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Placement and source effects of phosphate fertilizers on phosphorus availability and reaction products in two reduced-till soils: A greenhouse study

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Abstract

Crop yields are limited primarily by unavailability of nutrients in agricultural soil. Adoption of reduced tillage and no-tillage systems 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 the reaction products of P under greenhouse conditions using soil columns. 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 5 weeks after P application 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 analysis (SEM-EDXA) and synchrotron-based X-ray absorption near-edge structure (XANES) spectroscopy were used to understand P speciation. Results for P fertilizer sources and placement with respect to resin-extractable P showed no clear differences between the treatments except for granular broadcast and granular deep-placed treatments in the Ottawa soil. Reaction products formed after application of P in two soils showed some clear differences. The XANES speciation revealed that Fe-P-like forms dominated in the acidic soil, whereas adsorbed and Fe and Ca-P-like forms dominated in the neutral to slightly acid soil. No clear trends in reaction products were detected with respect to P source or the P placement method. Furthermore, SEM-EDXA analysis of incubated fertilizer granules extracted from soils at 5 weeks showed enrichment of Al, Fe, and

Ca in the zones of remaining P in incubated granules, indirectly indicating that these cations enter and or remaining in the granules and begin to react with P before the granules dissolve completely.

Introduction

Reduced tillage is becoming popular in the United States and worldwide (Hobbs et al., 2008). The approach has various advantages, but granular P fertilizer applications in reduced-tillage systems have been found to lead 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 that is ideal for high-speed operations and high application rates; however, increased adoption of reduced tillage coupled with broadcast fertilization has raised both agronomic and environmental concerns about P management. Concerns related to nutrient stratification include potential impact on nutrient uptake and subsequent reduction in crop yield due to the inability of crops to access nutrients (Mallarino and Borges, 2006). Holanda et al. (1998) found that P stratification stimulated root growth in conservation systems compared with conventional systems. Bordoli and Mallarino (1998) suggested that deep placement of nutrients (below the first 5 to 10 cm of the soil) should be superior to other placements in terms of avoiding nutrient stratification, but they found no response to P placement at any site for corn yield; that is, deep placement did not change yield compared with broadcast P treatment. Because of differential plant yield responses observed by the reduced-till researchers and the lack of insight into mechanisms responsible for variable responses, the need remains for knowledge of how different placements of P fertilizers in reduced-tillage systems affect P reaction pathways and products in relation to plant growth (Khatiwada et al., 2012). Deep

application of P fertilizers can minimize ammonia volatilization in moisture-deficit conditions and reduce surface P runoff to aquatic systems. Furthermore, studying the dominant solid P species found in soil following application of P fertilizers and making P available to plants would help producers manage P efficiently in reduced-tillage systems.

Liquid fertilizers have shown better performance than granular forms of P fertilizers in highly calcareous soils. Holloway et al. (2001) reported that fluid monoammonium phosphate was four to five times as effective as granular monoammonium phosphate in a field trial in the calcareous soils of South Australia. Lombi et al. (2004) showed that the liquid forms of P fertilizers are more isotopically exchangeable in highly calcareous soils than their granular forms, and thus more available to crops. Studies conducted thereafter in similar soils showed that 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 than broadcast or strip-applied fertilizers, liquids warrant further investigation because they may be a suitable alternative to enhance P availability, especially in reduced-tillage systems established on high P-fixing soils. Our main hypothesis was that liquid fertilizers would perform better than granulated fertilizers in terms of plant availability for deep placed treatments in contrast to broadcast application in reduced tillage system.

A study focused on evaluating the influence of placement (broadcast vs. deep-band P), fertilizer source (granular vs. liquid P), and time on the reaction of P products under field conditions without plants suggested that deep banding of liquid P in reduced tillage systems would most likely help maintaining better P availability compared to broadcast liquid or granular and deep-band granular fertilizers (Khatiwada et al., 2012). Combining the effect of plant growth in studies focusing on P fertilizer reaction products would

be more appropriate, and may give a different outcome than research conducted without plants as continual removal of P and other soil chemical changes induced by plant growth may affect soil P speciation. Therefore, assessing P reaction products after plant growth will allow us to study differences in P sources and P placement methods in reduced tillage systems more realistically.

Plant availability of P can be determined directly through plant uptake studies and indirectly through various extraction procedures. Labile P in soil appears to be isotopically exchangeable or anion resin-extractable. The resin-extractable P method mimics the soil/soil solution/plant root model (Bernardo et al., 2009), which makes the indirect resin-extractable P method superior to most other common extraction procedures for determining plant available P (such as Olsen P, Bray 1-P, Mehlich P) (Saggar et al., 1990).

Speciation of contaminants and nutrients in soils plays a major role in determining their availability and their fate in the environment (Nolan et al., 2005). Speciation of P reaction products in soils can be achieved using X-ray absorption near-edge structure (XANES) spectroscopy. This technique is advantageous in studying reaction products in soils due to its elemental specificity, superior detection limits, insensitivity to crystallinity, and capability of probing the element of interest in situ (i.e., with minimal sample preparation). The XANES technique allows determination of the oxidation state and the local chemical and structural environment of an element (Fendorf and Sparks, 1996), which enables speciation. This technique has 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 a 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 five different soils used for the study, with a high proportion in the more acidic soils and some in slightly alkaline soils. Although XANES is useful to identify P species in soils directly, the method also has weaknesses. The XANES speciation based on fitting techniques is limited by (i) data quality and (ii) how well the chosen set of standards represents real species in samples (Beauchemin et al., 2002). The speciation of P in broadcast and deep placed system would give us an insight into possible mineral phases formed in the soil under these system and help better predict their fate and availability.

Scanning electron microscopy with energy dispersive X-ray analysis (SEM-EDXA) is a technique that can be used to probe enriched samples or enriched zones of samples (at least about 1000 mg of element of interest/kg) to collect direct information on crystal morphology, size, shape, locations, and their associations. Because EDXA provides chemical compositional information, SEM combined with EDXA can be used to get indirect information about chemical species present in a sample; therefore, SEM-EDXA 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 the SEM-EDXA technique to identify compounds present in a single superphosphate produced from Brazilian phosphate rock and were able to identify compounds such as calcium phosphate monohydrate, triiron potassium octahydrogen hexaphosphate hexahydrate, triiron 15-hydrogen octaphosphate tetrahydrate, triiron potassium 14-hydrogen octaphosphate tetrahydrate, and barium sulfate. This technique would help us determine the possible mechanism associated with the mineral precipitation and availability in the zone of fertilizer application. The objectives of this greenhouse experiment were to: 1)

study plant growth (corn for 5-wk), fertilizer placement (broadcast vs. deep-placed) and source (granular vs. liquid) effect on reaction products of P, 2) establish availability of P using resin-extractable P measured at different distances from the point of fertilizer application, and 3) compare resin-extractable P with soil P chemistry in two Kansas soils under no- or reduced-tillage systems for many years. This information may aid in designing better P formulations and management practices for no- or reduced-tillage systems.

