

DIVISION S-2—SOIL CHEMISTRY

Aluminum Transformations and Solution Equilibria Induced by Banded Phosphorus Fertilizer in Acid Soil

J. J. Sloan, N. T. Basta,* and R. L. Westerman

ABSTRACT

Banded P fertilizer may alleviate Al toxicity in strongly acid surface soils (pH < 5) and is a useful remediation management practice when liming is not possible. The objective of this study was to determine the effect of banded P fertilizer on Al transformations and soil solution composition in acid soils. Pond Creek silt loam (fine-silty, mixed, thermic Pachic Argiustoll; pH = 4.0) was amended with five P fertilizer rates and incubated at 24°C for 70 d. Dissolved Al, Mn, Ca, Mg, K, PO₄, SO₄, Cl, and NO₃, pH, electrical conductivity, and exchangeable cations were measured after 1, 5, 10, 15, 30, and 70 d of incubation. Soil solution Al, Ca, Mg, and Mn decreased but SO₄ increased with P fertilizer rate. The concentration of dissolved metals increased and soil solution pH decreased with time. Soil solution Al³⁺ decreased and Al-orthophosphate complexes increased with P fertilizer rate. Saturation indices derived using MINTQA2 suggest possible precipitation of Al as gibbsite at low P rates (<175 mg P kg⁻¹) and incubation times ≤ 15 d, K-taranakite at high P rates (>262 mg P kg⁻¹) and incubation times ≤ 30 d, and amorphous variscite analogs at all P rates. Soil solution was undersaturated with respect to Ca and Mg phosphates. Formation of MnPO₄·1.5H₂O was consistent with the well-aerated conditions of this study. Significant (*P* < 0.05) reductions in exchangeable Al, Ca, and Mg were correlated with P fertilizer rate. Phosphorus additions did not affect exchangeable Fe or Mn. Banded P fertilizer is a viable alternative method to reduce toxic forms of Al in strongly acidic soils.

CULTIVATED SOILS tend to become acidic in the surface horizon with time due to a combination of factors, such as loss of basic cations and the addition of acid-forming N fertilizers (Foy, 1987). Statewide testing of Oklahoma soils under continuous wheat (*Triticum aestivum* L.) production showed that 30% of the 17 560 samples tested were acid, with pH values < 5.5 (Johnson et al., 1991). The majority of these samples came from the central region of Oklahoma where extensive wheat production is managed for cattle grazing followed by grain harvest. Because lime sources are 80 to 160 km (50–100 miles) from this area, many producers have been unable to amend the soil with lime due to the high transportation cost. Consequently, pH values have decreased to levels as low as 4.0 in the surface layer of some soils and crop failure has become more prevalent (Boman et al., 1992b; Johnson et al., 1991). Under acid conditions, increased amounts of exchangeable Al can cause shallow rooting, poor use of soil nutrients, and Al toxicity (Ritchey et al., 1988; Sheppard and Floate,

1984; Wright et al., 1989). Aluminum toxicity to seedling wheat has been a major source of crop failure at extremely low pH in Oklahoma soils (Newton et al., 1979).

Greater increases in wheat yields when P fertilizer was band applied rather than broadcast to acid soils have been reported (Boman et al., 1992a,b; Havlin et al., 1987). In some cases, response of wheat to P fertilization was observed even when soil test values indicated no additional P requirement (Boman et al., 1992b). The fertilizer P apparently had an effect that was not directly related to P nutrition. Phosphorus fertilization may temporarily reduce the concentration of toxic forms of Al in the soil solution to a level where plant growth and development is not adversely affected. The banding of P fertilizer with or below the wheat seed concentrates the P in a region where it is most needed. Most plant uptake and accumulation of Al³⁺ occurs near the emerging root tips where the endodermis and casparian strip have not yet differentiated (Matsumoto et al., 1976; Wagatsuma, 1984; Zhang and Taylor, 1988). Wheat seedlings are especially susceptible to Al toxicity on soils with an acidic surface because the emerging radicle has not yet penetrated to a depth where Al concentrations are non-toxic. Reduced Al³⁺ concentration near the seed would give the emerging seedling roots a chance to pass through the acid-affected surface soil and into the less acid subsurface.

Soluble Al, Fe, and other metals quickly react with P fertilizer to form soluble complexes that may precipitate from solution or be adsorbed on the surface of Fe and Al oxides or on clay particles (Bell and Black, 1970; Lindsay and Stephenson, 1959; Lindsay et al., 1962; Martin et al., 1988; Vig and Dev, 1984). A variety of methods have been used to distinguish between adsorption and precipitation reactions of phosphate fertilizer.

Vig and Dev (1984) applied ³²P fertilizer after removing sesquioxides with citrate dithionite and concluded that >90% of the added P in acid soils was sorbed in Al and Fe phosphate forms. Pierzynski et al. (1990b) used electron optical techniques to describe P-rich particles in excessively fertilized soils and found that Al and Si were the dominant elements associated with P. These amorphous, mixed Al-Si-P substances occurred as discrete particles as well as coatings on other particles. Martin et al. (1988) used spectroscopic techniques to observe Fe-phosphate crystallites on the surface of goethite. They concluded that in an Fe oxide system, phosphate retention may be due primarily to precipitation rather than adsorption. Van Riemsdijk and Lyklema (1980) found that adsorption contributed very little to total sorption at P concentrations >1 mmol L⁻¹.

Department of Agronomy, Oklahoma State Univ., Stillwater, OK 74078. Contribution from Oklahoma Agric. Exp. Stn. Received 19 Oct. 1993. *Corresponding author (ntb@soilwater.agr.okstate.edu)

This study was designed to further investigate results that showed a greater wheat response to banded vs. broadcast P fertilizer in acid soils (Boman et al., 1992a,b). Results from work by Boman et al. (1992a) suggested that P fertilizer may remove toxic metals from soil solution in the root zone of the emerging wheat seedling. The objective of this study was to determine the effect of banded P fertilizer on Al chemistry and soil solution composition in acid soils.

