# IRON CHLOROSIS IN SOYBEANS AND PHOSPHORUS INFLUENCE ON DTPA EXTRACTABLE MICRONUTRIENTS AND SOIL SOLUTION CHEMISTRY

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# INTRODUCTION

The research reported in this dissertation included three separate parts, each a manuscript prepared for publication in a professional journal with minor modifications.

Two soil types which are different in their chemical properties were collected from western Oklahoma and used in these studies.

The first study, Part I, was a comparison of the tolerance of five soybean cultivars (Essex, Crawford, York, Gail, and Forrest) to iron chlorosis in a greenhouse experiment. Relationship of chlorophyll and nutrient concentrations in the leaves and the degree of iron chlorosis among the five cultivars were discussed in this part.

Part II, involves the study of the influence of five rates of three P sources on soil pH, Bray and Kurtz no. 1 extractable P, and DTPA extractable micronutrients in a laboratory experiment. A detailed discussion of the effects of P on DTPA extractable iron ratios and micronutrients were included in this part.

Part III, included the study of the effects of three P sources on the chemistry of the soil solution in a laboratory experiment. Immiscible displacement was used to obtain the soil solution. GEOCHEM program and Davis equation were used to determine the free ionic concentration and the activity coefficients of the soil solution component. Influence of P sources on the activities of selected ionic species, ionic pairs, and P complexes were discussed in this part.

# PART I

# IRON CHLOROSIS IN SOYBEANS

# ABSTRACT

Iron chlorosis in soybeans, _Glycine_ _max_ (L.) Merr., is a major problem in many soils in the western Great Plains. Tolerance to chlorosis differs significantly within soybean cultivars. Therefore, the objectives of this study were (a) to determine the tolerance of soybean cultivars to chlorosis; and (b) to determine the relationship of nutrient concentrations in leaves and the degree of chlorosis. A randomized complete block design consisting of four replications with a factorial arrangement of treatments (2 x 5 x 2) was used in a greenhouse experiment to study the objectives. The main factors were soil types (Quinlan cl, pH 8.1 and McLain si cl, pH 7.3), cultivars (Essex, Crawford, York, Gail, and Forrest), and fertilizer rates (0 and 0.2 kg Fe ha$^{-1}$). Chlorosis was more severe in all cultivars grown in Quinlan soil than in McLain soil. York and Forrest exhibited the most severe chlorosis in Quinlan soil while York was the most chlorotic in McLain soil. Essex exhibited the least chlorotic symptoms of the cultivars tested in both soils. Chlorophyll concentration in leaves was higher in Essex than in the other cultivars. There were no significant differences in Fe concentration of leaves among cultivars grown in both soils. Phosphorus in leaves of Forrest was significantly higher than in the other cultivars when grown in McLain soil. High Ca and Mn concentrations in leaves were usually associated with the most chlorotic cultivars. Other nutrient concentrations and micronutrient ratios varied among chlorotic and nonchlorotic cultivars.

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Key Words: Cultivars, iron fertilization, chlorophyll concentration, nutrient concentrations and ratios.

# INTRODUCTION

Iron chlorosis has been reported in many different crops and is usually associated with moist and alkaline soils (Boxma, 1972; Elgala and Maier, 1964; and Wallace et al., 1976). Iron deficiency and correction in small grains, grain sorghum, and Forrest soybeans in Oklahoma were reported and reviewed by Rogers (1972), Datin and Westerman (1982) and Silvertooth (1982). Causative factors for variation in tolerance to iron chlorosis among plant species and varieties within species were studied by several investigators and conflicting results have been reported.

Brown et al. (1955) reported that application of P and Cu induced Fe chlorosis in (PI) but not (HA) soybean cultivars and that Cu and P concentrations were higher but Fe was lower in chlorotic than in nonchlorotic plants. Bassiri et al. (1979) found that iron chlorosis in mungbeans was induced by high P applications. Tiffin et al. (1960) reported that high P concentration in the nutrient solution or inside the soybean plants decreased the uptake and the translocation of Fe. A high P/Fe ratio was associated with chlorotic soybean plants and the increase of P level significantly inhibited the increase in Fe uptake of Fe inefficient soybeans but only slightly affected the Fe efficient soybeans (Chaney and Coulombe, 1982). Watanabe et al. (1965) pointed out that the development of Fe deficiency symptoms in corn was associated with a decrease in the Fe/Zn ratio or an increase of P and the

P/Fe ratio in plant leaves. Mustard plants were shown to develop Fe deficiency when the P/Fe ratio in the leaves was more than 60 (De Kock, 1955). Phosphorus and Fe complexes with immobile organic molecules have been shown to occur in barley roots (Foster and Russel, 1958).

Vretta-Kouskoleka and Kallinis (1968) reported that the Mn content of the blades of Fe deficient cotton was much higher than for normal and "corrected" plants. Olomu and Racz (1974) reported that chlorosis and reduction in flax yield occurred whenever the Mn/Fe ratio exceeded 4. Brown and Jones (1962) found that more Fe and Mn were absorbed by chlorotic (HA) soybeans than by green (HA) and green or chlorotic (PI) soybeans. This was attributed to a greater reduction capacity of chlorotic (HA) soybean roots.

Procopiou and Wallace (1982) observed that some chlorotic leaves of lemon trees were higher in P, K, and Fe and lower in Ca than in green leaves. Brown and Jones (1977) reported that out of ten soybean cultivars, Forrest developed severe Fe chlorosis and contained less Fe in the leaves than the other cultivars. Different soybean genotypes were reported to induce different degrees of Fe chlorosis (Byron and Lambert, 1983). Biddulph and Woodbridge (1952) reported a precipitation reaction may occur in the conductive tissues of the stem and the leaves of bean plants if P and Fe are in excess quantities in the nutrient solution.

Internal inactivation of Fe in chlorotic (PI) soybeans was caused by the combined effect of P and Ca mainly because of the increase in P and Ca adsorption and the decrease in Fe adsorption (Brown, et al., 1959). Elgala and Maier (1964) and Jacobson (1945) both reported that Fe chlorosis was related to the low concentration of the active Fe (chloroplast Fe) or to the abnormal inactivation or precipitation of Fe.

Wallace et al. (1978) reported a decrease in Fe concentration in soybean roots grown in soils with high pH.

Elgala and Maier (1964) and Wallace et al. (1976) reported no differences in Fe concentration of chlorotic and nonchlorotic soybeans were observed under high moisture levels and they related the development of chlorosis to the ionic interaction, ionic balance, and active Fe concentration.