Materials and Methods

Site Description, Soil and Fertilizers

A greenhouse-based study was conducted using soils collected from the Department of Agronomy North Farm (Site I) in Manhattan, KS, and from the East Central Kansas Experiment Field (Site II) in 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: H₂O) 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) in this soil was 423 mg kg⁻¹ for surface soil (0 to 7 cm). Ottawa soil had a pH (1:5, soil:H₂O) 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) of the Ottawa soil was 774 mg kg⁻¹. The maximum water-holding capacities of Manhattan and Ottawa soils were 48.2% and 57.5%, respectively, which were determined with a modified method of the version described by Jenikson and Powlson (1976). The general properties of soil used for the study are given in [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 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 the DTPA extraction technique described by Whitney (1998). Potassium chloride–extractable aluminum (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 the 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). Granular monoammonium phosphate (MAP) (11-52-0, N:P₂O₅:K₂O) and technical grade monoammonium phosphate (TGMAP) (12-60-0, N:P₂O₅:K₂O) in liquid form were used as P fertilizer sources. The rates of N and P applied were 200 and 75 kg/ha, respectively. Phosphorus is often applied with N to meet nutrient needs of plants. Nitrogen fertilizers that are applied with P fertilizers may influence P chemistry in soils; thus, we applied urea with P to supply and balance nitrogen (N) in all treatments.

Experimental Approach

The treatments structure included: (1) urea broadcast (+N Control), (2) urea deep-placed (+N control), (3) MAP broadcast, (4) MAP deep-placed, (5) TGMAP broadcast, and (6) TGMAP deep-placed. Experimental design was a randomized complete block with five replications. Soil cores of 30-cm depth were extracted from the Agronomy North Farm (Site I) and the East Central Kansas

Experiment Field (Site II) using a tractor-mounted and -driven probe. Extracted soil cores were divided into 0- to 7-, 7- to 15-, and 15- to 30-cm depth and homogenized separately to maintain the nutrient stratification in soil. Depth-wise separated (and homogenized) soils were air-dried, ground, passed through a <2-mm sieve, and further homogenized. Our preliminary soil analysis data showed large variability in total P concentrations in surface soils collected from both these sites, therefore, homogenization and sieving were performed to get uniform samples for our column experiments. Soils were packed in Plexiglas columns of 6.8-cm inner diameter and 35.6-cm length (Busada Manufacturing Corporation, Louisa, VA) section by section to keep depth-wise differences intact and maintain the bulk density of 1.2 g cm^{-3} , a total of 1318 g for Site I and 1362.4 g for Site II. The average P concentration of MAP granules (weighing $42 \pm 0.5 \text{ mg}$) was $9.08 \text{ mg P} / 42 \text{ mg granule}$. Six granules per column were applied for the 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 $600 \mu\text{L}$ by mixing with water. This was spread over the entire surface (not injected in a band, and entire surface is considered as a band). Urea was applied for all treatments at a rate of 200 kg N/ha . Application rates were based on the total nutrient content of the fertilizers. The experimental design was a randomized complete block with a total of five replications. Initially, three corn (*Zea mays* L., DKC 64-79, a VT3 hybrid) seedlings were planted in each column after treatment applications, and a single healthy seedling was maintained per column for 5 weeks. An additional two replicates of columns without plants were established in parallel for SEM-EDXA analysis.

Greenhouse temperature was maintained at an average of about 25°C with a 14-h photoperiod (6:00 am to 8:00 pm). The study was conducted during summer (June–July) for Site I and during winter (November–December) for Site II.

The columns were maintained at 80% of maximum water-holding capacity by adding deionized (DI) water based on weight losses. At 5 weeks, aboveground plant biomass was harvested, and the soil cores were removed from the Plexiglas columns. Soils and remaining granules in MAP granular-added were separated into 2.5-cm slices for wet chemical-based analysis, XANES analysis and SEM-EDXA analysis.

Wet Chemical Analysis of Soils

Wet chemical 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:water (NCRRP, 1998) was used for the determination of pH. Total P was determined with the modified salicylic sulfuric acid digestion method described by Bremner and Mulvaney (1982); the method uses inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 720-series ICP-OES, Walnut creek, CA). Resin-extractable P was determined 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 the resin P extraction procedure. The resin membrane comes in a pack of six 12.5- x 12.5-cm sheets. The resin membrane was cut to 5 cm x 2.5 cm and saturated with 0.5 M NaHCO₃. Two strips were used for 1.0g of soil, and P was extracted as described by Myers et al. (2005). Briefly, 1.0 g of soil was placed in polyethylene bottle containing 80 mL of water. Two resin strips were added to the polyethylene bottle and shaken in a reciprocal shaker for 24 h. After shaking, the resin strips were removed from the polyethylene bottle, washed with DI water to remove adhering soil particles, and

transferred to another polyethylene 250-mL bottle containing 50 mL of 0.5 M hydrochloric acid (HCl). The resin strips were further shaken with this solution for 1.5 h, filtered using Whatman No. 42 Filter Paper, and analyzed colorimetrically with a UV/VIS spectrophotometer (Beckman 800, Brea, CA) following the method described by Murphy and Riley (1962).

Plant Analysis

The aboveground plant parts harvested at 5 weeks were washed with DI water and blot-dried. Fresh weights were determined, and plants were dried in a forced-air oven at 60°C for a minimum of 4 days and weighed for biomass calculation. Dried plant material was ground with a Wiley grinder, 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. All data were analyzed with PROC MIXED in SAS (SAS 9.1, 2007). The pairwise Bonferroni method was used for pairwise comparisons between treatments at $\alpha = 0.05$ level of significance.

Speciation of Phosphorus

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

At five weeks, soil-applied MAP granules from columns 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 extracted granules were cross-sectioned with a stainless steel blade and mounted on an aluminum sample holder for SEM-EDXA analysis. The cross-sections were sputter-coated with a 40% palladium conductive coating of ~4 nm thickness and dried. Palladium coating helps minimize static

electric charge accumulation on the specimen during electron irradiation and increase the signal and surface resolution of images. This technique is an indirect, less sensitive method; therefore, only granules were used for the SEM-EDXA analysis, and soil samples were analyzed using X-ray absorption near-edge structure spectroscopy (XANES).

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

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 a maximum current of 100 mA. This beamline has an energy range of 2.1 to 23 keV and is equipped with an Si (III) monochromator with a focused beam size of 500 μ m x 500 μ m. The sample compartment was He-purged, and data were collected in fluorescence mode using a Ge solid-state detector. The phosphorus pentoxide (P₂O₅) standard was used for monochromator calibration. Correction in energy drifts caused by monochromator drifts were done by collecting spectra of P₂O₅ daily during run time. 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.

Samples were extracted from the field before application of the fertilizer treatments. The top 0 to 7 cm of soil for broadcast (Control broadcast) and the 12.5- to 15-cm depth for deep-placed (Control deep-placed) 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 depth for broadcast

treatments and 12.5- to 15-cm depth for deep-placed 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 further ground to very fine powder with an agate mortar and pestle. Soil pellets with a diameter of 4 mm were prepared using a KBr Quick Press Kit with a 7-mm die set (International Crystal Laboratories, Garfield, NJ) to get a better signal. The samples were then mounted on Teflon tape and fixed onto aluminum sample holders. 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 the pre-edge region (2110 to 2140 eV), 0.125 eV in the near-edge region (2140 to 2165 eV), and 0.5 in the post-edge region (2165 to 2400 eV), with a 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).

