³⁺				
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 pentaacetic acid-extractable iron and manganese; Al_{KCl}³⁺, potassium chloride extractable aluminum; OM, organic matter content; SiL, silty loam; SiCL, silty clay loam.

arrangement for running a twine on the deep-banded zone for relocating the exact position for sampling. The distance between the rows for each deep-band treatment was maintained at 76.2 cm (i.e., two rows 76.2 cm apart per treatment). The total amount of fertilizer for each deep-band treatment was divided equally between these two rows and applied uniformly along the bands/rows. The study was conducted without plants, and weeds were controlled with periodic hand-weeding. Soil samples were collected at 5 wk and 6 mo from treatment application time. Sampling was done by extracting 30-cm soil cores using a probe and separating 2.5-cm-long soil sections for separate analysis. For broadcast treatments, six representative soil cores from each plot were taken, separated into 2.5-cm-long soil sections, and mixed depth-wise. For deep-band treatments, three 30-cm soil cores from each row were extracted, separated into 2.5-cm-long sections, and mixed depth-wise. Soil samples were then air-dried and sieved with a 2-mm sieve before analysis. For broadcast treatments, soil samples from the top three layers (i.e., 0–2.5, 2.5–5, and 5–7.5 cm) 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. Statistical analysis of all data was performed using the PROC MIXED procedure in SAS (SAS 9.1, SAS Institute, 2007). The pairwise Bonferroni method was used for pairwise comparisons between treatments at $\alpha = 0.05$ level of significance.

Wet Chemical Analysis

The wet chemical-based analysis included measurement of pH, total P, and resin-extractable P (using anion exchange resin membrane) at different distances from the point of fertilizer application. Soil pH was determined using a 1:5 soil/water ratio (Thomas, 1996). Total P was determined using the modified salicylic sulfuric acid digestion method using inductively coupled plasma optical emission spectroscopy (ICP-OES) as described by Bremner and Mulvaney (1982). Resin-extractable P was determined following the procedure of Myers et al. (2005). Resin membrane BDH product no. 55164 S was used for the resin P extraction procedure (U.S. distributor: CTL Scientific Supply Corp., Deer Park, NY). The resin membrane comes in a pack of six 12.5- by 12.5-cm sheets. The resin membrane was cut into 5- by 2.5-cm pieces, 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 a polyethylene container containing 80 mL of water. Two resin strips were added to the container and shaken in an orbital shaker for 24 h. After shaking, the resin strips were removed from the container, washed with deionized water to remove any adhering soil particles, and transferred to another polyethylene container with 50 mL of 0.5 M hydrochloric acid (HCl). The resin strips in 0.5 M HCl solution were shaken for an additional 1.5 h, filtered using Whatman filter paper no. 2, and analyzed colorimetrically using method of Murphy and Riley (1962).

Speciation of Phosphorus

X-ray Absorption Near Edge Structure Spectroscopy Data Collection

Phosphorus K-edge XANES data were collected at Sector 9-BM-B, Advanced Photon Source (APS), Argonne National Laboratory, Argonne, IL. The electron storage ring at the APS is operated at 7 GeV with a maximum current of 100 mA. This beamline has an energy range of 2.1 to 23 keV and is equipped with a Si (III) monochromator with a focused beam size of 500 by 500 μm . The sample compartment was He-purged, and data were collected in fluorescence mode using a four element Vortex Si-Drift detector (SII Nano Technology USA Inc., Northridge, CA). The 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 runtime. All samples and standards were calibrated using a common energy scale by setting the first derivative spectrum of apatite to 2149.25 eV for analysis.

Pre-application samples were extracted from the field before application of the fertilizer treatments. The top 0 to 7 cm of soil for broadcast and the 7- to 15-cm depth for deep-band treatments were used as two additional controls (zero N and P) for the XANES study. A single replication of soil samples from the top 0 to 2.5 cm for broadcast treatments and 7.5- to 10-cm depth for deep-banded treatments was used for the speciation study. The soil samples were air-dried and ground to pass through a <150- μm sieve. The samples were ground further with an agate mortar and pestle, and soil pellets 4 mm in diameter were prepared using a KBr quick press kit with a 4-mm die set (International Crystal Laboratories, Garfield, NJ) to compact samples for a better signal. The quality of P-XANES collected improved with a decrease in particle size (data not shown). Grinding of samples below 150 μm enhanced the quality of P-XANES data compared with samples that passed only the 150- μm sieve. The samples were then mounted on Teflon tape and fixed on Al sample holders ready for analysis. Four to six scans of samples were taken with a scan range from 2110 to 2400 eV. The step size was 2.0 eV on the pre-edge region (2110–2140 eV), 0.125 eV in the near-edge region (2140–2165 eV), and 0.5 in the post-edge region (2165–2400 eV) with a reading time of 3 to 6 s per point. Four to six scans of collected spectra for particular samples were averaged, the edge energy was calibrated, the pre-edge was subtracted (by a linear function), and the spectrum was normalized to the second-order polynomial to be equal to 1. Normalization was done using Athena software version 0.8.056 (Ravel and Newville, 2005).

The P standards used in this study were purchased or synthesized. Berlinite (AlPO_4), brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$), hydroxyapatite [$(\text{Ca}_5(\text{PO}_4)_3(\text{OH}))$], monetite (CaHPO_4), and rock phosphate were purchased from Sigma Aldrich (St. Louis, MO). Strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) was synthesized following the procedure of Dalas (1991). Strengite with different crystallinities was synthesized. Variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$) was synthesized following the procedure of Hsu and Sikora (1993). Vivianite and apatite standards were obtained from the 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 X-ray diffraction. The powdered phosphate standards were spread as a thin layer over double-sided C tape and mounted on Al samples holders for XANES data collection. Two scans per each standard in fluorescence mode were collected as previously described.

Data Analysis

Principal Component Analysis

The normalized XANES spectra were analyzed using PCA. Principal component analysis was conducted with the LabView software package available from Beamline 10.3.2 of Advanced Light Source (Marcus et al., 2004) to see how many spectra were linearly independent in samples and how many principal components (PC) were needed to reproduce the spectrum. Principal component analysis first considers the statistical variance within an experimental dataset composed of a group of unknown samples. The dataset is then redefined into a reduced number of independent sources of variability. A subsequent analysis, the target transformation, offers the possibility of testing which standard species are most likely to contribute to the PC.