No appreciable difference in the total N of green and chlorotic corn plants was observed, but Fe chlorosis reduced 82 percent of the chloroplast protein while the cytoplasmic protein was not changed (Perur et al., 1961).

Boxma (1972), Brown and Holmes (1956), Inskeep and Bloom (1984) and Wallace et al. (1976) each reported that Fe chlorosis was associated with high $CaCO_3$ concentration in soil. Coulombe et al. (1984) and Lindsay and Thorne (1954) each found that bicarbonate content of soil was the direct factor for Fe chlorosis development. Inskeep and Bloom (1984) reported that bicarbonate activities were correlated with chlorosis score of one soybean transect but that high soil P was correlated with all chlorotic cultivars.

The tolerance of different soybean cultivars to Fe chlorosis in Oklahoma and the causative factors for developing chlorosis inside the plant have not been investigated. Therefore, a greenhouse experiment was designed to:

1. Determine the tolerance of soybean cultivars to iron chlorosis.
2. Determine the relationship of nutrient concentrations in leaves and degree of chlorosis.

# MATERIALS AND METHODS

Two soils (Quinlan cl, Typic Ustochrepts, and McLain si cl, Pachic Argiustolls) were collected from western Oklahoma for the experiment. These soils were analyzed for soil pH using 1:1 soil-water ratio, electrical conductivity (ECe) of the saturation extract, Rhoades (1982), soil P, Bray and Kurtz (1945) No. 1 P 1:20 soil-solution ratio, organic matter, Walkley-Black (1934), $CaCO_3$, Nelson (1982), $NO_3^-$-N, Keeney and Nelson (1982), $HCO_3^-$, Rhoades (1982) and DTPA extractable micronutrients, Lindsay and Norvell (1978).

The soils were kept field moist, mixed and passed through a 2 mm screen. Ammonium nitrate (20 kg N $ha^{-1}$) was applied to both soils and phosphoric acid (50 kg P $ha^{-1}$) was applied to the Quinlan soil to correct N and P deficiencies. Soils were mixed and passed through a 2 mm screen and 2 kg of each soil were placed in plastic pots in the greenhouse. Treatments included two soil types (Quinlan cl and McLain si cl), five soybean cultivars (Essex, Crawford, York, Gail, and Forrest) and two Fe fertilizer levels (0.0 and 0.2 kg Fe $ha^{-1}$) in a factorial arrangement (2 x 5 x 2) in a randomized block design with four replications.

Two soybean seeds, Glycine max (L.) Merr., per quadrant were planted 1 cm below the soil surface after being treated with Rhizobium Japonicum inoculum and later thinned to four plants per pot. Deionized water was used two or three times daily throughout the growing period to water the plants. Sequestrine 330 (0.2 kg Fe $ha^{-1}$, foliar application) was applied after six weeks of growth. At the end of the experiment (after two months of growth) and during the flowering stage, mature and young leaves were scored for chlorosis development. The chlorosis score ranged from 1 to 4 (1 refers to non-chlorotic plants and 4 refers to moderately chlorotic plants).

Young mature leaf samples were collected and washed four times with deionized water, dried at 65 °C for 12 h, ground to pass through a 200 mesh screen, and saved for chemical analysis.

Chlorophyll content was determined in leaf samples by a methanol extraction procedure outlined by Johnson (1974). Leaf samples were digested using HNO3-HC104, (Isaac and Kerber, 1971) and Fe, Mn, Zn, Cu, Na, K, Ca, and Mg were determined by atomic absorption and flame emission spectrometric procedures using acetylene-air-flame. Total P was determined colorimetrically (Murphy and Riley, 1962) after digestion. Total nitrogen was determined by micro-Kjeldahl (Bremner and Mulvaney, 1982).

Significant differences among treatments were determined using analysis of variance and LSD procedures outlined by Steel and Torrie (1960). All comparisons were made at the 0.05 level of probability.

# RESULTS

The initial soil test indices and micronutrient concentrations in both Quinlan and McLain soils are reported in Tables 1 and 2, respectively. The Quinlan soil was higher in soil pH and $CaCO_3$ concentration and was initially lower in soil P than the McLain soil. DTPA extractable Fe, Mn, Zn, and Cu were lower in Quinlan soil than in McLain soil, regardless of whether or not soils were kept moist or dried. Drying soils prior to DTPA extraction increased Fe and Mn concentrations markedly which was also observed by Leggett and Argyle (1983).

## Chlorosis Score and Concentration

In general, all soybean cultivars grown in Quinlan soil developed a higher chlorosis score than in McLain soil (Table 3).

In Quinlan soil without foliar Fe fertilization, York and Forrest had the highest chlorosis score while Essex had the lowest chlorosis score. Crawford, York, Forrest, and Gail cultivars had significantly higher chlorosis scores than Essex, but York and Forrest were significantly higher than Crawford.

In McLain soil without foliar Fe fertilization, York had the highest chlorosis score and was significantly higher than Essex and Forrest.

TABLE 1

Initial soil test indices.

| Soil | pH | ECe | P | O.M. | $CaCO_3$ | $NO_3$-N | $HCO_3$ |
|---|---|---|---|---|---|---|---|
| | (1:1) | (S $m^{-1}$) | ( g $g^{-1}$) | (mg $g^{-1}$) | (mg $g^{-1}$) | (kg $ha^{-1}$) | ($mML^{-1}$) |
| Quinlan | 8.1 | 0.035 | 23 | 11 | 127 | 38 | 1.97 |
| McLain | 7.3 | 0.22 | 116 | 22 | 18 | 61 | 3.12 |

TABLE 2

Micronutrient concentrations in moist and dry soils.

| | Soil Type | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Quinlan | | | | McLain | | | |
| | Fe | Mn | Zn | Cu | Fe | Mn | Zn | Cu |
| | ---------------------- ug $g^{-1}$ ----------------------- | | | | | | | |
| Moist | 1.0 | 5.5 | 0.3 | 0.3 | 6.7 | 7.4 | 0.5 | 1.8 |
| Dry | 2.1 | 17.1 | 0.4 | 0.4 | 28.4 | 38.0 | 0.8 | 2.0 |

TABLE 3

Chlorosis score at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| Essex | 1.50 | 1.00 | 1.00 | 1.00 |
| Crawford | 2.50 | 2.00 | 1.50 | 1.25 |
| York | 3.25 | 3.00 | 2.00 | 2.00 |
| Forrest | 3.25 | 1.50 | 1.25 | 1.75 |
| Gail | 3.00 | 1.75 | 1.50 | 1.50 |

LSD (0.05) = 0.65

Foliar application of Fe fertilizer usually decreased the chlorosis of all soybean cultivars grown in Quinlan soil, but not in McLain soil.