MATERIALS AND METHODS

Soil Collection and Preparation

The soil in this study was collected from the surface horizon (upper 15 cm) of a Pond Creek silt loam at Carrier, OK. The soil was stored at 4°C, maintained at field moisture, and passed through a 2-mm sieve before use. Soil pH was 4.0 (1:1 soil/H₂O). The initial Mehlich 3 extractable P was 60.8 mg P kg⁻¹ (134 P kg ha⁻¹). The soil contained 6.4 g kg⁻¹ organic C by the modified Mëbius procedure (Nelson and Sommers, 1982). Cation-exchange capacity was determined by summation of cations to be 4.24 cmol_c kg⁻¹. The soil contained 11% sand, 74% silt, and 15% clay and had a field-capacity water content of 0.21 kg kg⁻¹ soil.

Fertilizer Treatments

Phosphorus fertilizer solutions were prepared from reagent-grade NaH₂PO₄·2H₂O and were applied to the soil as follows. Soil (350 g) was evenly spread in a 30 by 25 by 12 cm plastic tub, fertilizer solution was sprayed in small increments evenly over the soil, and the soil was thoroughly mixed. These steps were repeated until the appropriate amount of P fertilizer had been applied.

Five P fertilizer rates were applied: 0, 88, 175, 262, and 350 mg P kg⁻¹ soil. These rates corresponded to the approximate P concentration found in fertilizer bands following application of 0, 15, 30, 45, and 60 kg P ha⁻¹. Rates were based on P fertilizer deposited in a band with cross-sectional area of 1.61 cm² and subsequent diffusion of 2 cm in all directions (Heslep and Black, 1954), giving a total cross-sectional area of 29 cm². Following fertilizer application, the soil water content was brought to 0.21 kg kg⁻¹ soil and samples were placed in an incubator at 25°C. Deionized water was added every 2 to 3 d to maintain the soil moisture content at field capacity. At the same time, soils were thoroughly mixed in their containers. Perforated container lids and thorough mixing ensured well-aerated conditions throughout the incubation period.

Soil Solution Analysis

At 1, 5, 10, 15, 30, and 70 d after fertilizer application, two 25-g subsamples of moist soil were removed for soil solution extraction using a modified, rapid centrifugation method (Elkhahtib et al., 1987). Each 25-g sample was weighed directly from the bulk sample into a centrifuge tube designed for collection of soil solution and centrifuged for 45 min at a relative centrifugation force of 39 410 m s⁻². Approximately 2 mL of soil solution per 25 g of moist soil were collected. Both soil solution fractions were then combined before chemical analysis.

Mononuclear Al was determined by the ferron method (Jardine and Zelazny, 1986; Parker et al., 1988). Absorbance of the reaction between ferron and mononuclear Al was monitored for 180 s at 363 nm. Absorbance increased quickly up to 30 s but very little after 60 s. The 30-s absorbance reading

was used to calculate mononuclear Al because it provides a good estimate of mononuclear Al in an acid solution (Jardine and Zelazny, 1987; Parker et al., 1988). Since Al solutions with low organic matter-ligand/Al ratios react with ferron similarly to pure monomeric Al solutions, "mononuclear" forms in this study include monomeric and some dissolved Al-organic matter complexes.

Soil solution pH was measured by using a flat-surface, combination electrode. Orthophosphate was measured colorimetrically using the modified Murphey-Riley method (Olson and Sommers, 1982). Other anions (F, Cl, NO₃, and SO₄) were determined by ion chromatography, and cations (Ca, Mg, Mn, K, and Na) were measured by flame atomic absorption spectroscopy.

The geochemical assessment model MINTEQA2 (Allison et al., 1991) was used to calculate activities of dissolved chemical species. Total dissolved concentrations of ions measured by laboratory methods and soil solution pH were input data for MINTEQA2. Equilibrium constants were adjusted using the ionic strength calculated by MINTEQA2. Saturation indices were calculated by MINTEQA2 for all possible solids with respect to the soil solution. The saturation index (SI) is defined as:

$$SI = \log \frac{IAP}{K}$$

where IAP is the ion activity product of the appropriate chemical species and *K* is the solubility product of the possible solid phase. Ion activity products are based solely on the speciation of the soil solution and can be used to determine whether the dissolution-precipitation reaction is actually at equilibrium (Sposito, 1989). For any specific mineral, SI > 0 indicates that the soil solution is oversaturated and SI < 0 indicates that

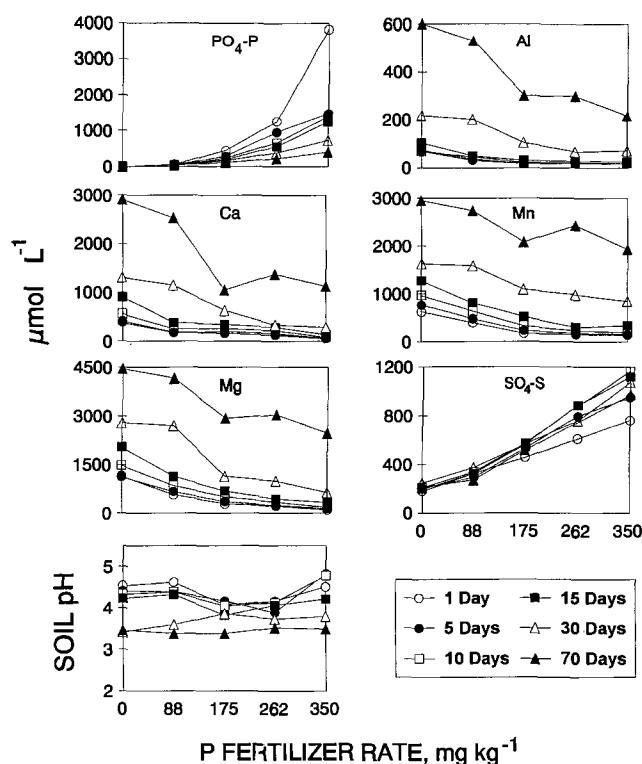


Fig. 1. Changes in soil solution composition following the banding of P fertilizer in an acidic soil (pH 4.0) after incubation periods of 1, 5, 10, 15, 30, and 70 d.

it is undersaturated. As the dissolution-precipitation reaction nears equilibrium, the SI value approaches zero.