Standards for Phosphorus K-edge XANES

The phosphorus 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). Phosphorus pentoxide (P_2O_5) was purchased from Alfa Aesar (Ward Hill, MA). Two strengites ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) with different crystallinities were synthesized following the procedure of Dalas (1991) by mixing KH_2PO_4 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at ambient temperature and heating hydrothermally at 100°C for 24 h and 3 days, respectively. 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 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 sample holders for XANES data collection.

Principal Component Analysis

Principal component analysis (PCA) was done using the Labview software package available from Beamline 10.3.2 from Advanced Light Source (Marcus et al., 2004) to see how many spectra were linearly independent in samples and how many principal components were needed to reproduce the spectrum. The dataset was then redefined into a reduced number of independent sources of variability. A subsequent analysis, the target transformation, offered the possibility of testing which standard species were most likely to contribute to the principal components (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 criterion described by Beauchemin et al. (2002) was used to define the number of significant components. The standards for linear combination fitting 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 lies between 3 and 6, and unacceptable if the value is >6 (Malinowski, 1991). The SPOIL values for standards are listed in [Table 3](#).

Linear Combination Fitting

The reduced spectra were analyzed using linear combination fitting (LCF) in Athena. The linear combination XANES fitting procedure was used to reconstruct the soil spectra using all combinations of the standard spectra reduced as previously described. The fitting was done in the normalized space using quaternary combinations of standards in fitting range from 2144 to 2179 eV. The weighting factors were forced to sum to 1, 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.

Results

Soil Wet Chemical Analysis

Site I (North Farm, Manhattan)

Surface soil (0 to 7 cm) had an initial pH of 5.9, and pH was more or less constant throughout the soil depth of 30 cm. Soil texture changed depth-wise and clay content increased slightly (26.3 to 37%) with increasing depth ([Table 1](#)). Diethylenetriamine

pentaacetic acid (DTPA)–extractable iron (Fe) (~8 mg/kg) and manganese (Mn) (~58 mg/kg) concentrations were relatively similar through the 15-cm depth but were quite different from the rest of the samples at the 15- to 30-cm depth ([Table 1](#)). This soil had a 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- to 7-cm and 7- to 15-cm depths, respectively, and slightly higher (3174 mg/kg) after 15 cm. Cation exchange capacity was in the range of 16.1 to 20.3 meq/100g (cmol_c/kg) through the 30-cm depth.

[Table 3](#) shows a statistical comparison of various treatments and parameters at the point of fertilizer application; i.e., at 0- to 2.5-cm depth for the broadcast treatments and 12.5- to 15-cm depth for the deep-placed treatments. Total soil P concentration was found to differ for the surface soil (0 to 7 cm) and the deeper layer (7 to 15 cm). For broadcast treatments, granular MAP showed significantly higher resin-extractable P followed by the liquid MAP ([Table 2](#)); however, no clear differences were found between liquid and granular fertilizers for deep-placed treatments with respect to resin-extractable P, and both treatments had significantly lower resin-extractable P than the broadcast P treatments. In deep-placed treatments added fertilizer P distributed in both 12.5- to 15-cm and 15- to 17.5 cm soil depths ([Figure 1](#)), we believe as a consequence of this dilution, deep placed- treatments had lower resin-extractable P at 12.5- to 15-cm depth as compared to broadcast treatments (0-to 2.5-cm depth). When comparing resin-extractable P expressed as a percentage of total P values ([Figure 2](#)), 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 with the urea control treatment.

Plants were P-responsive, and all P treatments showed significantly higher P uptake than the control. No significant differences were found among P treatments for P uptake except between TGMAP broadcast and TGMAP deep-placed treatments. Broadcast TGMAP had significantly higher P uptake compared with TGMAP deep-placed treatments, but P uptake for broadcast TGMAP was not significantly higher than that of the MAP broadcast or the MAP deep-placed treatments (data not shown). Site II (Eastern Kansas Experiment Site, Ottawa)

This site had a soil texture of silt loam throughout the 30-cm profile. The soil had slightly higher pH (5.9 to 6.6) than that of Site I (5.7 to 6.1). In addition, the soil pH decreased with increasing depth ([Table 1](#)). Diethylenetriamine pentaacetic acid (DTPA)-extractable Mn concentration was higher in surface soil (55 mg/kg) and decreased with increasing depth (25 mg/kg at 30-cm depth), but the trend was opposite for the DTPA-extractable Fe. Surface soil had relatively lower extractable Fe concentration (84 mg/kg) that increased with depth (116 mg/kg at 30-cm depth). Ammonium acetate-extractable Ca concentration of this soil was slightly higher than that of Site I; furthermore, Ca was relatively higher for the surface soil (3732 mg/kg) and decreased with increasing depth. The cation exchange capacity of this soil was higher (53 to 65 meq/100g or cmol_c/kg) than that of Site I (16 to 20 meq/100g or cmol_c/kg). Total P (774 mg/kg for Site II compared with 423 mg/kg for Site I surface soil) and total N (2395 mg/kg for Site II compared with 1598 for Site I surface soil) concentrations of this soil were higher than that of Site I soil, but both P and N decreased with increasing depth ([Table 1](#)).

No significant pH differences were detected between the soils that received different P treatments at 5 weeks ([Table 2](#)). Total P concentrations of the P-added fertilizer treatments were not significantly different from each other ([Table 2](#)). Resin-extractable P for

both the broadcast granular and broadcast liquid MAP were significantly higher than for deep-placed P fertilizer treatment. The urea control had significantly lower resin-extractable P than all P applied treatments ([Table 2](#)); however, no significant difference was detected in percentage resin-extractable P between the broadcast or deep-placed treatments ([Figure 1](#)). Plant biomass and P uptake were significantly higher for the broadcast MAP treatment compared with the deep-placed MAP, but plant biomass did not differ significantly from the respective liquid P treatments (data not shown).

SEM-EDXA Results

We were able to extract the remaining MAP granules intact after 5 weeks of incubation from Site I and Site II soil columns. The original MAP granules and the incubated MAP granules extracted were analyzed using SEM-EDXA. Energy dispersive X-ray spectroscopy analysis showed that the original MAP granules did not contain significant amounts of Al, Ca, and Fe as expected ([Figure 3](#)), but the incubated granules in soils from both the broadcast and deep-placed treatments showed significant enrichment of Al, Ca, and Fe. Significant amounts of P remained in incubated granules.

XANES Results

The SPOIL values for all standards used for the study are shown in [Table 3](#). The whole-spectrum (2144 to 2179 eV) PCA component plot ([Figure 4](#)) showed significant differences between principal components of Site I and Site II samples. Site I samples were quite close to each other, suggesting that the treatment and placement effects were relatively smaller, but the Site II samples were

widely dispersed, suggesting differences in treatment and placement effects. The Site I samples were also closer to standards for apatite, vivianite, brushite, etc., and the Site II samples were closer to standards for aluminum phosphate, variscite, goethite-P, etc.