Chlorophyll concentration in leaves of Essex grown in both soils was higher than observed in all other cultivars, regardless of whether or not foliar Fe was applied (Table 4). Chlorophyll concentration in leaves of cultivars with foliar Fe fertilization tended to be less than without foliar Fe fertilization. This was attributed to some leaf burn and necrosis due to the application of foliar Fe.

TABLE 4

Chlorophyll concentration in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| | $\text{g kg}^{-1}$ | | | |
| Essex | 0.09 | 0.09 | 0.12 | 0.11 |
| Crawford | 0.06 | 0.05 | 0.11 | 0.09 |
| York | 0.06 | 0.05 | 0.10 | 0.07 |
| Forrest | 0.06 | 0.07 | 0.11 | 0.08 |
| Gail | 0.06 | 0.05 | 0.10 | 0.08 |

LSD (0.05) = 0.01

## Nutrient Concentrations

There were no differences in Fe concentration in leaves of cultivars grown in either soil without foliar Fe fertilization (Table 5). However, foliar Fe fertilization increased Fe concentration in all cultivars except Crawford grown in McLain soil. Essex contained significantly higher Fe concentration in leaves than the other cultivars grown in Quinlan soil when Fe was applied foliarly. Iron concentrations in leaves of Essex and York cultivars were significantly higher than in Crawford and Forrest grown in McLain soil. However, Fe concentration in leaves of Gail was signficantly higher than observed in Crawford.

TABLE 5

Iron concentration in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| | $g\ kg^{-1}$ | | | |
| Essex | 0.11 | 0.23 | 0.14 | 0.19 |
| Crawford | 0.11 | 0.20 | 0.14 | 0.15 |
| York | 0.11 | 0.20 | 0.14 | 0.19 |
| Forrest | 0.11 | 0.21 | 0.14 | 0.16 |
| Gail | 0.12 | 0.20 | 0.13 | 0.18 |
| LSD (0.05) = 0.02 | | | | |

There were no differences in P concentration in leaves among soybean cultivars grown in Quinlan soil without foliar Fe fertilization (Table 6). However, in McLain soil without Fe foliar fertilization, P concentration in leaves of Forrest was higher than observed in all other cultivars. Phosphorus concentration in leaves of Forrest with foliar Fe fertilization was higher than in Gail when grown in Quinlan soil and higher than all other cultivars when grown in McLain soil.

Total N in leaves of York soybeans grown in Quinlan soil without foliar Fe fertilization was lower than observed in Crawford and Forrest cultivars (Table 7). However, with foliar Fe fertilization, total N in leaves of Gail was higher than observed in York. In McLain soil without foliar Fe fertilization, there were no differences in total N in leaves of Gail and York cultivars or among Crawford, Forrest and

Essex cultivars. However, total N in leaves of Crawford, Forrest, and Essex was higher than observed in both Gail and York cultivars.

TABLE 6

Phosphorus concentration in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| | $g\ kg^{-1}$ | | | |
| Essex | 1.22 | 1.53 | 3.30 | 4.18 |
| Crawford | 1.40 | 1.86 | 3.97 | 3.64 |
| York | 1.28 | 1.50 | 3.56 | 4.24 |
| Forrest | 1.53 | 2.12 | 5.67 | 5.41 |
| Gail | 1.14 | 1.28 | 3.42 | 3.69 |
| LSD (0.05) = 0.67 | | | | |

TABLE 7

Total nitrogen concentration in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| | $g\ kg^{-1}$ | | | |
| Essex | 36.9 | 35.2 | 46.3 | 44.6 |
| Crawford | 37.8 | 35.9 | 44.2 | 41.7 |
| York | 33.9 | 34.7 | 40.8 | 38.6 |
| Forrest | 38.2 | 37.1 | 44.9 | 40.3 |
| Gail | 35.4 | 38.5 | 39.5 | 39.4 |
| LSD (0.05) = 3.5 | | | | |

With foliar Fe fertilization, total N concentration in leaves of Essex was higher than observed in York, Gail, and Forrest cultivars. There were no differences in total N concentration in leaves of Essex and Crawford or among York, Gail, and Forrest cultivars.

Data in Table 8 indicate there was a higher Mn concentration in leaves of York, Forrest, and Gail than in the other cultivars grown in Quinlan soil without foliar Fe fertilization. Forrest grown in Quinlan soil with foliar Fe fertilization contained higher Mn in leaves than all other cultivars; whereas, the lowest Mn concentration in leaves was observed in the York cultivar. In McLain soil, Crawford had a lower Mn concentration in leaves than the other cultivars without foliar Fe fertilization.

TABLE 8

Manganese concentration in leaves at the flowering stage of soybeans with and without foliar Fe fertlization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| | $g\ kg^{-1}$ | | | |
| Essex | 0.12 | 0.12 | 0.08 | 0.07 |
| Crawford | 0.12 | 0.12 | 0.07 | 0.07 |
| York | 0.13 | 0.11 | 0.08 | 0.08 |
| Forrest | 0.13 | 0.13 | 0.08 | 0.07 |
| Gail | 0.13 | 0.12 | 0.08 | 0.07 |

LSD (0.05) = 0.01

But with foliar Fe fertilization, Mn concentration in leaves of York was higher than in leaves of all other cultivars. Even though there were differences in Mn concentration in soybean leaves with respect to foliar Fe fertilization and soils, the Mn concentrations were not excessively high.

In Quinlan soil without foliar Fe fertilization, Essex was lower in Ca concentration in leaves than all other cultivars (Table 9). There were no differences in Ca concentration in leaves of Crawford and Gail cultivars; however, both were lower than observed in leaves of York and Forrest. Calcium concentration in leaves was higher in York than in all other cultivars. In McLain soil without foliar Fe fertilization, Ca concentration was higher in leaves of York than in all other cultivars. There were no differences in Ca concentration among leaves of Essex, Crawford, Forrest, and Gail cultivars. In Quinlan soil with foliar Fe fertilization, Ca concentration was highest in leaves of York. Calcium concentration in leaves of Gail was lower than in leaves of Essex and Forrest cultivars. In McLain soil with foliar Fe fertilization, Ca concentration was lowest in Essex and highest in York cultivars. There were no differences in Ca concentration of leaves among Crawford, Forrest, and Gail cultivars.