A mechanical mixture of chemical species obviously results in a linear combination of the corresponding spectra; however, if different species have similar XANES spectra, the spectra may be linearly dependent even for a set of pure chemical species. The spectra subjected to PCA or target transformation are defined on the same energy grid. By loading sample spectra into PCA software, we obtained eigenvalues, indicator (IND) values, and signal and reconstructed curves. The eigenvalues measure the amplitude of the abstract spectra of the factors. Factors with large eigenvalues influence the data more than factors with small eigenvalues. The eigenvalue rule is one way to determine the number of significant principal components. If the eigenvalues are very small or do not change significantly, we could consider the eigenvalues insignificant. The criterion described by Beauchemin et al. (2003) and Nachtegaal et al. (2005) was used to define the number of significant components. The IND function is an empirical method that relies on the secondary eigenvalues; it should reach a minimum value when the correct number of significant components is reached. The standards were selected based on the SPOIL value. The SPOIL function indicates whether the vector of the soil standard tested fits well or increases the error in the matrix reproduced in the target transformation. A target is considered acceptable if its SPOIL value is <3 , moderately acceptable if the value is 3 to 6, and unacceptable if the value is >6 (Malinowski, 1991). The SPOIL values for standards are listed in Table 2.

Table 2. SPOIL+ factors for the reference spectra constructed from principal components.

Reference	5-wk samples	6-mo samples
Al. phosphate	1.43	1.47
Apatite	1.85	1.85
Brushite	1.66	1.73
Hydroxyapatite	1.83	1.88
Pot. Dihydrogen phosphate	1.79	1.90
Monetite	1.82	1.93
Monoammonium phosphate	1.80	1.92
Alumina adsorbed P	2.27	2.77
Ferrihydrite adsorbed P	2.26	2.58
Gibbsite adsorbed P	1.90	1.95
Goethite adsorbed P	1.98	2.03
Rock phosphate	1.96	2.02
Poorly crystalline Strengite	1.97	2.07
Strengite	1.80	1.90
Variscite	1.95	1.95
Vivianite	2.07	2.16

† SPOIL factors <1.5 indicate an excellent fit; 1.5 to 3 a good fit; 3 to 4.5 a fair fit; and 4.5 to 6 a poor fit. Factors >6.0 are unacceptable. All standards are a good fit.

Linear Combination Fitting

The XANES data were analyzed with Athena software. Speciation was done using linear combination fitting (LCF). The linear combination XANES fitting procedure reconstructs the sample (or experimental) spectra using all combinations of the standard spectra. The weighting factors were forced to sum to 1, and no energy shifts were permitted in LCF fitting. Out of all possible combinations, the combination with the lowest reduced χ^2 value was chosen as the most likely set of components or the best fit. The fitting was done in the normalized space using quaternary combinations of all standards with the fitting range from 2144 to 2179 eV because the PCA indicated that four principal components were needed to reproduce the soil P-XANES spectra.

RESULTS AND DISCUSSION

Wet Chemical Analysis

Figure 1 for the response variables shows a statistical comparison of various treatments at the point of fertilizer application; that is, at 0- to 2.5-cm depth for the broadcast treatment with 7.5- to 10-cm depth for deep-banded. The initial soil pH values for the top 0- to 7-cm and 7- to 15-cm soil depths were 5.9 and 5.7, respectively (Table 1). Addition of fertilizers showed a decrease in soil pH at 5 wk; however, pH moved toward initial soil pH at 6 mo for most of the treatments. Mixed results (lower, higher, or no significant difference) were observed for soil pH when comparing pH changes among the urea-added plots and the plots with both urea and MAP (as granular or liquid) added (Fig. 1). Many researchers have reported acidification effects of MAP on soil pH (Hanson and Westfall, 1985; Moody et al., 1995), but hydrolysis of urea consumes 2 moles of protons for each mole of urea hydrolyzed, thereby resulting in an increase in pH. Therefore, a combination of these