Spectra for Fe-phosphate standards showed a pre-edge feature between 2144 and 2147 eV that 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 bonded with calcium, aluminum, and iron have been well documented (Hesterberg et al. 1999; Peak et al. 2002; Beauchemin et al. 2003; Khare et al. 2005; Lombi et al. 2006) and help us determine the association of phosphate with different elements in soil samples. The LCF results and samples data for both Site I and Site II soils are shown in Figure 5.

Site I

The speciation results of soil samples from Site I and Site II are shown in [Table 4](#). Speciation of P in the original soil showed that adsorbed-P species were dominant in the 0- to 7-cm surface soils (Control broadcast), whereas Al and Fe P-like forms dominated the P speciation in the 7- to 15-cm layer (Control deep-placed). For P-treated soils, speciation results showed predominance of Fe-P in all treatments. Site I had relatively lower pH (5.7 to 5.9) than Site II (6.1 to 6.6). At the 5-week time period, the soil pH was in the range of 5.2 to 5.3. No significant differences were measured in pH between the broadcast treatments, but Site I deep-placed TGMAP had significantly lower pH compared with other deep-placed treatments ([Table 2](#)); however, when compared with the original soil pH addition of urea and phosphate, fertilizers reduced the pH of the soil up to 0.6 units. The adsorbed P species were one of the second dominating species found in this soil, and they were in aluminum oxide-adsorbed P-like forms. For liquid TGMAP treatments in

addition to adsorbed P species, a significant amount of Al-P like species were found. It appears that adsorbed P species were in relatively higher proportion in the broadcasted treatments (surface soils) than in the deep-placed treatments. In the MAP deep-placed treatment, the dominant P species in soil were Fe-P-like forms, and no Ca-P phosphate species were identified at this time period. For the liquid P treatment, the speciation results did not show distinct differences due to P placement.

Site II

The speciation results for Site II soil are shown in [Table 4](#). For P-treated soils, speciation results showed the combination of Fe, Ca, and adsorbed P species as reaction products formed in this soil at 5 weeks after P fertilizer application, but a significant number of P species were found in adsorbed forms as well. For broadcast and deep-placed MAP, a majority of the reaction products were found to be in Ca-P forms followed by adsorbed P forms, but no Ca-P forms were revealed for TGMAP treatments. Aluminum-P-like minerals were seen only in treatments that added no P. For TGMAP treatments, the adsorbed P species were the dominant forms. The XANES fitting results are shown in [Figure 4](#) for both soils.

Discussion

Wet Chemical Analysis

Fertilizers reduced the pH of the soil up to 0.6 units for Site I. Acidification effects of MAP on soil pH have been reported by many researchers (Hanson and Westfall 1985; Moody et al. 1995). The hydrolysis of urea consumes two moles of protons for each mole of urea hydrolyzed. A combination of neutralization of the initial acidification effect of MAP by hydrolysis of urea and extra proton consumption through urea hydrolysis resulted in an initial increase in pH, but in the long run, the conversion of ammonium to nitrate decreases the soil pH. The decrease in pH from P fertilizer applied to soil might be due to the combined effects of various reactions (nitrification of NH_4^+ , hydrolysis of urea, and other reactions such as formation of different reaction products).

Originally, the surface soils (0 to 7 cm) had relatively higher initial total P concentration (480 mg/kg and 774 mg/kg for Site I and II soils, respectively) than the deep layer (329 mg/kg and 559 mg/kg for Site I and II soils, respectively). This difference probably caused the total P concentration differences observed between broadcast and deep-placed P fertilizer treatments ([Table 2](#)). For both broadcast and deep-placed treatments, granular and liquid fertilizers were spread across the surface, which might have resulted in the differences between the treatments. Granular MAP could have released P slowly, and this might have helped P to remain in more extractable form longer; on the other hand, liquid P spread across (i.e., not banded) the soil surface or deep layer might have reacted with soil to transform P to an unavailable form within a short time after application. Site I soil had relatively lower organic matter content on top (0-7cm) and shallow (7-15) layers as compared to site II ([Table 2](#)). High organic matter content promotes microbial activity which would enhance the rate of P fertilizer solubilization and solubilization of newly precipitated inorganic P thereby increasing bioavailability (Kucey et al., 1989).

Resin-extractable P as a percentage of total P allows evaluation of resin-extractable P independent of the total P concentration in each soil section. Lack of P placement effect was observed by other researchers when soil test P levels were high (for example, greater than 13 mg/kg Bray- I P in the 0- to 7.5-cm layer, Bordoli and Mallarino, 2000). Previous research also suggested that the subsurface application of P fertilizers should only be considered if soil test P is highly stratified within the surface 0- to 15-cm layer, and soil test P values are medium or below (Schwab et al., 2006). So, lack of P source or placement effect could partly be due to soils ability to provide solubilized P under studied conditions. On the other hand, when P fertilizer is applied, root growth is stimulated, and plants begin building well-developed healthy root systems, thereby, enhancing plants ability to extract P from deeper layers (McBeath et al., 2011). Importance of an expanded root system for the acquisition of nutrients, especially immobile nutrients such as P, and the role of root exudate on P availability are well known (Mollier and Pellerin 1988; Lynch, 2007).

SEM-EDXA

For granular fertilizer treatments, the granules were found intact in the soil even after 5 weeks of the experiment. The SEM-EDXA of granules showed enrichment with cations, most likely the result of 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 granules incubated for 5 weeks in soil also indicates 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 into the granules, cations enter the granules and precipitate P inside the granules (Lombi et al. 2004; Hettiarachchi et al. 2006), thereby making applied P potentially less available for plants. This could also partly reflect a selective loss of some elements (N and P) and an increase in less soluble components (i.e.,

non-congruent dissolution of P granules). It should be noted here that Al and Fe enrichment in granules upon granule dissolution could also be due to enrichment of “immobile” Fe and Al originally present in these granules as impurities. Energy dispersive X-ray of soil adjacent to the granule and soil itself did not show enrichment with P ([Figure 3](#)), which may be due to the technique’s lack of sensitivity. Detection limits of EDXA can vary depending on the instrument, but EDXA generally can measure elements at concentrations of 0.1 weight percentage (1000 mg/kg) or more. This might have been why we did not detect P in the soil adjacent to the granule or in the bulk soil.

XANES

Non-P treated control soils at site I had more adsorbed-P, whereas site II had more precipitated-like P forms. This can be explained by soil pH (site I soils was more acidic compared to site II soils) as well as soil total P concentrations (site I had lower total P concentrations compared to site II soils). There is more evidence of Fe and Al hydroxide-adsorbed P or mixed precipitates of P than a discrete precipitation of Fe- and Al-P in acid soils (Lindsay et al., 1962). Some attributed this to low Fe and Al concentrations in soil solution as compared to Ca in solution (McLaughlin et al., 2011; Degryse et al., 2014). The phosphate solids formed in the soils upon P addition was found to be related to the pH of the soil. The predominance of Fe-P-like forms may be attributed to the slightly greater acidic pH condition of the Site I soil at 5 weeks, which favored the formation of Fe-P-like forms (Lindsay, 1979). Resin-extractable P

at this site was lower for both broadcast and deep-placed treatments compared with Site II ([Table 2](#)), and this may be due to low total P concentrations in site I soils ([Figure 1](#)). For the site I soil, resin-extractable P was higher for the broadcast granular P treatment, followed by the broadcast liquid P and the deep-placed granular and liquid treatments; although resin-extractable P calculated as a percentage of total P (percentage resin-extractable P) was not different for fertilizer source or placement methods ([Figure 2](#)). It appears that the formation of Al-P was promoted by addition of liquid MAP treatments as compared to their granular counterpart. This may be due high initial acidification that can be expected for liquid P added soils compared to granular P added soils. Both speciation ([Table 4](#)) and percentage resin-extractable P results ([Figures 2](#)) indicated no significant or contrasting differences between the broadcast and deep-placed fertilizer treatments for this soil. This lack of effect of P placement could mainly due the effect of geochemical and biological processes induced by plant root.