TABLE 9

Calcium concentration in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| | ------------- g $kg^{-1}$ | -------------- | | |
| Essex | 13.1 | 14.3 | 11.8 | 10.8 |
| Crawford | 14.4 | 13.4 | 12.4 | 13.1 |
| York | 17.2 | 17.2 | 14.2 | 15.8 |
| Forrest | 15.8 | 14.1 | 12.5 | 13.3 |
| Gail | 14.7 | 13.1 | 11.9 | 13.3 |

LSD (0.05) = 0.9

## Nutrient Ratios

There were no differences in P/Fe ratio in leaves of soybeans grown in Quinlan soil, regardless of whether or not foliar Fe was applied (Table 10). However in McLain soil, the P/Fe ratio in leaves of Forrest were higher with and without foliar Fe fertlization than all other cultivars. There were no differences of P/Fe ratios in leaves of Essex, Crawford, York, and Gail cultivars.

TABLE 10

Phosphorus to iron ratio in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| Essex | 10.7 | 6.6 | 24.0 | 21.9 |
| Crawford | 12.9 | 9.4 | 28.0 | 24.2 |
| York | 11.5 | 7.5 | 25.7 | 21.9 |
| Forrest | 13.4 | 10.0 | 39.5 | 37.8 |
| Gail | 9.8 | 6.5 | 26.2 | 20.8 |

LSD (0.05) = 4.9

The Mn/Fe ratio in leaves of York was higher than in Essex when grown in Quinlan soil without foliar Fe fertilization. With foliar Fe fertilization in McLain soil, the Mn/Fe ratio in leaves of Crawford was higher than in leaves of Essex and Gail cultivars (Table 11).

There were no other differences in Mn/Fe ratios in leaves of other cultivars within soils regardless of whether or not foliar Fe was applied.

TABLE 11

Manganese to iron ratio in leaves at the flowering stage of soybeans with and without foliar Fe fertilization.

| | Quinlan | | McLain | |
|---|---|---|---|---|
| Cultivar | -Fe | +Fe | -Fe | +Fe |
| Essex | 1.09 | 0.52 | 0.55 | 0.38 |
| Crawford | 1.13 | 0.60 | 0.49 | 0.50 |
| York | 1.21 | 0.61 | 0.59 | 0.39 |
| Forrest | 1.11 | 0.61 | 0.52 | 0.48 |
| Gail | 1.15 | 0.63 | 0.59 | 0.38 |

LSD (0.05) = 0.12

# DISCUSSION

Differences in Fe chlorosis score among the five soybean cultivars grown in both soils were related to the different tolerances of these cultivars to Fe chlorosis (Brown and Holmes, 1956; Brown and Jones, 1977; and Byron and Lambert, 1983).

Chlorosis score and the chlorophyll concentration are associated with each other in most of the cultivars grown in the two soils without foliar Fe fertilization. De Cianzio et al. (1979) reported that both visual score and chlorophyll concentration were efficient methods for direct comparisons of the response of soybean cultivars to Fe chlorosis.

Nonassociation of the chlorosis score and the chlorophyll concentration with foliar Fe fertilization was mainly caused by the burn effect of the Fe fertilizer.

High soil pH, high $CaCO_3$, and low DTPA extractable Fe concentration in Quinlan soil were believed to be the causative factors for chlorosis development in most of the soybean cultivars grown in this soil (Boxma, 1972; Froehlich and Fehr, 1981; Inskeep and Bloom, 1984; and Wallace et al., 1976).

High P and $HCO_3^-$ concentration of McLain soil might be considered as the main reasons for chlorosis development in some soybean cultivars grown in this soil (Brown and Tiffin, 1960; Brown et al., 1959; Chaney and Coulombe, 1982; Hale and Wallace, 1960; Inskeep and Bloom, 1984; Tiffin et al., 1960; and Wallace et al., 1978).

However, because the Fe concentrations in leaves of the chlorotic and nonchlorotic soybean cultivars grown in the same soil were the same, it is possible to conclude that inactivation of Fe inside the plant tissue or different Fe requirements of different soybean cultivars were the direct reasons for Fe chlorosis (Brown and Jones, 1962; Elgala and Maier, 1964; Perur, 1960; Perur et al., 1961; and Wallace et al., 1976).

Since the previous causative factors were reported as being attributed to the nutrient differences in the plant tissue and the difference in the metabolical and physiological properties among plant cultivars, it is possible to state the following:

(a) The nonassociation of the total N concentration and the chlorosis score in soybean cultivars grown in the same soil was not related to the Fe concentration of leaves of plants because Fe chlorosis had little effect on the total protein content of the chlorotic plants (Perur, 1960; and Smith et al., 1950).

(b) The higher Mn concentration in leaves of the York cultivar grown in both soils, the higher Mn/Fe ratio in the same cultivar grown in Quinlan soil, and the higher Mn concentration in leaves of the Gail cultivar grown in Quinlan soil might be a causative factor for Fe chlorosis development in those cultivars (Brown and Jones, 1962; Olomu and Racz, 1974; Olsen and Watanabe, 1979; and Vretta-Kouskoleka and Kallinis, 1968).

(c) According to Bassire et al., 1979; Brown et al., 1959; Chaney and Coulombe, 1982; De Kock, 1955; Inskeep and Bloom, 1984; Patel et al., 1976; Procopiou and Wallace, 1982; and Watanabe et al., 1965, a good indication for Fe chlorosis development in Forrest cultivar grown in both soils is the high P concentration and P/Fe ratio in the plant leaves.

(d) The appearance of high Ca concentrations in most of the chlorotic cultivars grown in the two soils might be considered as another factor for chlorosis development (Brown and Jones, 1962). However, this finding does not agree with reports of other investigators (Procopiou and Wallace, 1982; and Smith et al., 1950); therefore, more investigation is required to determine specifically the influence of Ca on Fe chlorosis in cultivars grown under different experimental conditions.

(e) The lack of differences in other nutrient concentrations or variable nutrient ratios in the leaves of the Crawford cultivar might be considered as good reason for the moderate tolerance of this variety to Fe chlorosis. Also, the lack of differences in other nutrient concentrations and ratios among the chlorotic and the non-chlorotic cultivars grown in the same soil are good indications of the lack of effect of the other nutrients on Fe chlorosis development under these experimental conditions.