Exchangeable Metals

At 1, 5, 10, 15, 30, and 70 d after fertilizer application, 1.5 g soil (dry weight) was removed from each treatment and extracted with 1 M KCl for 1 h. Exchangeable Al in the extract was determined by the ferron method (Jardine and Zelazny, 1986; Parker et al., 1988). Exchangeable Ca, Mg, Fe, and Mn were also measured in the 1 M KCl extract by flame atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Soil Solution

Soil solution composition was strongly affected by phosphorus fertilizer rate and incubation time (Fig. 1). A curvilinear increase in orthophosphate concentration with P fertilizer rate was found. This effect was most pronounced 1 d after fertilizer application but became less pronounced with each successive sampling period. Chen and Barber (1990) reported similar results following fertilizer P application to three acid soils.

Reductions in solution P with time were largest for the 350 mg kg⁻¹ P rate, with the largest decrease occurring between the 1-d (3800 μmol L⁻¹) and 5-d (1400 μmol L⁻¹) sampling periods. Once P concentration had decreased below 1400 μmol L⁻¹, further decreases in solution P concentration were less pronounced. Large, rapid decreases in solution P concentration suggest that precipi-

tation processes occurred. Van Riemsdijk and Lyklema (1980) concluded that precipitation of P was the dominant mechanism for removal of dissolved P above 1000 μmol L⁻¹ P.

"Mononuclear" Al concentration decreased as P fertilizer rate increased at all sampling times. Because Al solutions with low organic matter-ligand/Al molar ratios react with ferron similarly to pure monomeric Al solutions (Jardine and Zelazny, 1987), "mononuclear" forms included monomeric and some dissolved Al-organic matter complexes in this study. Large decreases in Al concentration occurred between the control and the 175 mg P kg⁻¹ rate. Above 175 mg P kg⁻¹ (30 kg P ha⁻¹), further additions of P fertilizer decreased the total mononuclear Al concentration only slightly. Results from field studies conducted with the same acid soil showed that banded P up to 30 kg P ha⁻¹ increased wheat forage yields, but higher P rates did not result in further yield increases (Boman et al., 1992a,b). Decreases in monomeric Al concentration with increasing P rate suggest the formation and precipitation of an Al-P solid. Other studies have shown Al to be one of the major elements associated with sorbed P (Pierzynski et al., 1990a; Vig and Dev, 1984).

Chemical speciation results for soil solution collected from soil samples during the incubation period are shown in Fig. 2. The distribution percentage of the various Al soluble complexes was calculated by MINTEQA2 using total dissolved concentrations of ions measured by laboratory methods and soil solution pH as input data. Values

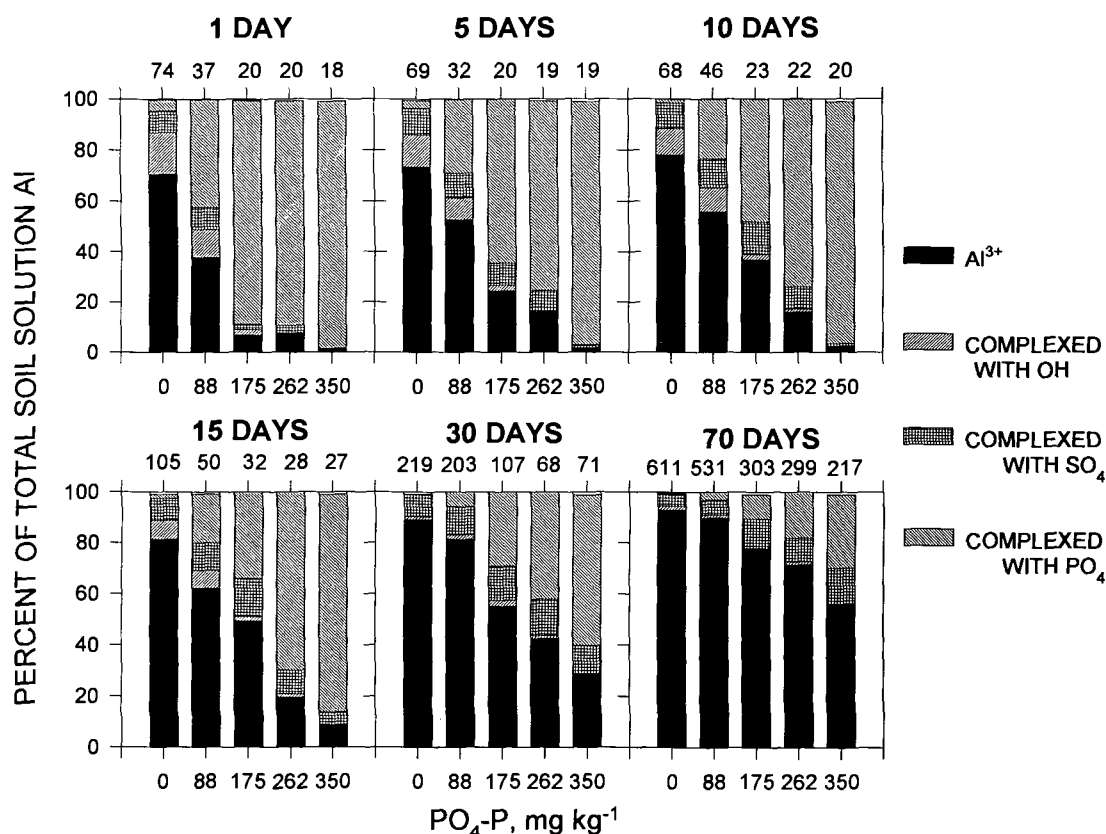


Fig. 2. Distribution of soluble Al complexes at 1, 5, 10, 15, 30, and 70 d after P fertilizer application.

at the top of each bar show the actual mononuclear Al concentration in micromoles per liter for that P fertilizer treatment. Free Al^{3+} was the predominant form of dissolved Al for application rates below 175 mg kg^{-1} P. Phosphorus fertilizer decreased free Al^{3+} and increased the amount of soluble Al complexed with orthophosphate. Aluminum complexed with phosphate was the predominant form of dissolved Al at rates above 175 mg kg^{-1} P and incubation times ≤ 30 d. Below the 175 mg kg^{-1} P rate, small amounts of soluble Al were complexed with OH. The only other significant anion forming a soluble complex with Al was SO_4 . In acid soil ($pH \leq 4.5$), toxic forms of Al are best approximated by the sum of the activities of $Al^{3+} + Al(OH)^{2+} + Al(OH)_2^+ + Al(OH)_3^0$ (Hodges, 1987; Parker et al., 1989). Phosphorus fertilizer decreased these toxic forms of Al in the soil solution, especially at rates $\geq 175 \text{ mg P kg}^{-1}$.