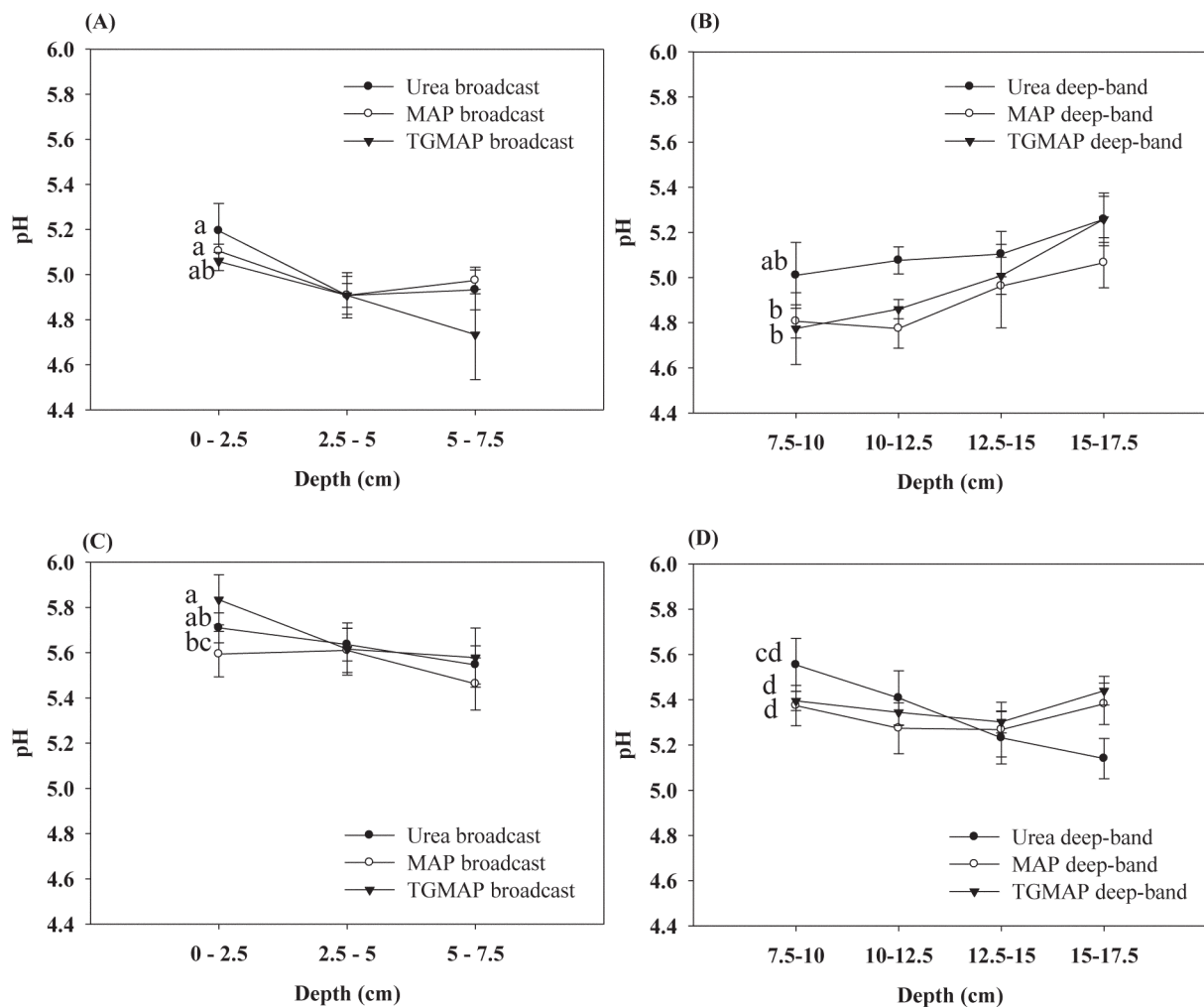


Fig. 1. pH at different distances from the point of fertilizer application over time: (A) 5 wk broadcast, (B) 5 wk deep-band, (C) 6 mo broadcast, and (D) 6 mo deep-band. Granular monoammonium phosphate (MAP) = MAP; liquid MAP = technical grade monoammonium phosphate (TGMAP).

reactions (nitrification of NH_4^+ and hydrolysis of urea) could in turn result in mixed effects on overall soil pH. At 5 wk, soil pH in both urea and MAP (as granular or liquid) added with broadcast and deep-banded treatments were significantly lower (0.6–1 units) than the original soil pH (5.9), whereas the soil pH of broadcast P treatments at 6 mo was found restored to initial soil pH (Fig. 1). At 6 mo, the soil pH for the deep-banded treatments was lower (0.2–0.6 units) than the soil pH at 5 wk from the same plots (i.e., that received same soil treatment). This result is most likely due to neutralization of treatment effects on soil pH with time and in-field seasonal variation of soil pH.

As expected, we found no difference in total P (Fig. 2) for granular MAP and liquid MAP treatments, and we observed no differences with respect to time. The broadcast urea had slightly higher total P content (average of 488.1 mg kg^{-1}) compared with the deep-banded urea treatment (average of 350.3 mg kg^{-1}), which might be due to the P stratification in the reduced-tillage system.

We used an anion exchange membrane technique (resin-extractable P) to estimate potential available P in soils (Fig. 3). The P supplying power of soils assessed by the anionic exchange membrane technique has been shown to correlate satisfactorily with P uptake and P concentration in the biomass; therefore,

resin-extractable P can be considered a reliable index of available P in soils (Myers et al., 2005). At 5 wk, deep-banded liquid MAP had the highest resin-extractable P compared with other treatments, and the trend continued even after 6 mo, when resin-extractable P remained significantly higher (Fig. 3). We also examined resin-extractable P as a percentage of total P because it allowed evaluating resin-extractable P independent of the total P concentrations in soils. At 5 wk for broadcast and deep-band urea plots, the percentages of resin-extractable P concentrations were 3.4 and 9.2, respectively (Fig. 4). For broadcast treatments at 5 wk, there was no significant difference in percentage resin-extractable P. For the deep-band treatments at 5 wk, liquid MAP deep-band had a significantly higher percentage of resin-extractable P followed by MAP deep-band. Additionally, percentage resin-extractable P at 5 wk for liquid MAP deep-band was significantly higher than all the other treatments. At 6 mo, we found no significant difference in percentage resin-extractable P for all broadcast treatments (Fig. 4). In the deep-band P plots, both the granular and liquid treatments had a significantly higher percentage of resin-extractable P than urea and MAP broadcast. For the deep-band treatments at 6 mo, liquid MAP deep-band had a significantly higher percentage of