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# APPENDIX

## CHLOROSIS SCORE, CHLOROPYLL AND NUTRIENT CONCENTRATIONS IN LEAVES

Key:

Cultivar 1 = Essex
Cultivar 2 = Crawford
Cultivar 3 = York
Cultivar 4 = Forrest
Cultivar 5 = Gail

Soil Type 1 = Quinlan cl
Soil Type 2 = McLain Sicl

Fertility Level 1 = 0.2 kg Fe $ha^{-1}$
Fertility Level 2 = 0.0 kg Fe $ha^{-1}$

Chlors = chlorosis
Chlorphl = chlorophyll in ppm
ppm = part per million
pct = percentage
T-N = total nitrogen
P-Fe = P/Fe
Mn-Fe = Mn/FE

| OBS | BLOCK | VARIETY | SOILTYPE | FERTTYPE | CHLORS | CHLORPHL | FE_PPM | P_PPM | T_N_PCT | MN_PPM | CA_PCT | P_FE | MN_FE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 1 | 1 | 90 | 270 | 1640 | 3 76 | 115 | 1.44 | 6.07 | 0.47 |
| 2 | 2 | 1 | 1 | 1 | 1 | 90 | 240 | 1320 | 3 31 | 118 | 1 45 | 5 50 | 0 53 |
| 3 | 3 | 1 | 1 | 1 | 1 | 82 | 214 | 1800 | 3 67 | 125 | 1 41 | 8 41 | 0.61 |
| 4 | 4 | 1 | 1 | 1 | 1 | 90 | 210 | 1360 | 3 35 | 120 | 1.40 | 6.48 | 0.60 |
| 5 | 1 | 1 | 1 | 2 | 1 | 85 | 132 | 1360 | 3 56 | 122 | 1 28 | 10 30 | 1 08 |
| 6 | 2 | 1 | 1 | 2 | 1 | 97 | 100 | 1240 | 4 02 | 124 | 1 32 | 12 40 | 1.44 |
| 7 | 3 | 1 | 1 | 2 | 2 | 84 | 128 | 1280 | 3 45 | 126 | 1.25 | 10.00 | 1.11 |
| 8 | 4 | 1 | 1 | 2 | 2 | 95 | 98 | 1000 | 3 74 | 120 | 1.38 | 10.20 | 1.53 |
| 9 | 1 | 1 | 2 | 1 | 1 | 115 | 198 | 3520 | 4 51 | 70 | 1.13 | 17.78 | 0 35 |
| 10 | 2 | 1 | 2 | 1 | 1 | 115 | 212 | 4720 | 4.55 | 72 | 1 02 | 22.26 | 0.34 |
| 11 | 3 | 1 | 2 | 1 | 1 | 113 | 182 | 5160 | 4.93 | 76 | 1 01 | 28.35 | 0.42 |
| 12 | 4 | 1 | 2 | 1 | 1 | 95 | 174 | 3320 | 3.84 | 68 | 1.14 | 19.08 | 0.39 |
| 13 | 1 | 1 | 2 | 2 | 1 | 120 | 120 | 3120 | 4.70 | 70 | 1.13 | 26 00 | 0 58 |
| 14 | 2 | 1 | 2 | 2 | 1 | 130 | 176 | 3880 | 4.71 | 80 | 1.23 | 22 05 | 0.45 |
| 15 | 3 | 1 | 2 | 2 | 1 | 98 | 128 | 3040 | 4 54 | 74 | 1.18 | 23.75 | 0 58 |
| 16 | 4 | 1 | 2 | 2 | 1 | 120 | 130 | 3160 | 4 68 | 78 | 1.16 | 24.31 | 0.60 |
| 17 | 1 | 2 | 1 | 1 | 2 | 46 | 180 | 1480 | 3 86 | 114 | 1.34 | 8 22 | 0 52 |
| 18 | 2 | 2 | 1 | 1 | 2 | 58 | 196 | 2280 | 3 90 | 118 | 1.35 | 11.63 | 0.50 |
| 19 | 3 | 2 | 1 | 1 | 2 | 56 | 234 | 2160 | 3 51 | 122 | 1 25 | 9 23 | 0.44 |
| 20 | 4 | 2 | 1 | 1 | 2 | 56 | 180 | 1520 | 3 10 | 116 | 1.43 | 8.44 | 0.55 |
| 21 | 1 | 2 | 1 | 2 | 1 | 71 | 120 | 1360 | 4 03 | 116 | 1.46 | 11.33 | 0.97 |
| 22 | 2 | 2 | 1 | 2 | 3 | 52 | 100 | 1480 | 3 63 | 122 | 1 53 | 14 80 | 1.22 |
| 23 | 3 | 2 | 1 | 2 | 3 | 78 | 110 | 1400 | 3 92 | 120 | 1 43 | 12.73 | 1.09 |
| 24 | 4 | 2 | 1 | 2 | 3 | 52 | 108 | 1360 | 3 55 | 134 | 1.33 | 12.59 | 1.24 |
| 25 | 1 | 2 | 2 | 1 | 1 | 97 | 134 | 3720 | 4.18 | 76 | 1.36 | 27 76 | 0.57 |
| 26 | 2 | 2 | 2 | 1 | 1 | 95 | 178 | 4640 | 4 48 | 66 | 1.25 | 26.07 | 0 37 |
| 27 | 3 | 2 | 2 | 1 | 2 | 88 | 168 | 2820 | 3 90 | 86 | 1.33 | 16 79 | 0.51 |
| 28 | 4 | 2 | 2 | 1 | 1 | 90 | 130 | 3400 | 4 10 | 70 | 1 28 | 26 15 | 0.54 |
| 29 | 1 | 2 | 2 | 2 | 1 | 140 | 160 | 3800 | 4.69 | 72 | 1 19 | 23.75 | 0.46 |
| 30 | 2 | 2 | 2 | 2 | 2 | 95 | 130 | 3520 | 4.29 | 60 | 1.25 | 27 08 | 0.68 |
| 31 | 3 | 2 | 2 | 2 | 1 | 110 | 146 | 5040 | 4 35 | 72 | 1.22 | 34.52 | 0 56 |
| 32 | 4 | 2 | 2 | 2 | 2 | 90 | 132 | 3520 | 4 34 | 74 | 1.30 | 26.67 | 0 61 |
| 33 | 1 | 3 | 1 | 1 | 3 | 44 | 210 | 1200 | 3 76 | 132 | 1.70 | 5 71 | 0.63 |
| 34 | 2 | 3 | 1 | 1 | 3 | 49 | 198 | 1600 | 3.28 | 124 | 1.60 | 8.08 | 0.63 |
| 35 | 3 | 3 | 1 | 1 | 3 | 49 | 202 | 1560 | 3 65 | 104 | 1.80 | 7.72 | 0 51 |
| 36 | 4 | 3 | 1 | 1 | 3 | 51 | 196 | 1640 | 3 19 | 130 | 1.79 | 8.37 | 0.66 |
| 37 | 1 | 3 | 1 | 2 | 4 | 62 | 112 | 1200 | 3 29 | 148 | 1.71 | 10.71 | 1.32 |
| 38 | 2 | 3 | 1 | 2 | 3 | 62 | 106 | 1480 | 3 03 | 140 | 1.78 | 13 96 | 1.32 |
| 39 | 3 | 3 | 1 | 2 | 3 | 64 | 128 | 1280 | 3 86 | 116 | 1.64 | 10.00 | 0.91 |
| 40 | 4 | 3 | 1 | 2 | 3 | 49 | 102 | 1160 | 3.36 | 130 | 1.76 | 11.37 | 1.27 |
| 41 | 1 | 3 | 2 | 1 | 2 | 63 | 188 | 5280 | 3.93 | 68 | 1 63 | 28.09 | 0 36 |
| 42 | 2 | 3 | 2 | 1 | 2 | 66 | 194 | 4600 | 3 77 | 68 | 1.63 | 23 71 | 0.35 |
| 43 | 3 | 3 | 2 | 1 | 2 | 72 | 208 | 3560 | 3 84 | 66 | 1.54 | 17.12 | 0.32 |
| 44 | 4 | 3 | 2 | 1 | 2 | 77 | 188 | 3520 | 3 89 | 60 | 1 52 | 18 72 | 0.32 |
| 45 | 1 | 3 | 2 | 2 | 2 | 95 | 164 | 4120 | 4 16 | 80 | 1 31 | 25.12 | 0.44 |
| 46 | 2 | 3 | 2 | 2 | 1 | 110 | 138 | 3640 | 4 24 | 82 | 1 33 | 26 38 | 0.43 |
| 47 | 3 | 3 | 2 | 2 | 2 | 92 | 150 | 3120 | 3 93 | 88 | 1 48 | 20.80 | 0.48 |
| 48 | 4 | 3 | 2 | 2 | 3 | 84 | 110 | 3360 | 3 97 | 74 | 1 54 | 30 55 | 0 67 |
| 49 | 1 | 4 | 1 | 1 | 2 | 68 | 232 | 2240 | 3.89 | 134 | 1.44 | 9.66 | 0 58 |
| 50 | 2 | 4 | 1 | 1 | 1 | 85 | 204 | 2080 | 3 72 | 120 | 1 35 | 10.20 | 0.59 |
| 51 | 3 | 4 | 1 | 1 | 1 | 63 | 224 | 2000 | 3 45 | 128 | 1.38 | 8 93 | 0 57 |
| 52 | 4 | 4 | 1 | 1 | 2 | 70 | 190 | 2160 | 3 78 | 130 | 1 45 | 11.37 | 0 68 |
| 53 | 1 | 4 | 1 | 2 | 3 | 60 | 104 | 1400 | 3 64 | 120 | 1 62 | 13.46 | 1 06 |
| 54 | 2 | 4 | 1 | 2 | 3 | 60 | 120 | 1640 | 3 93 | 124 | 1 52 | 13.67 | 0 87 |
| 55 | 3 | 4 | 1 | 2 | 3 | 68 | 116 | 1360 | 3 66 | 130 | 1 60 | 11 72 | 1 07 |
| 56 | 4 | 4 | 1 | 2 | 4 | 73 | 116 | 1720 | 4 03 | 132 | 1.56 | 14 83 | 1.14 |