Originally, Site II soil had higher pH (6.1 to 6.6) than Site I. Similarly, at the 5-week time period, the pH of the soil was significantly higher (6.6 to 6.7) than that of Site I (5.2 to 5.3). Concentration of ammonium oxalate-extractable Ca concentration was also higher (3136 to 3732 mg/kg) for this soil compared with the Site I soil (2426 to 2550 mg/kg). The dominance of Ca-P minerals found in this soil for MAP treatments may be attributed to the higher soil pH, which favored formation of Ca-P-like forms (Lindsay 1979), and to the high levels of extractable Ca in soil. 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), when inorganic P was added to slightly alkaline soils, Ca-P was the dominant P species; however, in acidic soil, a lower percentage of Ca-P species was in evidence. Resin-extractable P for Site II soil in the current study was relatively higher than that of Site I; Site II soil ranged from 40 to

45 mg/kg for the broadcast P treatments and 28 to 35 mg/kg for the deep-placed P treatments. High resin-extractable P levels can be explained by relatively high total P and 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 is reduced. A majority of adsorbed P species was found to be associated with alumina and ferrihydrite for this site. Beauchemin et al. (2003) also found a higher proportion of P adsorbed on Fe or Al-oxide minerals for most acidic soils. A relatively lower percentage of P reaction products was found to be associated with Fe and Al for the granular broadcast and the granular and liquid deep-placed treatments compared with the liquid-broadcast P treatment. The observed higher amounts of resin-extractable P in site II soils may also be contributed to inherent high organic matter content of the soil that favored microbial activity for solubilization of the applied P fertilizers and release of the soluble forms in the soil. In general, weakly adsorbed P species (via outer-sphere and diffuse-swarm adsorption) could be considered relatively more labile or resin-extractable than most P minerals in soils, especially sometime after P application. For site II soils, XANES data showed high adsorbed P species for broadcast P treatments as compared to deep-banded P treatments. Comparison of resin-extractable P data with speciation results for this soil showed a positive correlation of adsorbed P species with resin-extractable P, suggesting that adsorbed P species might be more available. This was not observed for the acidic site I soils, where adsorbed P was dominated originally but Fe-P precipitate-like P dominated the P speciation in treated soils.

Conclusions

Reaction products that formed 5 weeks after application of P in two different soils were highly correlated with soil pH. Speciation results for the soils from Site I with relatively lower pH at 5 weeks showed that the reaction products of P fertilizers were dominated by Fe-P- and Al-P-like forms, but speciation results of soil from Site II with neutral to slightly acid pH (6.6-6.7) showed that the reaction products of P fertilizers were dominated by Fe and Ca-phosphate adsorbed P-like forms. We found no clear trends in reaction products with respect to P source or P placement. Resin-extractable P concentrations as a percentage of total P, showed no placement or source effect, indicating that observed differences in resin-extractable P for broadcast granular MAP treatments could be due to differences in total P concentration in soils. Effect of plant growth (extended root system exploring deeper layers, root exudates and enhanced P solubility due to microbial activities) might have been partly responsible for the lack of differences observed in the percentage of resin-extractable P and P reaction products. Results from SEM combined with energy dispersive X-ray analysis of incubated fertilizer granules extracted from soils at 5 weeks showed enrichment of Al, Fe, and Ca in granules, indirectly indicating that these cations either remained in granules or enter the granules and begin to react with P hindering complete dissolution of granules

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TABLE 1. Basic properties of soil used for the study, (A) Site I and (B) Site II.

(A)

Sample depth	pH	CEC [†]	M3 P	Extractable				Total N	Total P	OM	Texture			Textural class
				Ca _{ac}	Fe _{dtpa}	Mn _{dtpa}	Al ³⁺ _{KCl}				Sand	Silt	Clay	
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	9.3	64.4	26.3	SiL
7-15	5.7	20.3	19.6	2540.0	8.2	57.8	0.4	1114.0	329.0	2.3	7.2	63.0	29.8	SiCL
15-30	6.1	18.8	5.9	3174.0	27.8	25.0	0.1	1119.0	278.0	2.2	5.0	58.0	37.0	SiCL

(B)

Sample depth	pH	CEC [†]	M3 P	Extractable				Total N	Total P	OM	Texture			Textural class
				Ca _{ac}	Fe _{dtpa}	Mn _{dtpa}	Al ³⁺ _{KCl}				Sand	Silt	Clay	
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	7.8	74.3	18.8	SiL
7-15	6.1	63.0	49.8	3136.0	112.0	50.0	0.1	1588.0	559.0	3.7	4.5	73.6	21.9	SiL
15-30	5.9	53.7	38.6	3202.0	116.0	25.0	0.2	1194.0	396.0	3.0	3.6	69.7	26.7	SiL

[†] 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; Al³⁺_{KCl}, potassium chloride-extractable aluminum; OM, organic matter content; SiL, silty loam; SiCL, silty clay loam.

TABLE 2. Soil pH, total P and resin extractable P at the point of fertilizer application after 5 weeks of treatment application at Site I and II. Granular MAP = MAP; liquid MAP = TGMAP. Broadcast = 0- to 2.5-cm; Deep-placed = 10- to 12.5-cm. Letters on the table indicate significance at the 0.05 probability level.

Treatments	pH	Total P (mg/kg)	Resin Extractable P (mg/kg)
Site I			
Urea broadcast	5.21 ± 0.02 ^{ab}	477.45 ± 18.51 ^c	12.34 ± 0.86 ^d
MAP broadcast	5.12 ± 0.02 ^{bc}	744.08 ± 50.14 ^a	36.52 ± 1.74 ^a
TGMAP broadcast	5.15 ± 0.04 ^{ab}	691.46 ± 42.38 ^a	29.53 ± 0.81 ^b
Urea deep-placed	6.59 ± 0.04 ^{bc}	343.67 ± 5.40 ^d	13.88 ± 1.17 ^d
MAP deep-placed	6.67 ± 0.15 ^c	571.26 ± 60.69 ^{bc}	23.68 ± 1.01 ^c
TGMAP deep-placed	6.68 ± 0.09 ^a	536.68 ± 34.61 ^b	24.36 ± 0.74 ^c
Site II			
Urea broadcast	6.65 ± 0.05 ^a	641.87 ± 20.30 ^b	15.84 ± 0.7 ^c
MAP broadcast	6.57 ± 0.07 ^a	939.41 ± 21.88 ^{ab}	45.31 ± 5.66 ^a
TGMAP broadcast	6.70 ± 0.04 ^a	953.51 ± 43.73 ^{ab}	38.67 ± 2.46 ^a
Urea deep-placed	6.65 ± 0.05 ^a	587.10 ± 28.45 ^b	16.92 ± 0.54 ^c
MAP deep-placed	6.57 ± 0.07 ^a	977.14 ± 189.83 ^{ab}	33.08 ± 1.11 ^b
TGMAP deep-placed	6.70 ± 0.04 ^a	730.59 ± 65.64 ^b	27.11 ± 2.30 ^b

TABLE 3. SPOIL[†] factors for the reference spectra constructed from principal components.