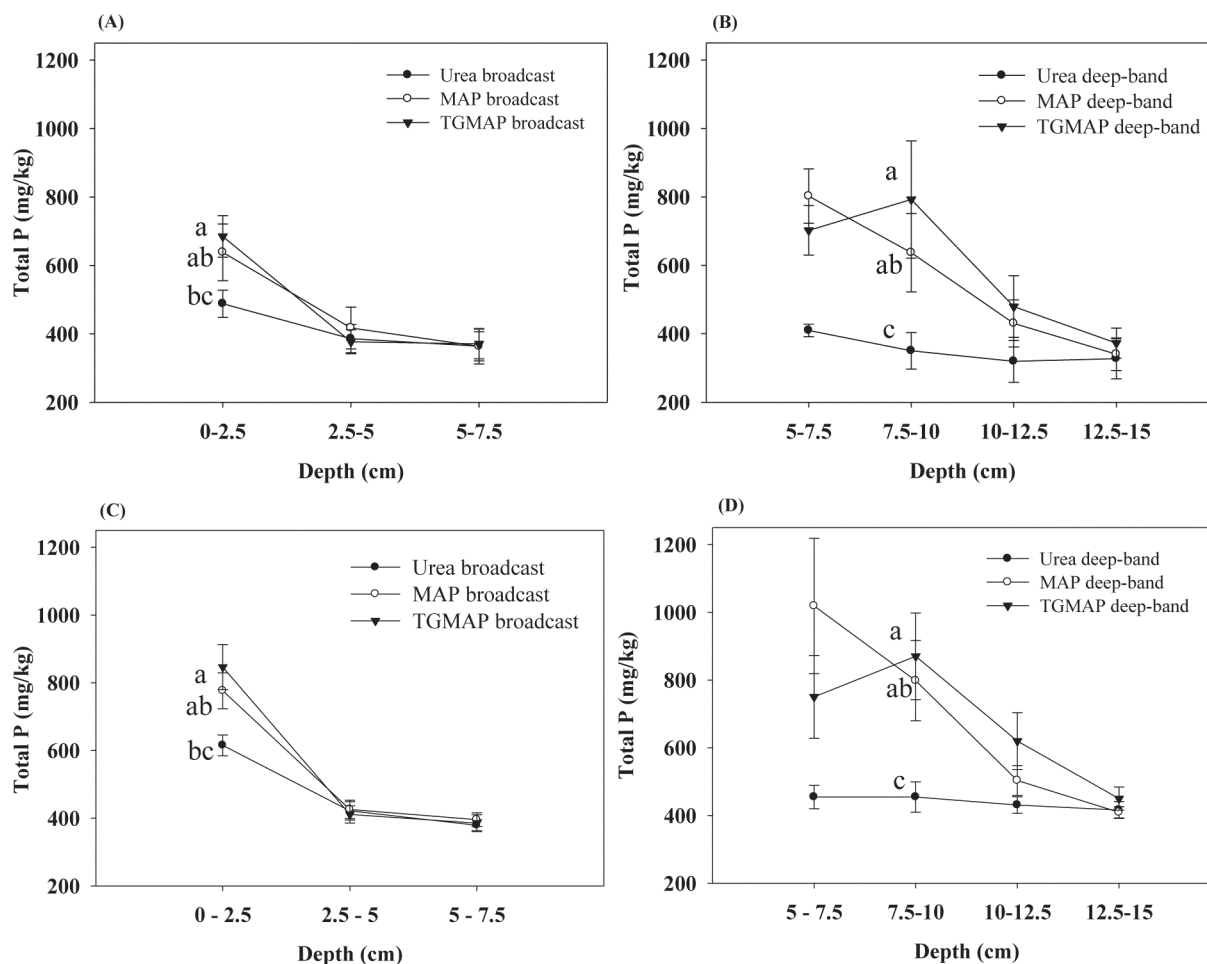


Fig. 2. Total P at different distances from the point of fertilizer application over time: (A) 5 wk broadcast, (B) 5 wk deep-band, (C) 6 mo broadcast, and (D) 6 mo deep-band. Granular monoammonium phosphate (MAP) = MAP; liquid MAP = technical grade monoammonium phosphate (TGMAP).

resin-extractable P. Despite liquid MAP deep-band's significantly higher percentage of resin-extractable P at 6 mo, MAP deep-band did not differ significantly from urea deep-band. Only the deep-band liquid treatment had a significantly higher percentage of resin-extractable P compared with all other treatments at 6 mo.

X-ray Absorption Near Edge Structure Analysis

X-ray absorption near edge structure spectra of standards used for the study are shown in Fig. 5. The white line peak was around 2149 eV. Spectra for Fe-phosphate standards showed a pre-edge feature between 2144 and 2147 eV, which increased with increasing crystallinity. All calcium phosphate minerals have a shoulder on the high-energy side between 2151 and 2155 eV. Aluminum phosphate minerals are characterized by weak pre-edge inflection at about 2148 eV. These spectral features of phosphate bond with Ca, Al, and Fe and have been well documented (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003; Khare et al., 2005; Lombi et al., 2006), which helps us determine the association of phosphate with different elements in soil samples.

The SPOIL values for all the standards used for the study were <3, indicating that all standards were suitable for linear combination (LC)-fitting (Table 2). In the whole-spectrum

(whole energy range) PCA component plot (Fig. 6), only the score plots for PC1 and PC2 are presented. The PC1 and PC2 explained 69.5 and 20.6% of the sample spectral variation, respectively. In the PCA component plot, more similar spectra are located closer to each other, so the PCA component plots can be used to identify groupings of samples. For example, the 5-wk samples were found to be closely located or similar to apatite, hydroxyapatite, monetite, brushite, vivianite, etc., whereas the 6-mo samples were closer to variscite, aluminum phosphate, and adsorbed P forms. Moreover, 6-mo samples were very similar to the spectra of the control soils, suggesting that with time, P reaction products transform into forms similar to the soil's original P forms. Further PCA of the samples within the pre-edge energy range (2145.5–2148 eV) and the post-edge energy range (2150–2155.5 eV) showed that the PC1 explained at least 91.5% of spectral variation.

The normalized P K-edge XANES spectra and linear combination fitting results of 5-wk and 6-mo samples are shown in Fig. 7. Phosphorus was present as adsorbed P (68%) and Fe-P mineral forms (32%) in the control soil at 5 wk based on XANES fitting analyses (Table 3). Addition of urea lowered adsorbed P and increased Fe-P forms. The broadcast placement of MAP in a granular form further increased the proportion of P associated

