

Speciation and Potential Availability of Phosphorus in Reduced Tillage System: Placement and Source Effect

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Abstract

Despite various advantages of reduced-till systems, it has been found that surface application of phosphorus (P), leads to an accumulation of P in the surface 0 to 5 cm soil layer and a depletion of available P deeper in the profile. We measured changes in soil pH, resin extractable P and speciation of P at 5 week and 6 month after P application to a soil system that was under long-term reduced tillage. Resin extractable P was lower for broadcast treatments as compared to deep band treatments for both the time periods. Resin extractable P was greater for the liquid P treated soils when compared to the granular P treated soils. Speciation results showed that granular-P fertilizers tended to form Fe-phosphate like products whereas liquid forms found to remain in adsorbed-P like forms in soil after 5-wk of application. Over 6 month time period, reaction products of broadcast-granular and broadcast-liquid and deep band-granular fertilizers transformed to Ca-phosphate- or mixtures of Ca-, Fe-, Al- and adsorbed-phosphate-like forms while deep band-liquid P continued to remain mainly as adsorbed-P like forms.

Introduction

Phosphorus management in reduced tillage systems has been a great concern for farmers. It has been found that P applications, mostly in granular forms, leads to an accumulation of available P on the surface 0 to 5 cm soil layer and a depletion of available P deeper in the profile (Schwab et al., 2006). Deep placement of nutrients below the first 5 to 10 cm of the soils should be superior to other placements when nutrient stratification, coupled with topsoil moisture deficit, reduces nutrient uptake from shallow soil layers (Bordoli and Mallarino, 1998). Inconsistent results have been obtained from the research conducted to study the effects of tillage and deep placement of P fertilizers on grain yields of crops grown in Kansas (Schwab et al., 2006). Knowledge of the dominant solid P species present in soil following application of P fertilizers and linking that to potential P availability would help understand how to manage P in efficiently reduced tillage systems. The objective of this research was to understand the influence of placement (broadcast- vs. deep band-P), fertilizer source (granular- versus liquid-P) and time on reaction products of P under field conditions.

Materials and Methods

A field based study was done at Agronomy North Farm site located in Manhattan, KS. This site has a history of more than five years of reduced tillage. Two P fertilizer sources were granular monoammonium phosphate (granular MAP) and technical grade MAP (liquid MAP). Phosphorus was applied at 75 kg/ha and N as urea was applied at 200 kg N/ha. The treatments were: Urea Broadcast (control), Urea Deep band (control), granular MAP (MAP) Broadcast; granular MAP Deep band; liquid MAP (TGMAP) Broadcast; and liquid MAP Deep band. Experimental design was a randomized complete block design with five replications and the plot size was 5' x 8' with 3' alley between the plots. Broadcast treatments were applied on the surface and gently mixed, whereas deep band treatments were applied approximately at 10 cm depth in two rows per plot. Soil sampling was done at 5 week and 6 months time after treatment application. Each time 30cm long soil cores were extracted using auger and divided into 2.5 cm slices, air dried and sieved <2mm. The wet chemical based analysis included pH (1:5 soil:water), total P (Bremner and Mulvaney, 1982) and resin extractable P (Myers et al., 2005). Resin extractable P was used to estimate plant available P. All data were analyzed using proc mixed procedure using SAS software (SAS 9.1, 2007). Pairwise Bonferroni method was used for pairwise comparisons of all the treatments at $\alpha=0.05$ level of significance.

Synchrotron-based bulk x-ray absorption near-edge structure (XANES) spectroscopy analysis (to determine chemical form of reaction products, was performed at sector 9 BM-B, Advanced Photon Source, Argonne, IL, U.S.A. The first derivatives of reduced spectra for the samples were analyzed by linear combination fitting (LCF) using IFEFFIT software (Newville, 2001). Spectra for the various standard compounds were reduced and normalized as for the spectra of the soil samples.

Results and Discussion

Mixed results (lower, higher or no significant difference) were observed for soil pH when comparing differences in soil pH among the urea added control plots and the both urea+ MAP (as granular or liquid MAP) added plots (data not shown). Acidification effects of MAP on soil pH have been reported by many researchers (Moody et al., 1995). However, hydrolysis of urea consumes two moles of protons for each mole of urea hydrolyzed, thereby resulting an increase in pH. So combination of these reactions (nitrification of NH_4^+ and hydrolysis of urea) in turn could result mixed effects on overall soil pH. At five weeks, soil pH in both urea and MAP (as granular or liquid) added zones were significantly lower (by about 0.2 to 0.5 units) than the original soil pH (5.3). However, soil pH of six month samples was higher (by about 0.2 to 0.6 units) when compared to the soils sampled from the same plots (i.e., that received same soil treatment) at 5 weeks. This could most likely be due to neutralization of initial treatment effects on soil pH with time and in-field seasonal variation of soil pH.