Dissolved Mn, Ca, and Mg were also inversely related to the P fertilizer rate (Fig. 1). Solution Mn, Ca, and Mg were significantly reduced by P fertilizer. The reduction in solution Mn, Ca, and Mg was similar to the reduction in solution Al in that the largest decrease occurred at P rates below 175 mg kg^{-1} . This suggests that similar mechanisms may be responsible for the removal of Mn, Ca, and Mg from soil solution. Manganese, Ca, and Mg form solid phases with orthophosphate of varying solubility. Following the addition of P fertilizer, Ca and Mg phosphates may initially form, but later disappear as more stable minerals are formed (Lindsay, 1979). Although Ca and Mg phosphates can be soluble in acid soils, P fertilizer decreased dissolved Ca and Mg at all sampling periods under the acidic conditions ($pH < 4.5$) in this experiment. Although Mn, Ca, and Mg concentrations increased with time, the effect of P fertilization remained apparent at all sampling periods (Fig. 1).

The concentration of dissolved metals (Al, Mn, Ca, and Mg) increased and soil solution pH decreased with incubation time (Fig. 1). Soil samples were maintained moist ($0.21 \text{ kg H}_2\text{O kg}^{-1}$ soil) and well aerated throughout the incubation study and optimal conditions for mineralization existed. Soil solution NO_3^- concentrations increased by a factor of three during the 70-d incubation period (data not shown). Elevated NO_3^- concentrations in the soil solution that increased with time suggest that mineralization occurred throughout the incubation study. Protons released through mineralization of organic matter contributed to the decrease in soil solution pH observed in this study. The decrease in pH probably increased the solubility of these metals.

A linear relationship was observed between P fertilizer rate and soil solution SO_4 (Fig. 1). A correlation coefficient of 0.99 was obtained for all sample times (excluding the 262 mg kg^{-1} rate on Day 70) whereas the best correlation was found for Day 1 data ($r = 0.999$). This linear relationship between soil solution SO_4 concentration and P fertilizer rate may suggest SO_4 desorption from soil by ligand exchange with orthophosphate (Bornemisza and Llanos, 1967; Chao et al., 1962). Phosphate forms a stronger bond at the sorption surface than does SO_4 (Kamprath et al., 1956; McBride, 1994). The ratio of SO_4 increase in solution to PO_4 decrease in solution

($\Delta SO_4/\Delta PO_4$ in micromoles) was calculated to further investigate this trend. The $\Delta SO_4/\Delta PO_4$ ratio ranged from 0.011 to 0.018 at 1 and 10 d respectively. Ratio values of ≤ 1 would be consistent with increases in SO_4 concentration due to ligand exchange of SO_4 by PO_4 . Because $\Delta SO_4/\Delta PO_4$ ratios were $\ll 1$, SO_4 desorption by phosphate may be responsible for increased concentrations of dissolved SO_4 . However, these results also suggest that most P removal from soil solution cannot be attributed to ligand exchange with SO_4 .

Solid-Phase Equilibria

Saturation indices were calculated by MINTEQA2 to investigate formation of solid phases. Table 1 shows soil solution saturation indices for five Al minerals whose dissolution-precipitation reactions may control Al activity in the soil solution. For any specific mineral, $SI > 0$ indicates that the soil solution is oversaturated and $SI < 0$ indicates that it is undersaturated. Equilibrium with a particular solid phase is indicated by $SI = 0$.

The underlined values in Table 1 indicate supersaturation of the soil solution with respect to that mineral and consequently possible precipitation of that mineral. In general, the soil solution was supersaturated with respect to the crystalline form of variscite ($AlPO_4 \cdot 2H_2O$, $pK_{SO} = 30.5$ [pK_{SO} is the negative log of the mineral solubility

Table 1. Soil solution saturation indices for several Al solid phases at P addition rates of 0, 88, 175, 262, and 350 mg kg^{-1} . Underlined values indicate supersaturation of the soil solution with respect to that particular mineral.

Time	Mineral†	0	88	175	262	350
d		mg P kg^{-1}				
1	KT	-7.81	-0.83	-2.68	<u>1.30</u>	<u>4.15</u>
	GA	-0.86	-1.14	-1.85	-3.34	-3.22
	GC	<u>0.76</u>	<u>0.48</u>	-0.23	-1.72	-1.60
	VC	<u>1.25</u>	<u>2.02</u>	<u>2.18</u>	<u>1.65</u>	<u>1.96</u>
	VA	-1.15	-0.38	-0.22	-0.75	-0.44
5	KT	-9.94	-3.16	-1.14	-1.22	<u>4.50</u>
	GA	-1.18	-1.70	-2.82	-3.94	-2.17
	GC	<u>0.44</u>	-0.08	-1.20	-2.32	-0.55
	VC	<u>0.96</u>	<u>1.58</u>	<u>1.52</u>	<u>1.23</u>	<u>2.29</u>
	VA	-1.44	-0.82	-0.88	-1.17	-0.11
10	KT	-12.64	-3.09	-2.77	-0.21	<u>4.53</u>
	GA	-1.48	-1.51	-3.20	-3.30	-2.13
	GC	<u>0.14</u>	<u>0.11</u>	-1.58	-1.68	-0.51
	VC	<u>0.46</u>	<u>1.65</u>	<u>1.23</u>	<u>1.50</u>	<u>2.30</u>
	VA	-1.94	-0.75	-1.17	-0.90	-0.10
15	KT	-10.93	-3.75	-3.99	<u>0.19</u>	<u>1.88</u>
	GA	-1.60	-1.76	-3.56	-3.14	-3.22
	GC	<u>0.02</u>	-0.15	-1.94	-1.52	-1.60
	VC	<u>0.65</u>	<u>1.49</u>	<u>0.99</u>	<u>1.58</u>	<u>1.75</u>
	VA	-1.75	-0.91	-1.41	-0.82	-0.65
30	KT	-16.65	-7.37	-1.57	-1.49	<u>0.56</u>
	GA	-3.69	-3.20	-2.74	-3.65	-3.56
	GC	-2.07	-1.58	-1.12	-2.03	-1.94
	VC	-0.42	<u>0.74</u>	<u>1.55</u>	<u>1.28</u>	<u>1.55</u>
	VA	-2.82	-1.66	-0.85	-1.13	-0.85
70	KT	-13.20	-8.20	-5.31	-2.48	-1.57
	GA	-3.03	-3.41	-3.71	-3.48	-3.75
	GC	-1.41	-1.79	-2.09	-1.86	-2.13
	VC	<u>0.09</u>	<u>0.60</u>	<u>0.87</u>	<u>1.27</u>	<u>1.33</u>
	VA	-2.31	-1.80	-1.53	-1.14	-1.07