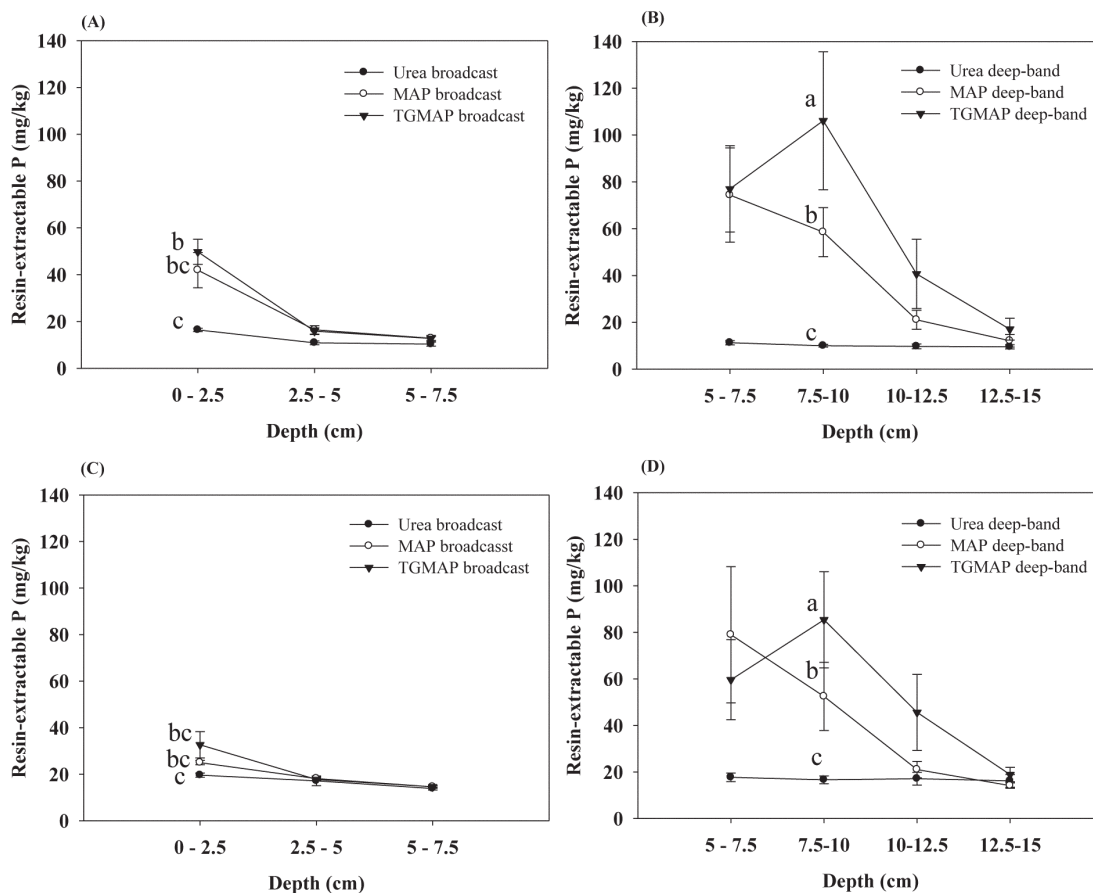


Fig. 3. Resin-extractable P at different distances from the point of fertilizer application over time: (A) 5 wk broadcast, (B) 5 wk deep-band, (C) 6 mo broadcast, and (D) 6 mo deep-band.

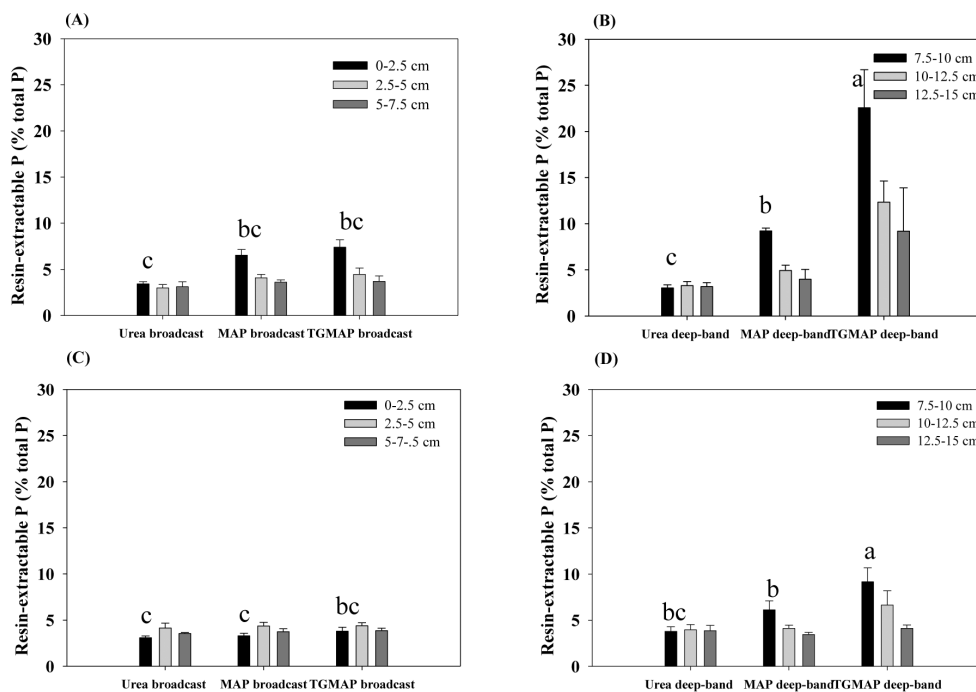


Fig. 4. Resin-extractable P (as percentage of total P) in soil sections collected at different distances from the point of fertilizer application. The resin-extractable P (as a percentage of total P) was calculated by dividing resin-extractable P values for each section by the corresponding total P concentration. Error bars represent standard errors of five field replicates. (A) 5 wk broadcast, (B) 5 wk deep-band, (C) 6 mo broadcast, and (D) 6 mo deep-band treatments. Granular monoammonium phosphate (MAP) = MAP; liquid MAP = technical grade monoammonium phosphate (TGMAP).

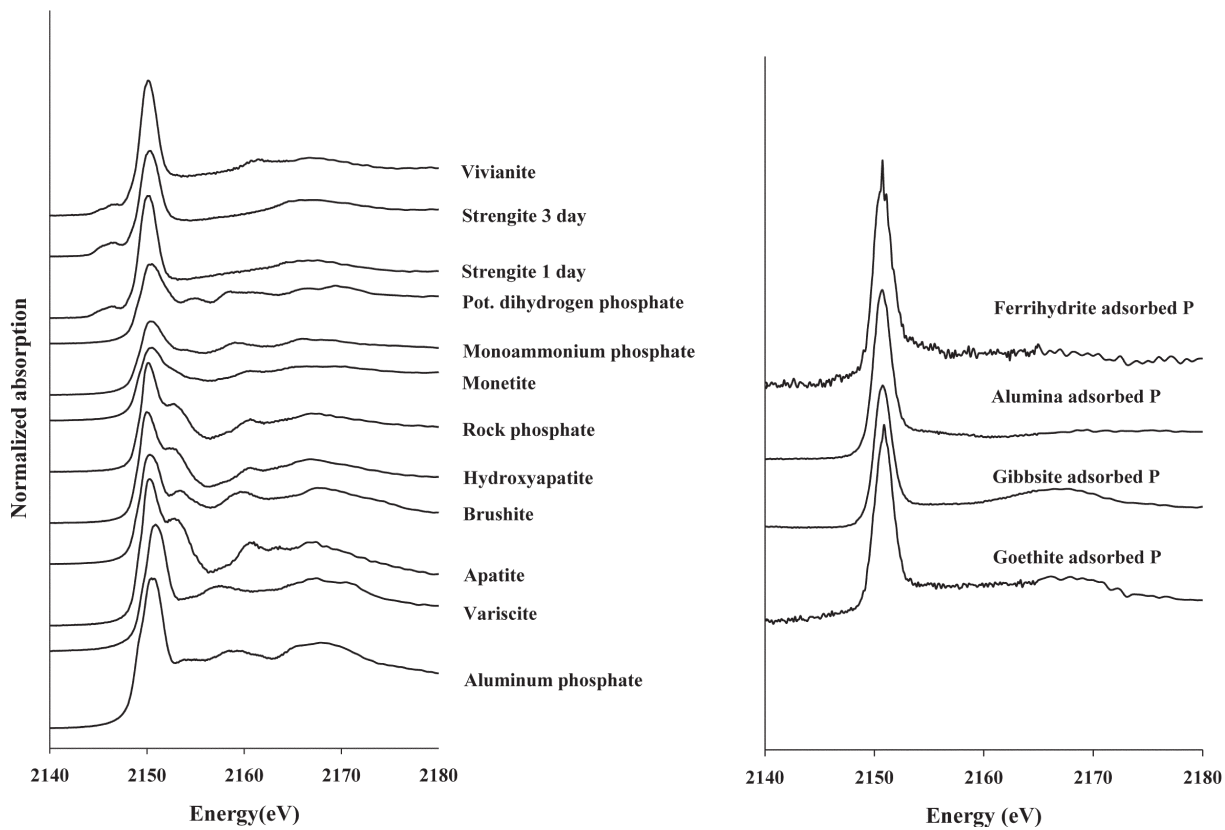


Fig. 5. Normalized P K-X-ray absorption near edge structure (XANES) of standards used for linear combination fitting.