Reference	Manhattan	Ottawa
Al. Phosphate	3.23	0.76
Apatite	1.98	1.41
Brushite	2.72	1.03
Hydroxyapatite	2.93	1.13
Pot. Dihydrogen Phosphate	2.38	0.87
Monetite	2.99	0.94
Mono ammonium Phosphate	3.28	0.94
Alumina adsorbed P	4.23	3.62
Ferrihydrite adsorbed P	3.83	2.14
Gibbsite adsorbed P	3.39	3.08
Goethite adsorbed P	3.81	2.51
Rock Phosphate	2.23	1.12
Strengite 1d	1.82	0.84
Strengite 3d	1.74	0.54
Variscite	2.55	1.41
Vivianite	1.68	0.93

†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. As rule of thumb, standards with SPOIL factors greater than 3 are not suitable for linear fitting.

TABLE 4. Fitting results for the final fit performed in normalized space in fitting range of 2144 to 2179 eV: 5-week samples at (A) Site I and (B) Site II.

(A)

Treatment	Ca-P minerals	Al-P minerals	Fe-P minerals	Adsorbed P	Red. χ^2_{\ddagger}
Control broadcast	-	-	32.0	68.0	0.010
Urea broadcast	-	-	69.8	30.2	0.090
MAP broadcast \ddagger	-	-	75.9	24.1	0.007
TGMAP broadcast \ddagger	-	25.2	64.8	10.0	0.007
Control deep-placed	6.4	39.7	53.9	-	0.098
MAP deep-placed	-	-	77.1	22.9	0.003
TGMAP deep-placed	7.8	13.4	67.2	11.6	0.017

(B)

Treatment	Ca-P minerals	Al-P minerals	Fe-P minerals	Adsorbed P	Red. χ^2_{\ddagger}
Control broadcast	9.0	21.6	43.1	26.3	0.026
Urea broadcast	-	-	-	100.0	0.166
MAP broadcast \ddagger	35.5	-	-	64.5	0.005
TGMAP broadcast \ddagger	-	-	-	100.0	0.020
Control deep-placed	32.9	-	53.3	13.8	0.092
Urea deep-placed	-	13.2	52.0	34.8	0.006
MAP deep-placed	36.0	-	19.6	44.4	0.002
TGMAP deep-placed	-	-	-	100.0	0.027

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

\ddagger MAP, monoammonium phosphate; TGMAP, technical grade monoammonium phosphate.

FIG 1. Total P at different distances from the point of fertilizer application: (A) 5 weeks after broadcast Site I, (B) 5 weeks after deep-placed Site I, (C) 5 weeks after broadcast Site II, and (D) 5 weeks after deep-placed Site II. Granular MAP = MAP; liquid MAP = TGMAP.

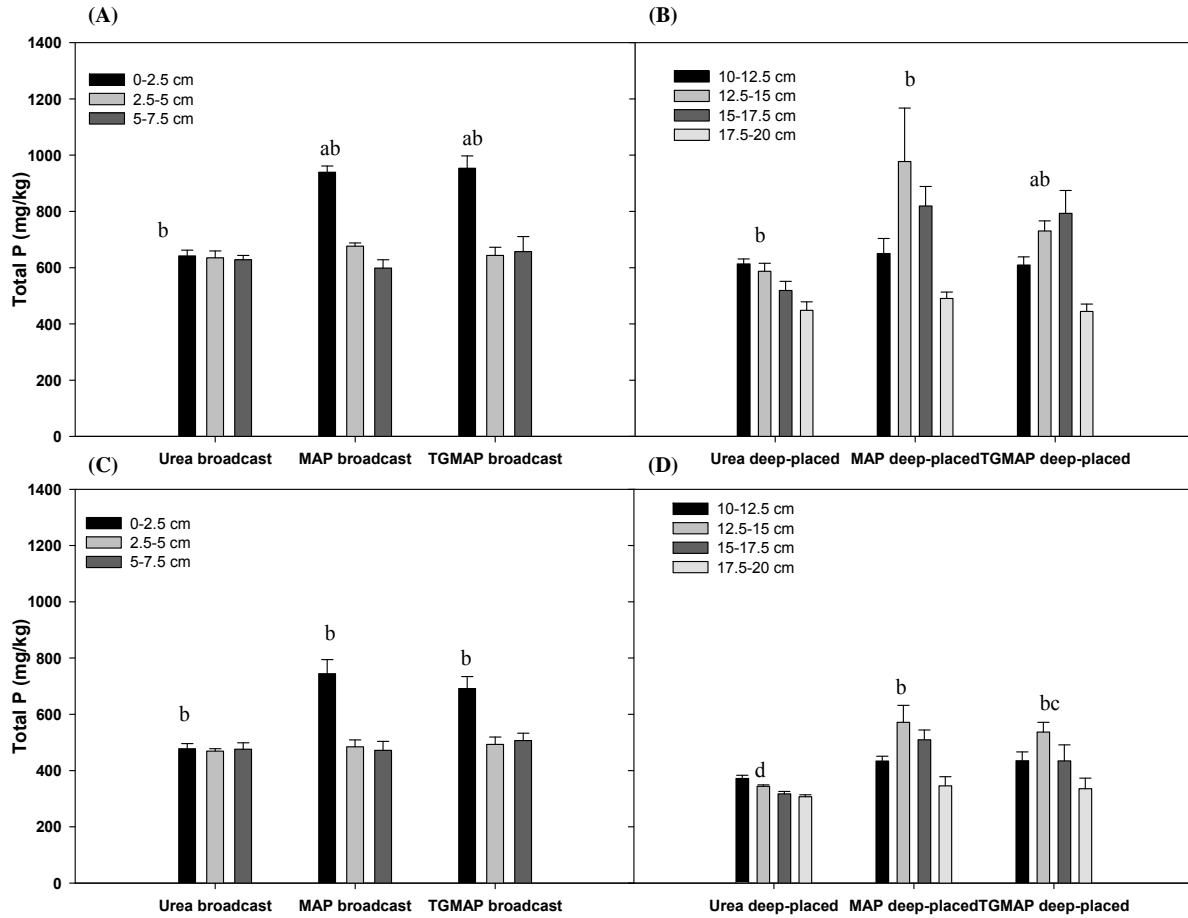


FIG 2. Resin-extractable P (as percentage of total P) at different distances from the point of fertilizer application: (A) 5 weeks after broadcast Site I, (B) 5 weeks after deep-placed Site I, (C) 5 weeks after broadcast Site II, and (D) 5 weeks after deep-placed Site II. Granular MAP = MAP; liquid MAP = TGMAP.