† KT = K-taranakite, GA = amorphous gibbsite, GC = crystalline gibbsite, VC = crystalline variscite (Lindsay, 1979); VA = amorphous variscite [$Al(OH)_2PO_4$] (Veith and Sposito, 1977).

product]) at all rates and all times. The saturation index for crystalline variscite was closest to 0 for the control treatment at the later incubation times and generally increased with P rate. In soil, the formation of pure crystalline mineral forms is less likely than the formation of less perfect crystalline forms (Sposito, 1989). Table 1 also shows the saturation index for an amorphous form of variscite ($\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$, $\text{p}K_{\text{SO}} = 28.1$) identified by Vieth and Sposito (1977). Although the soil solution was never supersaturated with respect to this mineral, the saturation index did approach zero for the 350 mg P kg^{-1} rate at 5 and 10 d. Amorphous variscite has been reported as an Al-phosphate reaction product by many researchers, with $\text{p}K_{\text{SO}}$ values ranging from 27.4 to 28.6 (Cole and Jackson, 1950; Coleman et al., 1960; Gephardt and Coleman, 1974; Taylor and Gurney, 1962). More recently, amorphous variscite was reported as a reaction product in an acidic, montmorillonitic soil (Traina et al., 1986). Amorphous variscite analogs were identified as solid phases in equilibrium with soluble P in excessively fertilized, acidic Alfisols (Pierzynski et al., 1989a,b). Precipitation of an amorphous analog of variscite with $\text{p}K_{\text{SO}}$ between crystalline and amorphous variscite is consistent with data in our study.

The soil solution was supersaturated with respect to the crystalline form of gibbsite ($\text{p}K_{\text{SO}} = -8.04$; Lindsay, 1979) for P fertilizer rates < 175 mg P kg^{-1} and incubation times ≤ 15 d. The soil solution was undersaturated with respect to an amorphous form of gibbsite (Table 1) ($\text{p}K_{\text{SO}} = -9.66$; Lindsay, 1979). The increase in dissolved SO_4 discussed above was attributed to ligand exchange between orthophosphate and SO_4 at anion sorption sites. Ligand exchange in acid soil ($\text{pH} < 5.5$) also results in the release of OH^- into soil solution (Alva and Sumner, 1990; McBride, 1994). Soluble hydroxy-Al complexes were found in soil solution at rates < 175 mg P kg^{-1} (Fig. 2). Consequently, it is possible that at low P rates and short periods of time, Al was removed from soil solution by precipitation as gibbsite or a gibbsite analog. Alva and Sumner (1990) reported a similar mechanism following the addition of phosphogypsum to an acid soil. In their study, alleviation of Al toxicity was partly attributed to ligand exchange reactions where SO_4 adsorption released OH^- ligands. This mechanism may also result in precipitation of gibbsite. Ligand-exchange reactions where phosphate adsorption released OH^- ligands may have occurred and contributed to gibbsite precipitation in our study.

Potassium taranakite [$\text{H}_6\text{K}_3\text{Al}_5(\text{PO}_4)_8 \cdot 18\text{H}_2\text{O}$] was also a possible precipitation product for P fertilizer rates ≥ 262 mg P kg^{-1} and incubation times ≤ 30 d. Potassium taranakites, as well as NH_4 -taranakites, have been identified in soils as initial reaction products following the addition of P fertilizer (Lindsay et al., 1962). However, taranakites are relatively unstable in the soil environment and probably do not endure for long periods of time. The saturation index for K-taranakite decreased rapidly 15 and 10 d after fertilizer application for the 262 and 350 mg P kg^{-1} rates, respectively. Therefore, although

initial precipitation of K-taranakite was thermodynamically feasible after application of high P rates (≥ 262 mg P kg^{-1}), K-taranakite was not stable at longer incubation times.

Saturation indices were examined for Ca, Mg, and Mn solid phases because the concentrations of these metals also significantly decreased with P fertilizer application (Table 2). Soil solution was greatly undersaturated with respect to Ca and Mg phosphates and sulfates. The Ca and Mg minerals listed in Table 2 were the least soluble minerals considered by MINTEQA2 (Allison et al., 1991), with SI values closest to zero. Soil Ca and Mg were the Ca and Mg "solid phases" with SI closest to zero. Lindsay (1979) defined "soil Ca" and "soil Mg" as reference activities for Ca^{2+} and Mg^{2+} in acid soils that may include unknown or unidentified solid phases. The soil solution was slightly undersaturated with respect to soil Ca at all P rates and all times. The soil solution was oversaturated with respect to soil Mg for fertilizer rates ≤ 88 mg P kg^{-1} at 30 d and for all P fertilizer rates at 70 d.

Solubility equilibria of Mn was also considered in this study. Redox was not measured but soils were well aerated at all times during the incubation. Although redox was not measured, pe values ≥ 10 would be consistent for a well-aerated, acid soil (pH 4 to 5) (Sposito, 1989; McBride, 1994). Calculated saturation indices (assuming $\text{pe} = 10$) for 14 divalent and trivalent Mn minerals in MINTEQA2 (Allison et al., 1991) showed the soil solution to be undersaturated with respect to all except the trivalent $\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O}$ (Boyle and Lindsay, 1985a). Soil solution was oversaturated with respect to $\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O}$ at: P rates ≥ 88 mg P kg^{-1} and incubation times ≤ 10 d, P rates ≥ 175 mg P kg^{-1} and incubation times ≤ 30 d and P rates ≥ 350 mg P kg^{-1} for all incubation times. Studies have found that solubility of $\text{MnPO}_4 \cdot 1.5\text{H}_2\text{O}$ was capable of controlling soil solution Mn in acid soils with $\text{pe} + \text{pH}$ values ranging from 15.5 to 17.5 (Boyle and Lindsay, 1986; Schwab, 1989).