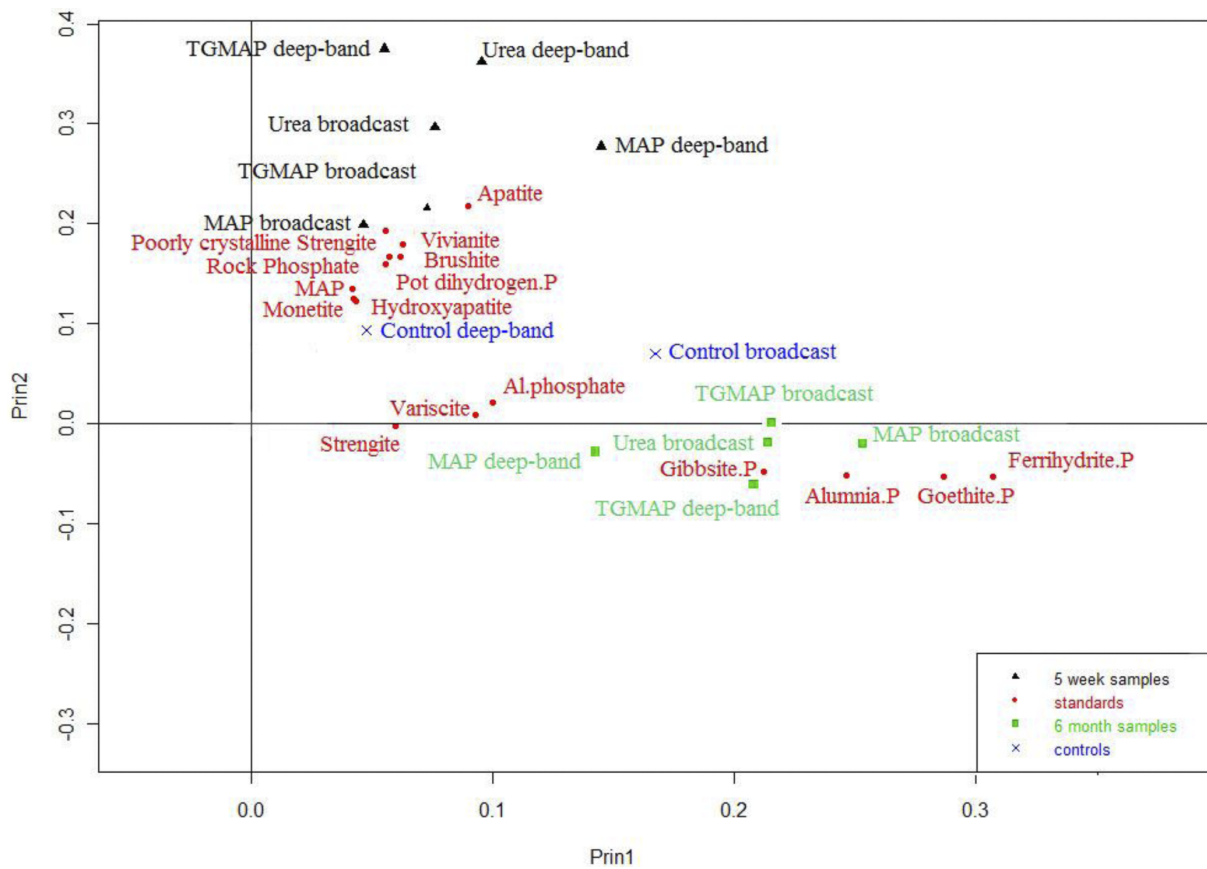


Fig. 6. Principal component (PC) loading plot of standards for 5-wk and 6-mo soil samples. Eigenvectors of all standards and samples across the full spectral range (2144–2179 eV) are presented in the loading plot.