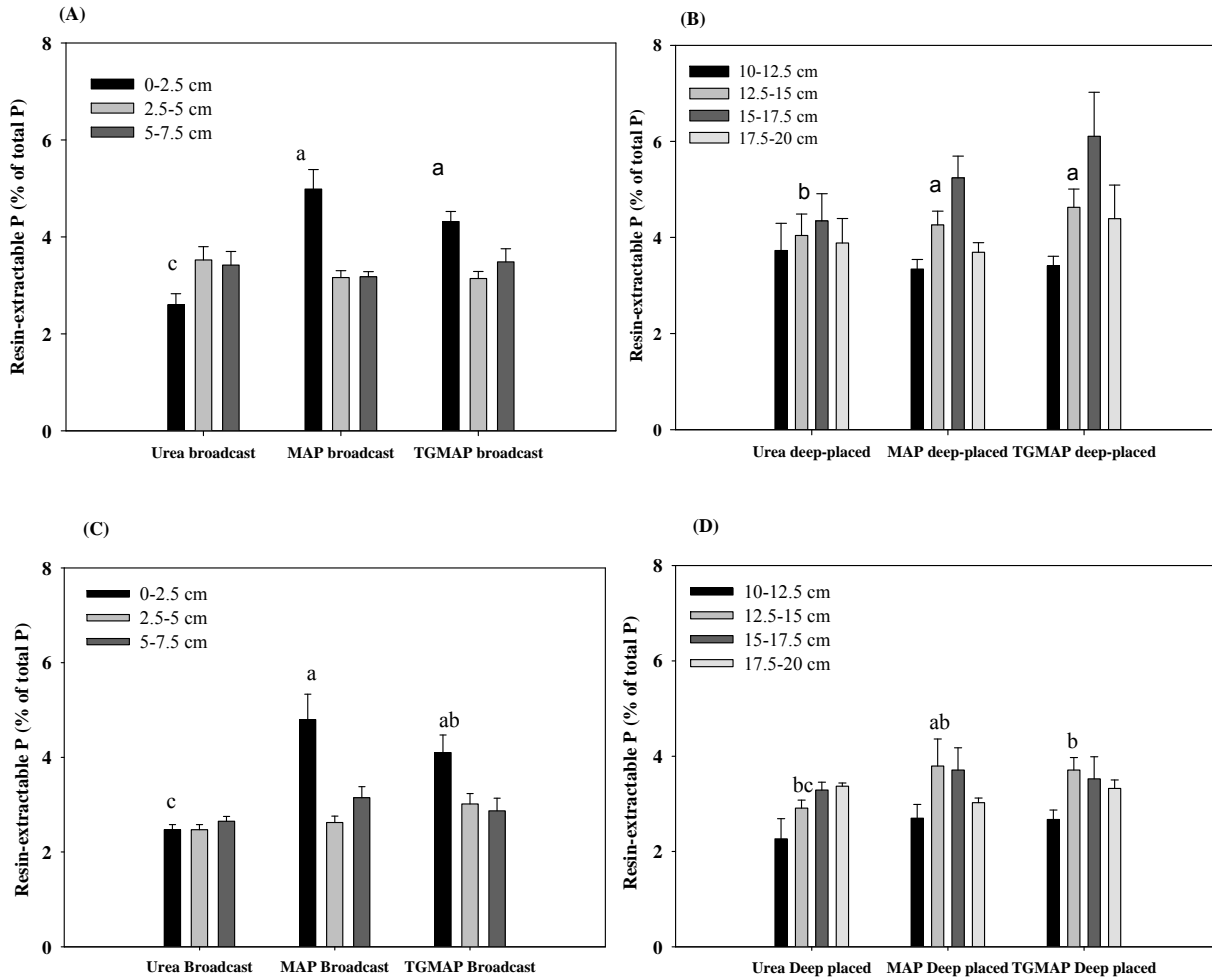
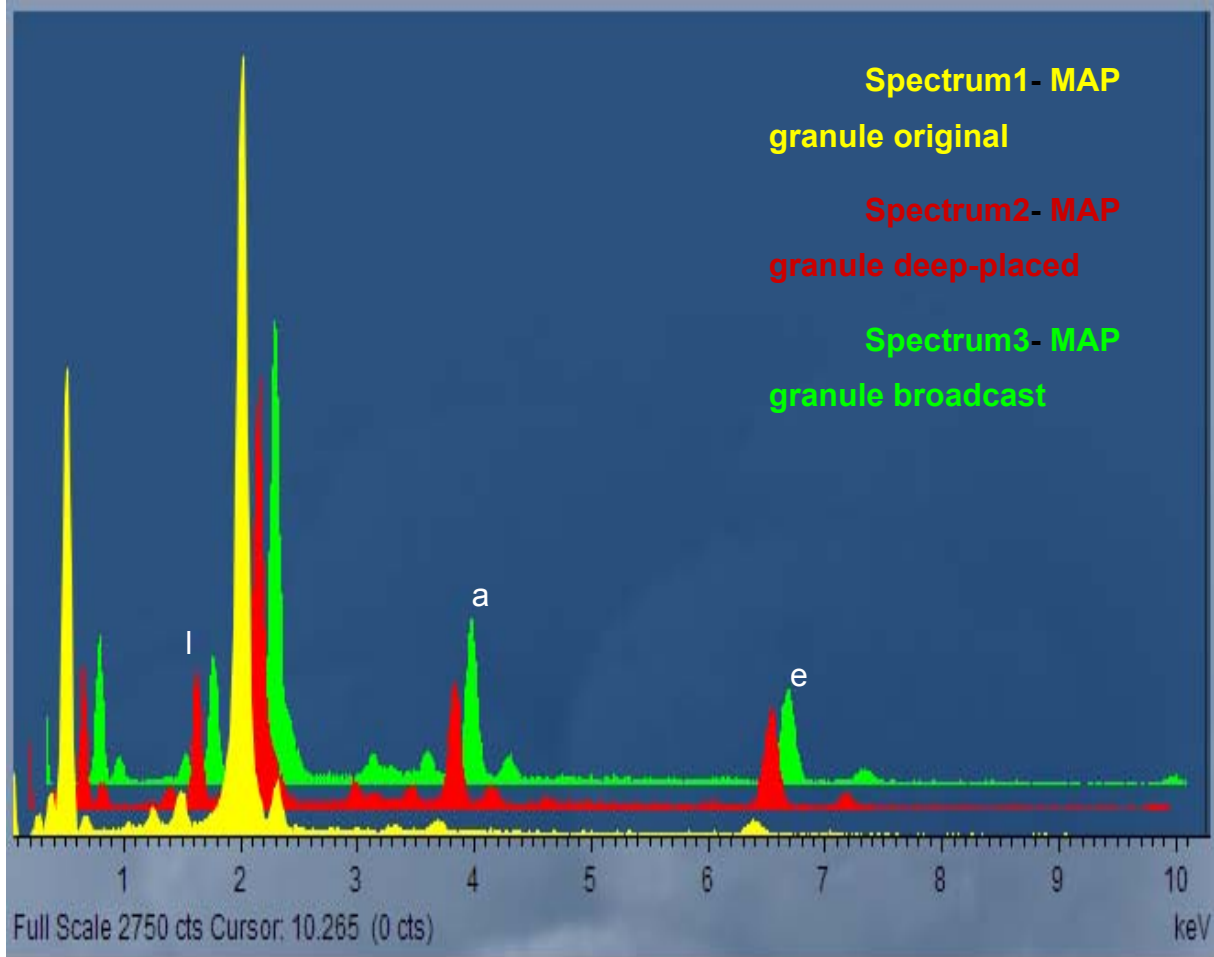


FIG 3. Scanning electron microscope with energy dispersive X-ray analysis (SEM-EDXA) comparison of original and soil-applied MAP granules: (A) Site I and (B) Site II.