Exchangeable Metals

The effect of P fertilizer treatments on exchangeable cations was investigated (Table 3). Analysis of variance was conducted for each dependent variable (Al, Fe, Mn, Ca, and Mg) to account for replication and treatment (P rate) sources of variation. Orthogonal contrasts were used to determine whether there were significant linear or quadratic trends between exchangeable metals and P rate. In general, orthogonal contrasts showed that the linear and quadratic effects for P rate on exchangeable Al were highly significant (Table 3). Exchangeable Al decreased in a linear fashion with P rate up to 262 mg P kg^{-1} and then slightly increased at 350 mg P kg^{-1} . Exchangeable Ca, and to a lesser degree Mg, responded to P rate similarly to exchangeable Al (Table 3). Phosphorus rate did not affect exchangeable Fe or Mn (Table 3).

Decreases in both soil solution and exchangeable concentrations of a particular cation suggest that cations

Table 2. Soil solution saturation indices for several Ca, Mg, and Mn solid phases following P addition at rates of 0, 88, 175, 262, and 350 mg kg⁻¹. Underlined values indicate supersaturation of the soil solution with respect to the mineral phase.

Time	Mineral	0	88	175	262	350
d		mg P kg ⁻¹				
1	Soil Ca	-1.09	-1.48	-1.53	-1.55	-2.12
	Gypsum	-2.99	-3.10	-2.99	-3.01	-3.40
	CaHPO ₄ ·2H ₂ O	-5.27	-4.41	-3.39	-3.57	-3.23
	Ca ₅ (PO ₄) ₃ OH	-17.68	-15.33	-12.00	-14.79	-13.50
	Ca ₅ (PO ₄) ₃ F	-13.88	-10.98	-6.98	-9.28	-7.95
	Soil-Mg	-0.14	-0.45	-0.77	-0.92	-1.31
	MgHPO ₄ ·3H ₂ O	-5.75	-4.86	-4.48	-4.47	-4.52
	MgSO ₄ ·7H ₂ O	-5.05	-5.09	-5.24	-5.28	-5.59
	MnPO ₄ ·1.5H ₂ O	-0.25	0.91	1.69	1.09	2.11
10	Soil Ca	-0.97	-1.35	-1.34	-1.45	-1.90
	Gypsum	-2.83	-2.91	-2.74	-2.55	-3.00
	CaHPO ₄ ·2H ₂ O	-5.72	-4.58	-4.20	-3.74	-3.15
	Ca ₅ (PO ₄) ₃ OH	-19.85	-16.77	-16.86	-15.28	-11.65
	Ca ₅ (PO ₄) ₃ F	-15.84	-12.49	-11.56	-9.87	-6.49
	Soil-Mg	-0.04	-0.29	-0.54	-0.74	-1.03
	MgHPO ₄ ·3H ₂ O	-5.05	-4.88	-4.55	-4.29	-3.54
	MgSO ₄ ·7H ₂ O	-4.91	-4.94	-4.95	-4.96	-5.14
	MnPO ₄ ·1.5H ₂ O	-0.84	0.48	0.27	0.74	2.40
30	Soil Ca	-0.54	-0.72	-0.99	-1.25	-1.37
	Gypsum	-2.55	-2.46	-2.48	-2.51	-2.51
	CaHPO ₄ ·2H ₂ O	-5.85	-4.87	-4.19	-4.23	-3.96
	Ca ₅ (PO ₄) ₃ OH	-23.78	-19.45	-16.55	-17.98	-16.99
	Ca ₅ (PO ₄) ₃ F	-19.48	-15.27	-12.19	-13.08	-12.03
	Soil-Mg	0.19	0.15	-0.21	-0.28	-0.51
	MgHPO ₄ ·3H ₂ O	-5.28	-5.24	-4.57	-4.50	-4.35
	MgSO ₄ ·7H ₂ O	-4.72	-4.58	-4.72	-4.54	-4.76
	MnPO ₄ ·1.5H ₂ O	-2.02	-0.79	0.29	0.28	0.67
70	Soil Ca	-0.35	-0.42	-0.80	-0.70	-0.80
	Gypsum	-2.45	-2.40	-2.44	-2.38	-2.18
	CaHPO ₄ ·2H ₂ O	-5.52	-4.90	-4.71	-4.24	-4.02
	Ca ₅ (PO ₄) ₃ OH	-21.46	-19.73	-19.78	-17.73	-17.25
	Ca ₅ (PO ₄) ₃ F	-17.71	-15.80	-15.54	-13.53	-12.79
	Soil-Mg	0.35	0.31	0.16	0.16	0.05
	MgHPO ₄ ·3H ₂ O	-5.08	-5.42	-5.00	-4.54	-4.42
	MgSO ₄ ·7H ₂ O	-4.77	-4.69	-4.49	-4.53	-4.34
	MnPO ₄ ·1.5H ₂ O	-1.68	-1.12	-0.67	-0.15	0.05

were precipitated or were converted to nonexchangeable forms. This was the case with Al, Ca, and to some degree Mg. This is consistent with other findings in this study. Saturation indices (Table 1) indicated possible precipitation of several Al solid phases. These include gibbsite at low P rates, amorphous variscite at all P rates, and K-taranakite at high P rates. No solid phases for Ca or Mg could be identified other than the nonspecific "soil Ca" and "soil Mg" forms suggested by Lindsay (1979) (Table 2).

Trends with time were less distinct than trends with fertilizer rate. Exchangeable Al decreased from 1 to 10 d but then increased after 10 d. The initial decrease of exchangeable Al was probably due to precipitation and the subsequent increase may be attributed to increased solubility of Al minerals as the pH decreased. The decrease in exchangeable Ca and Mg with time is possibly due to fixation by orthophosphate.

SUMMARY

Phosphorus fertilizer reduced total dissolved Al and toxic soluble Al³⁺. Initial Al solid phases that may have formed after P application include gibbsite and K-taranakite, but formation of amorphous forms of variscite were possible under all soil conditions and incubation

times investigated. Although other soluble metals (Ca, Mg, and Mn) were probably reduced by precipitation induced by P fertilizer, deduction of possible solid phases was less definite. Decreases in soil pH with incubation time increased dissolved and exchangeable amounts of some metal cations. Significant decreases in soil solution pH at 70 d were associated with increased soluble and exchangeable Al³⁺ concentrations. Decreases in soil pH and increases in exchangeable Al were not observed in a parallel study under field conditions. Perhaps, intense mixing and watering of soil and other incubation artifacts resulted in excessive amounts of mineralization and contributed to soil acidification.