Broadcast urea control (0 to 2.5 cm) had slightly higher total P concentration (~500 to 620 mg P/kg) when compared to that of deep band control (7.5 to 10 cm) (~400 to 450 mg P/kg), which can be attributed to P stratification due to reduced tillage practice. We used resin extractable P to estimate potential available P in soils. The P supplying power of soils assessed by anionic exchange resins have been shown to correlate satisfactorily with P uptake and P concentration in the biomass. Therefore, resin extractable P can be considered as a reliable index of available P in soils (Myers et al., 1995). At five weeks, in the urea broadcast (control) and urea deep band (control) plots, % resin extractable P concentrations were 3.4 and 9.2, respectively (Figure 1). In the deep band P plots both the granular and liquid treatments, had a significantly higher % resin extractable P in comparison to the No P urea broadcast or urea deep band treatments. At 6 months, only the deep band liquid treatment, had a significantly higher % resin extractable P in comparison to the both no P urea broadcast or no P urea deep band treatments.

Bulk XANES spectra suggested that the majority of P (69.2%) in the broadcast granular MAP treatment at 5 wk was vivianite ($\text{Fe(II)}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$)-like P form (Table 1). The spectra for broadcast liquid MAP- treated soil suggested two major form of P in this soil, strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$)- like (38.9%) and adsorbed P (43.4%). Similarly, for the deep banded granular-MAP-treated soils at 5 wk, the majority of P (64.5%) existed as vivianite-like form while adsorbed P accounted for the rest. The spectra of the deep band liquid MAP-treated soils suggested 46.7% of vivianite-like P and 53.4% as adsorbed-P (Table 1). Over 6 month time period, reaction products of broadcast-granular MAP and liquid-MAP treated soils were transformed to Ca phosphate-like, Al phosphate-like and Fe phosphate- like forms while the majority of P in deep banded liquid MAP treated soils continued to remain in adsorbed-P like forms. Lindsay (1979) suggested that the formation of sparingly soluble mixed Al- phosphates and/or Fe-phosphates as a possible mechanism restricting P solubility in acid soils. Similarly depending on activity of Ca^{2+} in soil solutions, precipitation of P as Ca-phosphates can also responsible for restricting P solubility in slightly acid, neutral and alkaline soils.

Conclusions

It appears that when liquid MAP is deep placed in no-till soil systems, more P remains in resin extractable P forms for six months after fertilizer application. In contrast, broadcasted P, either in granular or in liquid form, tended to transform into less extractable P forms after five weeks or six months time period. Formation of Fe-, Al-, and/or Ca- P solid species, with different solubilities, may have been the reason for the observed differences in extractability or potential availability of P between broadcasted and deep placed granular and liquid MAP evaluated in this study.