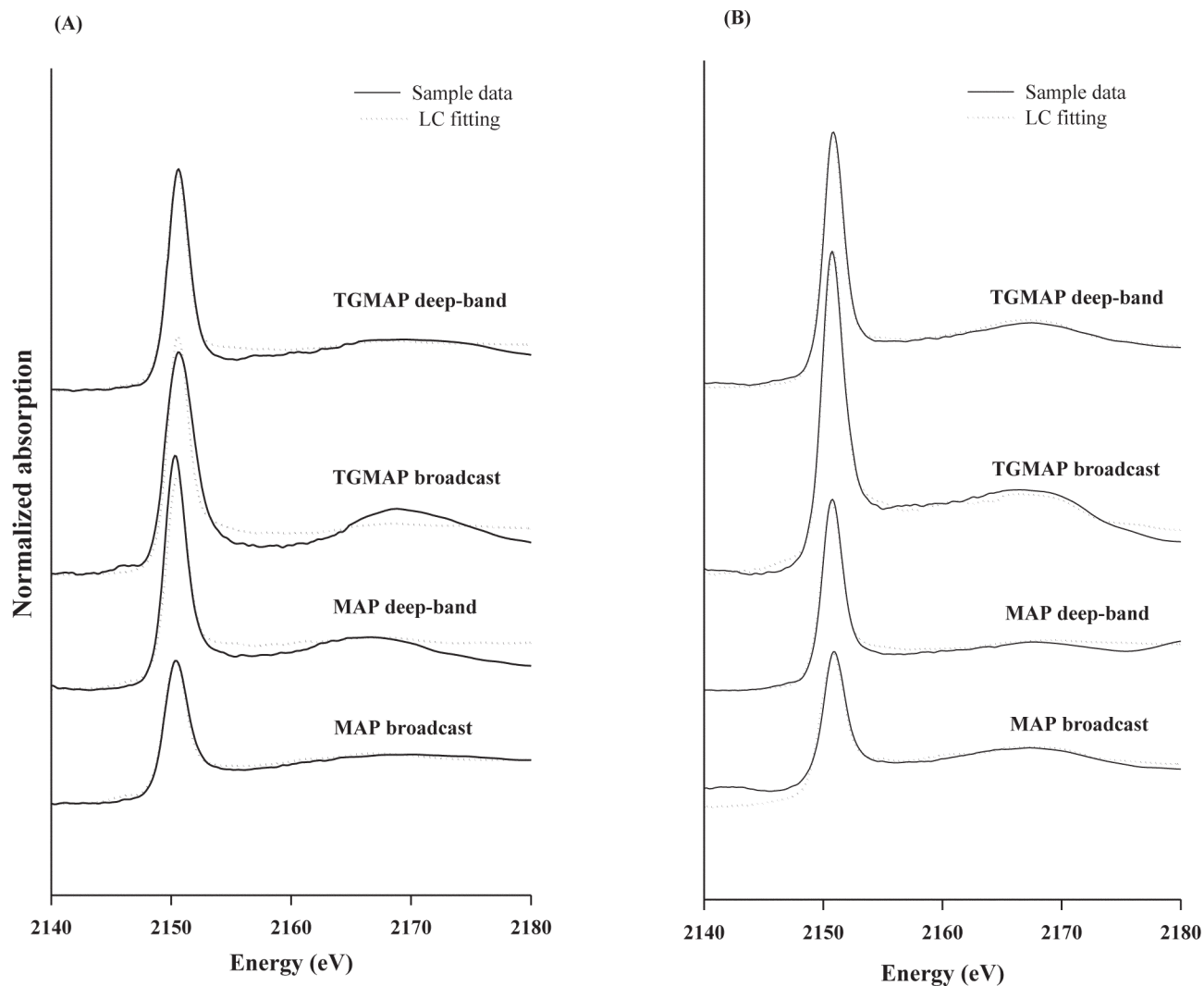


Fig. 7. Normalized P K-X-ray absorption near edge structure (XANES) spectra (solid lines) of soil samples. (A) 5-wk samples, (B) 6-mo samples. Dotted lines indicate the linear combination fits using all the standard compounds.

with Fe–P minerals to 72% and lowered the percentage of adsorbed P forms to 23%. The remaining P was present as Ca–P minerals (5%). The increase in precipitated Fe–P forms with

broadcast MAP in granular form could be due to the drop in soil pH from 5.9 in the control to 5.1 after 5 wk as previously mentioned (see Fig. 1). Iron phosphates are known to control solubility of P under acidic conditions (Lindsay, 1979). In addition, limited diffusion of P away from MAP granules might have encouraged locally high P concentrations and subsequent precipitation of Fe–P forms (Lombi et al., 2006).

Addition of MAP in a liquid, broadcast form (TGMAP broadcast) resulted in a majority of the P existing as adsorbed forms (76%) and the remainder as Ca–P minerals (24%) after 5 wk (Table 3). No Fe–P minerals were present in the TGMAP broadcast experiments. The lower proportion of precipitated forms of P in liquid P treatments when compared with granular P treatments agrees with our initial hypothesis. A plausible explanation

Table 3. Phosphorus K-X-ray absorption near edge structure (XANES) fitting results for 5-wk samples performed in normalized space with an energy range from 2144 to 2179 eV showing the relative proportion of phosphate minerals showing best fit.

Treatment‡	Ca–P minerals	Al–P minerals	Fe–P minerals	Adsorbed P	Red. χ^2 †
Control broadcast	–	–	32.0	68.0	0.010
Urea broadcast	–	–	56.8	43.2	0.053
MAP broadcast	5.0	–	72.5	22.5	0.004
TGMAP broadcast	24.0	–	–	76.0	0.077
Control deep-band	6.4	39.7	53.9	–	0.098
Urea deep-band	53.7	23.4	15.4	7.5	0.030
MAP deep-band	–	–	49.0	51.0	0.098
TGMAP deep-band	–	–	36.9	63.1	0.015

† $\chi^2 = \sum(\text{fit} - \text{data})/\epsilon)^2 / (N_{\text{data}} - N_{\text{components}})$ 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 $N_{\text{components}}$ 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%.

‡ MAP, monoammonium phosphate; TGMAP, technical grade monoammonium phosphate.

for the differences between granular and liquid treatments might be greater diffusion of P in liquid MAP. Lombi et al. (2006) showed that liquid MAP had a greater diffusion rate than granular MAP. We might expect this to result in more diffuse concentrations of P, and conditions might be undersaturated with respect to potentially precipitating Fe–P phases.

The second hypothesis was that deep-banding of P would result in lower precipitated forms of P than for broadcast placement. This was true of granular MAP. Linear combination fitting results showed granular MAP deep-banded into the soil lowered the proportion of precipitated P forms from 77% with broadcast placement to 49% in deep placement after 5 wk (Table 3). The rest of the P (51%) was present in adsorbed forms. Native P in the control and urea deep-placed treatments was present entirely in precipitated forms (>90%). Notably, these two soils did not receive any P and therefore had considerably low total P concentrations that resulted in noisier XANES spectra and weak fits. Addition of deep-placed liquid MAP resulted in a shift from Ca-associated P (with broadcast placement) to Fe–P forms, but the majority of the P (63%) was still present in adsorbed forms (Table 3). A possible reason for these trends with placement maybe attributed to the pH differences (Fig. 1a and 1b). Deep-banded liquid P had soil pH of ~4.8, whereas broadcast liquid P had soil pH of ~5.1. Low pH might have resulted more soluble Fe in soil solution, thus promoting Fe–P formation as opposed to Ca-associated P.

Comparison of resin-extractable P data with speciation results showed a positive correlation of adsorbed P species with resin-extractable P, suggesting that adsorbed P species might be more available. For liquid P treatments with higher resin-extractable P, the dominant P species were found in adsorbed P-like forms. The liquid MAP likely appeared to be in more “accessible” forms than the granular MAP due to the differences in diffusion of P from granular and liquid MAP. Lombi et al. (2006) found that liquid MAP remained in potentially plant-available form (as measured by isotopically exchangeable P) because of increased diffusion compared with the granular MAP in a highly calcareous soil. 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). Similarly, the current study shows that liquid MAP tended to form relatively more adsorbed-P forms and less Fe-phosphate-like P than the granular MAP treatment in this acid soil.