Banded application of P fertilizer is an efficient way to utilize P, especially in soils where Al toxicity may be a problem. The 88 mg P kg⁻¹ treatment corresponded to the P concentration in a 15 kg P ha⁻¹ fertilizer band. If an equivalent amount of fertilizer were broadcast and incorporated to a depth of 7.5 cm, the soil concentration would be only 15 mg kg⁻¹. Thus, banding fertilizer results in a much higher concentration of P in the soil solution in the region of the emerging wheat seedling. In addition to its nutritional value, banded P fertilizer complexes and precipitates Al in the region of the emerging wheat roots and may reduce the toxic effect of Al on wheat growth and development.

Table 3. Effect of P fertilizer rate and time on exchangeable cation concentrations.

Time	P rate	Al	Fe	Mn	Ca	Mg
d	mg kg ⁻¹	cmolc kg ⁻¹				
1	0	0.69	0.11	0.39	1.40	0.59
	88	0.55	0.11	0.40	1.35	0.55
	175	0.40	0.11	0.39	0.97	0.48
	262	0.35	ND†	0.35	0.53	0.46
	350	0.45	0.10	0.39	0.84	0.54
	SED‡	0.03	<0.01	0.01	0.03	0.02
10	Linear§	***	NS	NS	***	***
	Quadratic¶	***	NS	NS	***	***
	0	0.58	0.11	0.48	1.09	0.50
	88	0.45	0.11	0.47	0.99	0.50
	175	0.36	0.11	0.47	0.68	0.45
	262	0.26	ND	0.45	0.38	0.40
30	350	0.32	0.12	0.47	0.76	0.51
	SED	0.02	0.01	0.01	0.03	0.01
	Linear	***	NS	NS	***	*
	Quadratic	***	NS	NS	***	***
	0	0.78	0.11	0.47	0.76	0.49
	88	0.72	0.11	0.47	0.66	0.50
70	175	0.27	0.12	0.45	0.34	0.39
	262	0.49	ND	0.49	0.62	0.51
	350	0.42	0.11	0.45	0.44	0.48
	SED	0.04	<0.01	0.01	0.04	0.02
	Linear	***	NS	NS	***	NS
	Quadratic	***	NS	NS	***	**
70	0	0.91	0.10	0.52	0.65	0.50
	88	0.86	0.10	0.51	0.48	0.47
	175	0.78	0.11	0.49	0.47	0.49
	262	0.51	ND	0.44	0.25	0.37
	350	0.56	0.10	0.47	0.39	0.50
	SED	0.04	<0.01	0.01	0.06	0.02
70	Linear	***	NS	***	***	*
	Quadratic	NS	NS	NS	NS	**

*, **, *** Significant at 0.05, 0.01 and 0.001 levels of probability, respectively. NS = not significant.

† ND = not determined.

‡ Standard error of difference.

§ Linear effect for P rate.

¶ Quadratic effect for P rate.