| OBS | BLOCK | VARIETY | SOILTYPE | FERTTYPE | CHLORS | CHLORPHL | FE_PPM | P_PPM | T_N_PCT | MN_PPM | CA_PCT | P_FE | MN_FE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57 | 1 | 4 | 2 | 1 | 2 | 73 | 140 | 5680 | 3.87 | 74 | 1.28 | 40.57 | 0.53 |
| 58 | 2 | 4 | 2 | 1 | 1 | 66 | 130 | 5018 | 3.98 | 68 | 1.36 | 38.83 | 0.52 |
| 59 | 3 | 4 | 2 | 1 | 2 | 80 | 162 | 4640 | 4.15 | 70 | 1.35 | 28.64 | 0.43 |
| 60 | 4 | 4 | 2 | 1 | 2 | 84 | 146 | 6280 | 4.12 | 64 | 1.33 | 43.01 | 0.44 |
| 61 | 1 | 4 | 2 | 2 | 1 | 110 | 162 | 5040 | 4.18 | 74 | 1.34 | 31.11 | 0.46 |
| 62 | 2 | 4 | 2 | 2 | 1 | 120 | 148 | 5720 | 4.81 | 70 | 1.18 | 38.65 | 0.47 |
| 63 | 3 | 4 | 2 | 2 | 2 | 115 | 136 | 5640 | 4.24 | 82 | 1.25 | 41.47 | 0.60 |
| 64 | 4 | 4 | 2 | 2 | 1 | 125 | 134 | 6280 | 4.72 | 74 | 1.22 | 46.87 | 0.55 |
| 65 | 1 | 5 | 1 | 1 | 1 | 51 | 186 | 1360 | 4.05 | 128 | 1.43 | 7.31 | 0.53 |
| 66 | 2 | 5 | 1 | 1 | 2 | 55 | 218 | 1210 | 3.90 | 119 | 1.22 | 5.69 | 0.41 |
| 67 | 3 | 5 | 1 | 1 | 2 | 52 | 186 | 1240 | 3.84 | 122 | 1.33 | 6.67 | 0.55 |
| 68 | 4 | 5 | 1 | 1 | 2 | 56 | 201 | 1280 | 3.60 | 128 | 1.24 | 6.27 | 0.43 |
| 69 | 1 | 5 | 1 | 2 | 3 | 42 | 116 | 1000 | 3.45 | 136 | 1.40 | 8.62 | 1.17 |
| 70 | 2 | 5 | 1 | 2 | 3 | 65 | 111 | 1280 | 3.55 | 120 | 1.46 | 11.23 | 1.05 |
| 71 | 3 | 5 | 1 | 2 | 3 | 64 | 124 | 1240 | 3.91 | 130 | 1.53 | 10.00 | 1.05 |
| 72 | 4 | 5 | 1 | 2 | 3 | 56 | 110 | 1010 | 3.24 | 125 | 1.49 | 9.45 | 1.14 |
| 73 | 1 | 5 | 2 | 1 | 2 | 88 | 172 | 3760 | 4.25 | 68 | 1.45 | 21.86 | 0.40 |
| 74 | 2 | 5 | 2 | 1 | 2 | 78 | 116 | 4000 | 3.99 | 66 | 1.26 | 27.40 | 0.45 |
| 75 | 3 | 5 | 2 | 1 | 1 | 82 | 210 | 3480 | 3.72 | 72 | 1.30 | 16.57 | 0.34 |
| 76 | 4 | 5 | 2 | 1 | 1 | 63 | 204 | 3520 | 3.81 | 70 | 1.32 | 17.25 | 0.34 |
| 77 | 1 | 5 | 2 | 2 | 2 | 91 | 124 | 3120 | 3.85 | 74 | 1.18 | 25.16 | 0.60 |
| 78 | 2 | 5 | 2 | 2 | 2 | 120 | 142 | 4360 | 4.21 | 76 | 1.16 | 30.70 | 0.54 |
| 79 | 3 | 5 | 2 | 2 | 1 | 93 | 112 | 2880 | 3.68 | 80 | 1.19 | 25.71 | 0.71 |
| 80 | 4 | 5 | 2 | 2 | 1 | 103 | 142 | 3320 | 4.06 | 71 | 1.24 | 23.38 | 0.50 |