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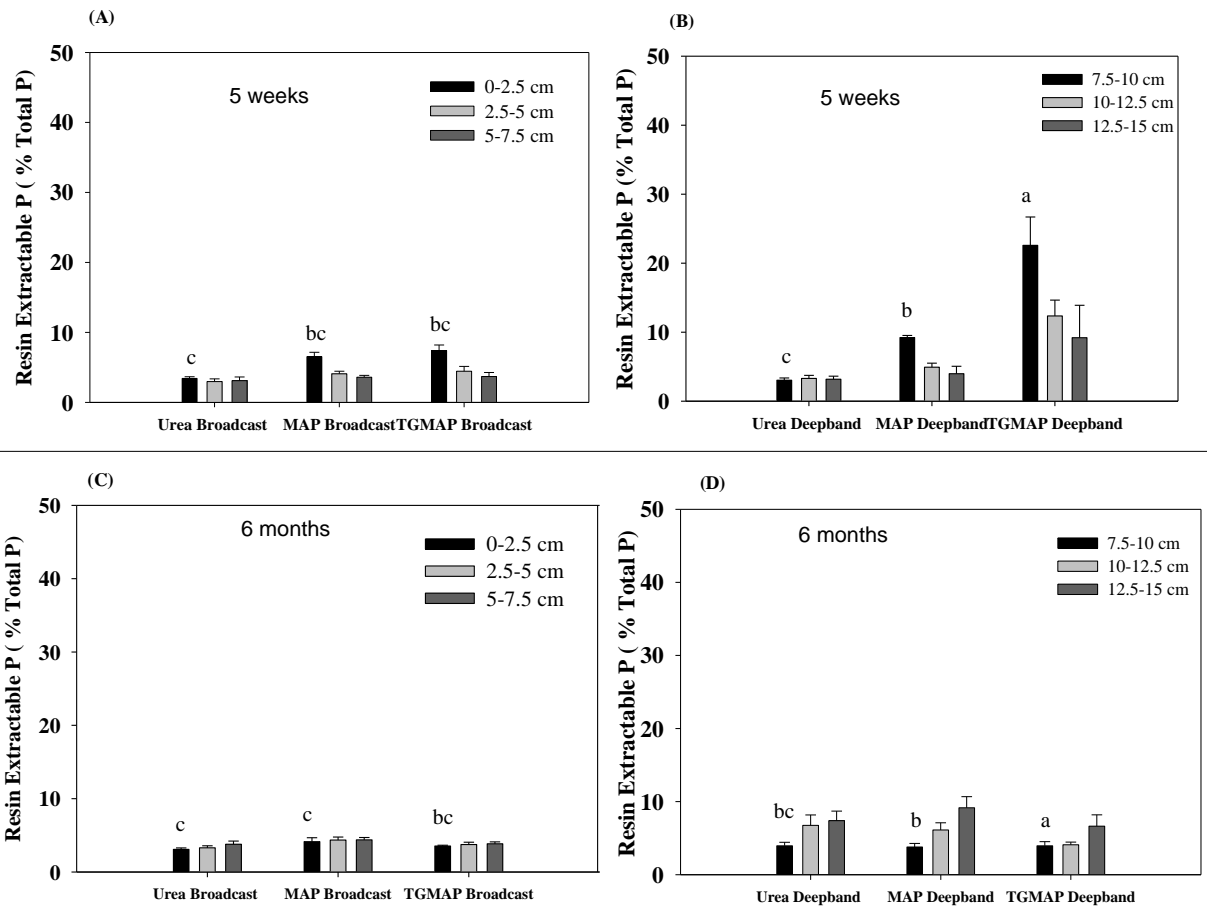


Figure 1. Resin extractable P (as % of total P) in soil sections collected at different distances from the point of fertilizer application. The resin extractable P (as a percent of total P) was calculated dividing resin extractable-P values for each section by the corresponding total P concentration. Error bars represent standard errors of five field replicates. (A) Five weeks broadcast, (B) Five weeks deep band, (C) Six months broadcast, and (D) Six months deep band treatments. Granular MAP= MAP; liquid MAP = TGMAP. Means with the same letter within a time period are not significantly different at $P < 0.05$.

Table 1. Percentages of P species in soils in the fertilized soil sections (0 to 2.5 cm for the broadcast and 7.5 to 10 cm for the deep band treatments) determined by linear combination fitting of the first derivative of XANES spectra

| Treatment | Al- Phosphates | Ca- Phosphates | Fe(III) Phosphate | Fe(II) Phosphate | Adsorbed P | Red. χ^2_* |
|-----------------------------|-------------------|-------------------|----------------------|---------------------|---------------|--------------------|
| <u>5 weeks</u> | | | | | | |
| Urea Broadcast (Control) | - | - | - | 57.9 | 42.1 | 0.06 |
| Gr. MAP Broadcast | 11.3 | - | - | 69.2 | 19.5 | 0.01 |
| Liquid MAP Broadcast | - | 17.7 | 38.9 | - | 43.4 | 0.06 |
| Urea Deep band (Control) | 40.5 | 47 | - | - | 12.5 | 0.01 |
| Gr. MAP Deep band | - | - | - | 64.5 | 33.5 | 0.12 |
| Liquid MAP Deep band | - | - | - | 46.7 | 53.4 | 0.01 |
| <u>6 months</u> | | | | | | |
| Urea Broadcast (Control) | 60.4 | - | - | 39.6 | - | 0.41 |
| Gr. MAP Broadcast | 46.3 | - | - | - | 53.6 | 0.01 |
| Liquid MAP Broadcast | - | 100 | - | - | - | 1.13 |
| Urea Deep band (Control) | - | 53 | - | 47 | - | 6.60 |
| Gr. MAP Deep band | - | 51.6 | - | - | 48.4 | 1.47 |
| Liquid MAP Deep band | - | 19.8 | - | - | 80.3 | 0.01 |

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