REFERENCES

- Allison, J.D., D.S. Brown, and K.J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems: Version 3.0 user's manual. USEPA Rep. 600/3-91/021. Environ. Res. Lab. Athens, GA.
- Alva A.K., and M.E. Sumner. 1990. Amelioration of acid soil infertility by phosphogypsum. *Plant Soil* 128:127-134.
- Bell, L.C., and C.A. Black. 1970. Crystalline phosphates produced by interaction of orthophosphate fertilizers with slightly acid and alkaline soils. *Soil Sci. Soc. Am. J.* 34:735-740.
- Boman, R.K., J.J. Sloan, R.L. Westerman, W.R. Raun, and G.V. Johnson. 1992a. Using phosphorus fertilizers to maintain wheat forage and grain yields on acid soils. *Better Crops* 76:16-19.
- Boman, R.K., R.L. Westerman, G.V. Johnson, and M.E. Jojola. 1992b. Phosphorus fertilization effects on winter wheat production in acid soils. p. 195-200. *In* J.L. Havlin (ed.) *Proc. Great Plains Soil Fert. Conf.* Denver, CO. Vol. 4.
- Bornemisza, E., and R. Llanos. 1967. Sulfate movement, adsorption, and desorption in three Costa Rican Soils. *Soil Sci. Soc. Am. Proc.* 31:356-360.
- Boyle, F.W., and W.L. Lindsay. 1985a. Preparation, x-ray diffraction pattern, and solubility product of Mn(III) phosphate hydrate. *Soil Sci. Soc. Am. J.* 49:758-760.
- Boyle, F.W., and W.L. Lindsay. 1986. Manganese-phosphorous equilibrium relationships in soils. *Soil Sci. Soc. Am. J.* 50:588-593.
- Chao, T.T., M.E. Harward, and A.C. Fang. 1962. Adsorption and desorption phenomena of sulfate ions in soils. *Soil Sci. Soc. Am. Proc.* 26:234-237.
- Chen, J.H., and S.A. Barber. 1990. Effect of liming and adding phosphate on predicted phosphorus uptake by maize on acid soils of three soil orders. *Soil Sci.* 150:844-850.
- Cole, C.V., and M.L. Jackson. 1950. Solubility equilibrium constant of dihydroxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. *Soil Sci. Soc. Am. Proc.* 15:84-89.
- Coleman, N.T., J.T. Thorup, and W.A. Jackson. 1960. Phosphate-adsorption reactions that involve exchangeable aluminum. *Soil Sci.* 90:1-7.
- Elkhahtib, E.A., J.L. Hern, and T.E. Staley. 1987. A rapid centrifugation method for obtaining soil solution. *Soil Sci. Soc. Am. J.* 51:578-583.
- Foy, C.D. 1987. Acid soil tolerances of two wheat cultivars related to soil pH, KCl extractable aluminum and degree of Al saturation. *J. Plant Nutr.* 10:609-623.
- Gephardt, H., and N.T. Coleman. 1974. Anion adsorption by allophanic tropical soils. III. Phosphate adsorption. *Soil Sci. Soc. Am. Proc.* 38:263-266.
- Havlin, J., A. Schlegel, and J. Zupancic. 1987. Phosphorus rate and placement effects on winter wheat. *Kansas Fert. Res. Rep. Prog.* 531. Agric. Exp. Stn., Kansas State Univ., Manhattan.
- Heslep, J.M., and C.A. Black. 1954. Diffusion of fertilizer phosphorus in soils. *Soil Sci.* 78:389-401.
- Hodges, S.C. 1987. Aluminum speciation: A comparison of five methods. *Soil Sci. Soc. Am. J.* 51:57-64.
- Jardine, P.M., and L.W. Zelazny. 1986. Mononuclear and polynuclear aluminum speciation through differential kinetic reactions with ferron. *Soil Sci. Soc. Am. J.* 50:895-900.
- Jardine, P.M., and L.W. Zelazny. 1987. Influence of inorganic anions on the speciation of mononuclear and polynuclear aluminum by ferron. *Soil Sci. Soc. Am. J.* 51:889-892.
- Johnson, G.V., R.L. Westerman, E.R. Allen, and R.K. Boman. 1991. Managing acid soils for wheat production. OSU Extension Facts no. 2240. Coop. Ext. Serv., Stillwater, OK.
- Kamprath, E.J., W.L. Nelson, and J.W. Fitts. 1956. The effect of pH, sulfate, and phosphate concentrations on the adsorption of sulfate by soils. *Soil Sci. Soc. Am. Proc.* 20:463-466.
- Lindsay, W.L. 1979. *Chemical equilibria in soils.* John Wiley & Sons, New York.
- Lindsay, W.L., A.W. Frazier, and H.F. Stephenson. 1962. Identification of reaction products from phosphate fertilizers in soils. *Soil Sci. Soc. Am. Proc.* 26:446-452.
- Lindsay, W.L., and H.F. Stephenson. 1959. Nature and reaction of monocalcium phosphate monohydrate in soils: II. Dissolution and precipitation reactions involving iron, aluminum, manganese, and calcium. *Soil Sci. Soc. Am. Proc.* 23:18-22.
- Martin, R.R., R.St.C. Smart, and K. Tazaki. 1988. Direct observation of phosphate precipitation in the goethite/phosphate system. *Soil Sci. Soc. Am. J.* 52:1492-1500.
- Matsumoto, H., E. Hirasawa, H. Torikai, and E. Takahashi. 1976. Localization of adsorbed aluminum in pea root and its binding to nucleic acids. *Plant Cell Physiol.* 17:127-358.
- McBride, M.B. 1994. *Environmental chemistry of soils.* Oxford Univ. Press, New York.
- Nelson, D.W., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-579. *In* A.L. Page et al. (ed.) *Methods of soil analysis. Part 2. 2nd ed.* Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Newton, K.K., R.L. Westerman, B.B. Tucker, and L.W. Reed. 1979. Effect of lime and nitrogen on aluminum and manganese in acid soils. p. 178. *In* Agronomy abstracts ASA, Madison, WI.
- Olson, S.R., and L.E. Sommers. 1982. Phosphorus. p. 413-414. *In* A.L. Page et al. (ed.) *Methods of soil analysis. Part 2. 2nd ed.* Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Parker, D.R., T.B. Kinraide, and L.W. Zelazny. 1989. On the phytotoxicity of polynuclear hydroxy-aluminum complexes. *Soil Sci. Soc. Am. J.* 52:67-75.
- Parker, D.R., L.W. Zelazny, and T.B. Kinraide. 1988. Comparison of three spectrophotometric methods for differentiating mono- and polynuclear hydroxy-aluminum complexes. *Soil Sci. Soc. Am. J.* 52:67-75.
- Pierzynski, G.M., T.J. Logan, and S.J. Traina. 1990a. Phosphorus chemistry and mineralogy in excessively fertilized soils: Solubility equilibria. *Soil Sci. Soc. Am. J.* 54:1589-1595.
- Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990b. Phosphorus chemistry and mineralogy in excessively fertilized

- soils: Descriptions of phosphorus-rich particles. *Soil Sci. Soc. Am. J.* 54:1583-1589.
- Ritchey, K.D., V.C. Baligar, and R.J. Wright. 1988. Wheat seedling responses to soil acidity and implications for subsoil rooting. *Commun. Soil Sci. Plant Anal.* 19:1285-1293.
- Schwab, A.P. 1989. Manganese-phosphate solubility relationships in an acid soil. *Soil Sci. Soc. Am. J.* 53:1654-1660.
- Sheppard, L.J., and M.J.S. Floate. 1984. The effects of soluble Al on root growth and radicle elongation. *Plant Soil* 80:301-306.
- Sposito, G. 1989. *The chemistry of soils*. Oxford Univ. Press, New York.
- Taylor, A.W., and E.L. Gurney. 1962. Solubility of amorphous aluminum phosphate. *Soil Sci.* 93:241-245.
- Traina, S.J., G. Sposito, D. Hesterberg, and U. Kafkafi. 1986. Effects of pH and organic acids on organophosphate solubility in an acid montmorillonitic soil. *Soil Sci. Soc. Am. J.* 50:45-52.
- van Riemsdijk, W.H., and J. Lyklema. 1980. Reaction of phosphate with gibbsite ($\text{Al}(\text{OH})_3$) beyond the adsorption maximum. *J. Colloid Interface Sci.* 76:55-66.
- Veith, J.A., and G. Sposito. 1977. Reactions of aluminosilicates, aluminum hydrous oxides, and aluminum oxide with *o*-phosphate: The formation of x-ray amorphous analogs of variscite and montebasite. *Soil Sci. Soc. Am. J.* 41:870-876.
- Vig, A.C., and G. Dev. 1984. Phosphorus adsorption characteristics of some acid and alkaline soils. *J. Indian Soc. Soil Sci.* 32:235-239.
- Wagatsuma, T. 1984. Characteristics of upward translocation of aluminum in plants. *Soil Sci. Plant Nutr.* 30:345-358.
- Wright, R.J., V.C. Baligar, K.D. Ritchey, and S.F. Wright. 1989. Influence of soil solution aluminum on root elongation of wheat seedlings. *Plant Soil* 113:294-298.
- Zhang, G., and G.J. Taylor. 1988. Effect of aluminum on growth and distribution of aluminum in tolerant and sensitive cultivars of *Triticum aestivum* L. *Commun. Soil Sci. Plant Anal.* 19:1195-1205.