# PART II

# INFLUENCE OF P SOURCES AND RATES ON SOIL pH, EXTRACTABLE P, AND DTPA EXTRACTABLE MICRONUTRIENTS

# ABSTRACT

Phosphorus fertilization has been reported to influence micronutrient availability. Influence of applied P on extractable micronutrients depends mainly on chemical characteristics of soil and P sources. Soils in the western Great Plains are typically high in soil pH and are saturated with Ca which has a marked effect on micronutrient availability. Therefore, the objectives of this study were to determine the effect of different P sources and rates on (a) soil pH (b) Bray and Kurtz No. 1 P and (c) DTPA extractable Fe, Mn, Zn, and Cu.

Two soils (Quinlan clay loam - Typic Ustocrept and McLain silty clay loam - Pachic Agriustolls), which differed in micronutrient content and chemical characteristics, were collected from western Oklahoma for laboratory study. Soils were passed through a 2 mm screen and placed in plastic petridishes, and five phosphorus levels (0, 20, 40, 60 and 80 kg P $ha^{-1}$) were applied as monocalcium phosphate (MCP), monoammonium phosphate (MAP), and ammonium polyphosphate (APP) and mixed uniformly. Soils were moistened to approximately 0.033 MPa and incubated for two months at room temperature.

Phosphorus sources in both soils decreased soil pH, but APP decreased soil pH more than MCP. Bray and Kurtz No. 1 P increased with P application in both soils.

In the McLain soil, MCP and MAP decreased DTPA extactable Fe, Mn, and Cu. However, high levels of applied P as APP increased DTPA extractable Fe, Mn, and Cu. DTPA extractable Zn was not affected by P application, regardless of source.

Monocalcium phosphate and MAP decreased DTPA extractable Mn in the Quinlan soil, however, high levels of applied APP increased DTPA extractable Fe. Phosphorus application did not affect DTPA extractable Zn and Cu.

Application of MAP or MCP fertilizer to McLain soil decreased DTPA extractable Fe and increased P/Fe ratio, but application of high levels of APP fertilizer increased DTPA extractable Fe and decreased P/Fe ratio. Phosphorus fertilization caused different effects in Zn/Fe, Mn/Fe and Cu/Fe ratios, depending on P sources and soil type.

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Additional Keywords: Monocalcium phosphate, MCP, monoammonium phosphate, MAP, ammonium polyphosphate, APP, Bray and Kurtz No. 1 P, P/micronutrient ratios, micronutrient ratios, Fe, Mn, Zn, and Cu.

# INTRODUCTION

High P content of soil is one of the major factors which affect the availability of micronutrients to plants (Tisdale and Nelson, 1975; and Buckman and Brady, 1969).

Under satisfactory conditions of aeration, Fe and Mn are bound in most soils as precipitates of oxides and phosphates, while the other micronutrients appear to be regulated by reactions with minerals and organic surfaces (Hodgson, 1963).

Application of P fertilizers influence soil micronutrient status in different manners, depending on kind of fertilizer and soil characteristics. Mandal and Haldar (1980) found that applied P decreased DTPA extractable Zn, Cu, Fe, and Mn in soil. Haseman et al. (1950a, 1950b) reported that rapid fixation of P was caused by the reaction of phosphate with readily available Al and Fe and that Fe and Al phosphates were the reaction products in the soil fertilizer system. Slow precipitation reactions of K and Fe phosphates as K[Fe(OH)1.33)]3.-$(H_2PO_4)_6$. $2H_2O$ and (Fe-K-tarankite) occurred mainly because of reactions of P with Fe and K ions in the soil solution (Kim et al., 1983).

Ryan et al. (1985) pointed out that the amount of amorphous or acid oxalate Fe significantly influenced the loss of P from the solution of P treated soil. Harter (1969) proposed that P was initially bound to anion exchange sites on soil organic matter by the substitution of the phosphate ions for the hydroxyl ions, and subsequently, transformed into less soluble Fe and Al phosphate. A decrease in available Zn, Cu, and Mn was caused by the application of P fertilizers in acid soils (Badanur and RAO., 1973). Murphy et al. (1981) reported that the availability of Zn, Fe, Cu, and Mn is low in calcareous soils and that added P can antagonize micronutrient deficiencies more easily under high pH conditions. He also noticed that a large amount of free $CaCO_3$ in soil can depress the availability of P, which would tend to mask the P-micronutrient interaction. Mortvedt and Osborn (1977) reported that soluble micronutrient concentrations in calcareous and neutral soils were not affected by P fertilizer application. They related the temporary increase in micronutrient concentrations in acid soils after the addition of ortho and polyphosphates to the solubilization of organic matter by these fertilizers.

Lindsay (1979) reported that monocalcium phosphate application released $H_3PO_4^0$ and precipitated P as dicalcium phosphate dihydrate and dicalcium phosphate. Taylor and Gurney (1965) found that calcium ferric phosphate, $CaFe_2(HPO_4)_4.5H_2O$, was the principal product of the reaction of geothite with acid calcium phosphate solution in the absence of K and a mixture of $CaHPO_4.2H_2O$ and $KFe_3\ H8(PO_4)_6.\ 6H_2O$ was formed in the presence of K.