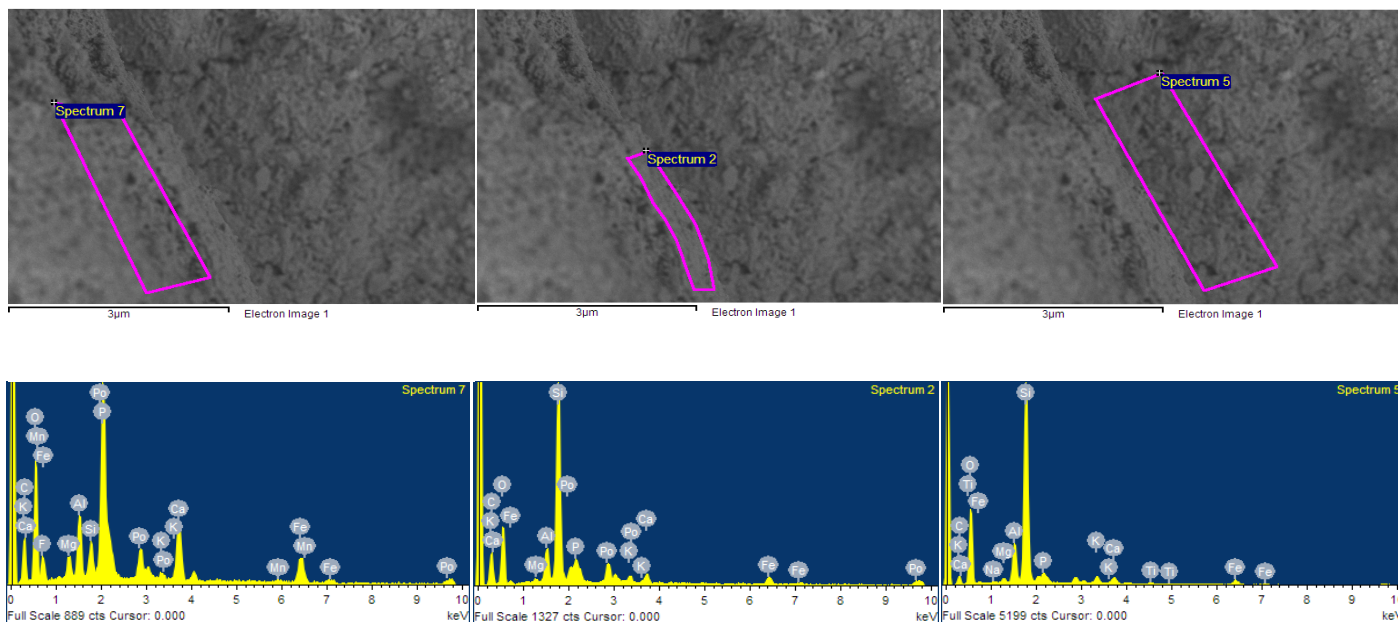
(A)



Elemental composition

Treatments	Weight %			
	Al	P	Fe	Ca
MAP granule original	0.87	19.92	1.47	0.45
MAP granule broadcast	3.93	15.30	12.95	8.05
MAP granule deep-placed	5.50	17.67	16.75	7.93

(B)



Spectrum 7 = Granule, Spectrum 2 = Soil-granule interface, and Spectrum 5 = Soil

Elemental composition

Treatments	Weight %			
	Al	P	Fe	Ca
Granule	2.36	7.07	3.89	3.27
Soil-granule interface	1.88	0.29	1.97	0.79
Soil	3.98	0.28	2.07	1.12

FIG 4. Principal component loading plot of standards for Site I and Site II soil samples and PCA of all standards and samples across the full spectral range.

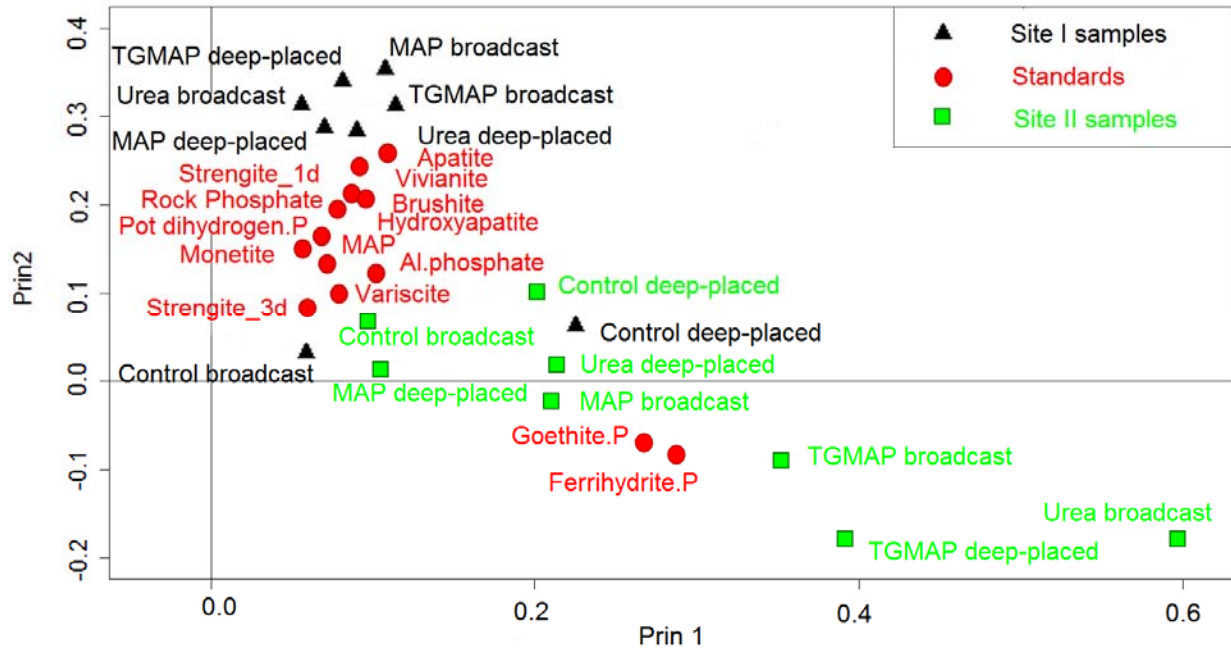


FIG 5. Normalized P K-XANES spectra (solid lines) of soil samples: (A) Site I and (B) Site II. Dotted lines indicate the linear combination fits using all standard compounds.