Time Effect

At 6 mo in the urea broadcast treatment (broadcast +N control), a greater portion of P was found to be

in adsorbed-P forms (82.6%), whereas in the added urea deep-band treatment (broadcast +N control), P transformed to more Ca–P like forms (83.4%) over time. The increase in pH over time might have favored formation of more adsorbed- or Ca–P-like forms compared with their 5-wk samples (after perturbation of the system by adding urea). For MAP added treatments, with time P reaction products changed from more Fe–P-like forms to Ca–P forms (5 and 24% of Ca–P at 5 wk increased to 66 and 39% at 6 mo for MAP broadcast and MAP deep-band treatments, respectively). In both liquid MAP broadcast and deep-band treatments, P continued to be in more adsorbed P-like forms (79.2 and 80.2%, respectively) (Table 4).

The surface soil had relatively lower resin-extractable P (25 mg kg⁻¹ for MAP and 32.65 mg kg⁻¹ for TGMAP) (Fig. 3) compared with deeper (7–15 cm) soil (52.45 mg kg⁻¹ for MAP and 85.38 mg kg⁻¹ for TGMAP). Consequently, the relative differences in reaction products in broadcast and deep-band treatments over time might be related to resin-extractable P levels at given time periods. Soils layered with higher resin-extractable P after P application showed relatively more soluble species of P compared with soil layers with low resin-extractable P. Lindsay (1979) suggested the formation of sparingly soluble mixed Al-phosphates and/or Fe-phosphates as a possible mechanism that restricts P solubility in acid soils. Calcium phosphates such as apatite are the stable P species formed in alkaline soil through time after P fertilizer applications (Lindsay, 1979). Similarly, depending on the activity of Ca²⁺ in soil solutions, precipitation of P as Ca-phosphates also can be responsible for restricting P solubility in slightly acid, neutral, and alkaline soils.

Anions such as phosphate can bind strongly to the mineral surfaces of Fe and Al oxides, particularly at lower pH values (Hingston et al., 1967, 1968). Adsorbed P was prominent in a majority of the treatments, especially where liquid MAP was added. The Fe–P forms were also present in granular P treatments after 5 wk. The standards included in our study were P adsorbed on ferrihydrite, goethite, alumina, and gibbsite, each of which displays complex behavior with P in pure mineral systems (Arai and Sparks, 2007); thus, teasing out the exact nature of

Table 4. Phosphorus K- X-ray absorption near edge structure (XANES) fitting results for 6-mo samples performed in normalized space with an energy range from 2144 to 2179 eV showing the relative proportion of phosphate minerals showing best fit.

Treatment	Ca–P minerals	Al–P minerals	Fe–P minerals	Adsorbed P	Red. χ^2
Control broadcast	–	–	32.0	68.0	0.010
Urea broadcast	–	–	17.4	82.6	0.031
MAP broadcast ‡	66.2	–	5.1	28.7	0.013
TGMAP broadcast ‡	20.8	–	–	79.2	0.015
Control deep-band	6.4	39.7	53.9	–	0.098
Urea deep-band	83.4	–	16.6	–	0.214
MAP deep-band	38.5	–	7.6	53.9	0.009
TGMAP deep-band	19.8	–	–	80.2	0.010

† $\chi^2 = \sum(\text{fit} - \text{data})^2 / \epsilon^2 / (N_{\text{data}} - N_{\text{components}})$ 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 $N_{\text{components}}$ 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%.

‡ MAP, monoammonium phosphate; TGMAP, technical grade monoammonium phosphate.

the adsorbed P complex is difficult. Moreover, adsorption and precipitation of P are known to occur on a continuum (Arai and Sparks, 2007).

Notably, a portion of P is associated with Ca in liquid MAP broadcast treatment despite the low soil pH conditions (Table 3 and Fig. 1). Co-existence of adsorbed P and Ca–P forms is not uncommon in acidic soils. Previous P K-edge XANES results indicated that P was adsorbed on Fe and Al oxides as well as Ca–P forms in acidic soils (Beauchemin et al., 2003). Using chemical extractions, Simard et al. (1995) found co-existence of Ca–P forms, assessed by HCl extractions, and Fe/Al–P, evaluated by NaOH extraction. After 6 mo, there was a negligible change in distribution of P in liquid MAP treatments, but granular MAP broadcast treatments increased in the proportion of Ca–P forms to 66%. The soil pH values increased with time (Fig. 1) and could have promoted conditions for Ca–P precipitation to occur (Lindsay, 1979). Soil in the current study had higher extractable Ca concentration than extractable Al and Fe (Table 1). Adsorption interactions between Ca and P also might be in operation, because these interactions have been reported in pure mineral systems (Helyar et al., 1976; Rietra et al., 2001). These results underscore the complexity of P speciation in heterogeneous soil samples.

CONCLUSIONS

When liquid MAP is deep-banded in a reduced-till soil system, more P appears to remain in resin-extractable P forms for 6 mo after fertilizer application. In contrast, broadcast P, either in granular or in liquid form, tended to transform into less extractable P forms after 5 wk to 6 mo. Speciation results showed that granular P fertilizers tended to form Fe P-like products, whereas liquid forms were found to remain in adsorbed P-like forms in soil after 5 wk of application. When comparing deep-band granular MAP treatment to broadcast granular MAP treatment, speciation results showed a reduction in precipitated P forms and higher resin-extractable P in the deep-band granular MAP treatments compared with the broadcast granular MAP treatments at 5 wk, thus proving our second hypothesis that deep-banding would result in lower precipitated forms of P than broadcast placements. In a 6-mo period, reaction products of broadcast granular and broadcast liquid and deep-band granular fertilizers transformed to Ca-phosphate or mixtures of Ca-, Fe-, and adsorbed-phosphate-like forms, whereas deep-band liquid P continued to remain mainly as adsorbed P-like forms. Formation of Fe- and/or Ca–P solid species, known to have different solubilities, may have been the reason for the observed differences in resin extractability or potential availability of P between broadcast and deep-banded granular and liquid MAP evaluated in this study. Spectroscopic investigations appeared to agree with resin-extractable P results and suggest that when liquid or granular P is deep-banded, more P remains in comparatively more soluble forms of P in soil, whereas surface-applied granular and liquid P tend to transform into comparatively less soluble P forms in 6 mo.

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