Amer. et al., (1980) and Blanchar and Caldwell (1966) both reported that monocalcium phosphate application reduced soil pH in the fertilizer zone. The reaction of the acid fertilizer solution TPS ($Ca(H_2PO_4)_2.H_2O$, $CaHPO_4$, and $H_3PO_4$) with soil initially dissolves Fe, Al, Mn, and other constituents. But as more soil comes in contact with the solution, the pH of the solution increases and certain phosphate compounds precipitate when the solution becomes saturated with respect to these compounds (Lindsay and Stephenson, 1959). The precipitation of P and Fe in soil was caused by the formation of a colloidal ferric aluminum phosphate (Fe, Al, X)$PO_4.nH_2O$ after the application of monocalcium phosphate monhydrate $Ca(H_2PO_4)_2.H_2O$ (Lindsay et al., 1962). Application of triple superphosphate fertilizer to calcareous soils caused the accumulation of octacalcium phosphate (OCP) at a $NaHCO_3$ extractable P level 32 mg kg$^{-1}$. Below 32 mg kg$^{-1}$ of extractable P β-tricalcium phosphate (TCP) controlled P solubility (Havlin and Westfall, 1984).

Taylor et al. (1965) observed very little reaction of iron oxides (geothite) with $NH_4H_2PO_4$ solution at any pH value. An increase in soil pH and the precipitation of P as tarankite were caused by the application of monoammonium phosphate in some soils. However, adding $Fe_2O_3$.-$H_2O$ to the monoammonium phosphate treated soil caused the presence of a precipitated phase of colloidal (Fe, Al, X)$PO_4.nH_2O$ which coated the remaining $Fe_2O_3.H_2O$ particles (Lindsay et al., 1962).

Super phosphate produced a greater amount of Al phosphate than Fe and Ca phosphates (Manning and Salomon, 1965). Aluminum phosphate and lesser amounts of Fe phosphate were formed by the application of both superphosphate and polyphosphate (Miner and Kamprath, 1971; and Manning and Salomon, 1965). Due to the sequestration effect of ammonium polyphosphate, no solid Fe or Al compounds were formed by the reaction of polyphosphate with clay minerals or their impurities (Philen and Lehr, 1967). The ability of ammonium polyphosphate to sequester soil Fe and Al did not prevent the precipitation of these phosphates (Khasawneh et al., 1974). Condensed phosphate (di-, tri-, and tetraammonium pyrophosphate, and tri-, and pentaammonium tripolyphosphate) was reported to sequester all Fe and Al that were released by soil minerals; furthermore, the reaction of tripolyphosphate with soil minerals required at least a week for initiation and continued for months (Philen and Lehr, 1967). Little precipitation of $MnNH_4PO_4.H_2O$ and $Mn(NH_4)_2P_2O_7.H_2O$ occurred with low pH orthophosphate or with decreasing pyro-to orthophosphate content (Hossner and Blanchar, 1970). The limited availability of P in alkaline-calcareous soils after the addition of ammonium polyphosphate was caused by the formation of $Ca(NH_4)_2P_2O_7.H_2O$ (Subbarao and Ellis, 1975).

Richter and Matzel (1976), and Sarkar et al. (1977) reported that phosphate precipitated as tarankite in soil solution. Crystalline $CaHPO_4.2H_2O$ and trace amounts of $CaHPO_4$ were formed by $Ca(H_2PO_4)_2.H_2O$ application, while $CaHPO_4.2H_2O$, which depends on the amount of Ca present initially in the exchangable sites and the carbonate forms, was formed with $NH_4H_2PO_4$, but $Mg3(PO_4)_2.22H_2O$ and $MgNH_4PO_4.6H_2O$ were identified in a high exchangeable Mg soil after the addition of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, respectively (Bell and Black, 1970).

The relation of one micronutrient to another has been reported to be more important to plant growth than the absolute level (Tisdale and Nelson, 1975; and Dekock, 1955). Watanabe et al. (1965) reported that decreasing Fe/Zn or Fe/P ratio in calcareous soils accentuated Fe deficiency symptoms in corn plants. Fe/Mn ratio was very important in supplying Fe to sorghum plants when the Fe level supplied was about 0.5 ppm (Carlson and Olson, 1950). Olson and Carlson (1949) pointed out that exchangeable Mn and easily reducible Mn/Fe ratios were greater in soils from chlorotic than nonchlorotic sorghum.

The objectives of this study were to determine the effect of P fertilizer sources and rates on soil pH, Bray and Kurtz No. 1 P, and DTPA extractable Fe, Mn, Zn, and Cu.

# MATERIALS AND METHODS

Quinlan cl and McLain sicl soils were collected from western Oklahoma for the experiment. Basic characteristics and micronutrient concentrations of these soils are reported in Table 1.

Soils were mixed and passed through a 2 mm screen and 50 g of each soil was placed in 8 cm diameter plastic petridishes in the laboratory. Treatments consisted of five P rates, 0, 20, 40, 60, and 80 kg $ha^{-1}$, supplied with monocalcium phosphate (MCP) 0-25-0 (chemical grade), monoammonium phosphate (MAP) 12-27-0 (chemical grade), and ammonium polyphosphate (APP) 11-24-0 (commercial grade). Fertilizers are expressed in elemental form.

Treatments were arranged in a randomized complete block design with three replications. All P was mixed uniformly with soils. Deionized water was used throughout the experimental period to moisten the soils to 0.033 MPa moisture content of soils and was maintained by watering every other day.

After two months incubation at room temperature, soils were air dried, ground, mixed, and passed through a 2 mm screen and saved for analysis.

Micronutrients were extracted with DTPA (Lindsay and Norvell, 1978), soil pH was determined in 1:1 soil-$H_2O$ paste, and soil P was determined in a 1:20 soil-solution extract (Bray and Kurtz, 1945).

Table 1. Initial soil characteristics.

| Soil Type | Classification | pH | P[+] | Fe | Mn | Zn | Cu | O.M. | $CaCO_3$ |
|---|---|---|---|---|---|---|---|---|---|
| | | (1:1 $H_2O$) | ----------mg $kg^{-1}$---------- | | | | | ---mg $g^{-1}$--- | |
| McLain scl | Pachic Argiustolls | 7.7 | 110 | 8.4 | 7.5 | 0.8 | 1.1 | 23 | 20 |
| Quinlan cl | Typic Ustocrept | 8.3 | 16 | 0.7 | 8.0 | 0.6 | 0.4 | 11 | 127 |

[+] Bray and Kurtz No. 1 (1:20) P.

Significant differences among treatments were determined using orthogonal contrasts according to procedures outlined by Steel and Torrie (1960). All comparisons were made at 0.05 level of probability.

# RESULTS AND DISCUSSION

## McLain Soil

### pH, and P and micronutrient concentrations

Application of P decreased soil pH (Tables 2 and 3). Amer et al. (1980) and Blancher and Caldwell (1966) reported that monocalcium phosphate reduced soil pH in the fertilizer zone. MAP application decreased soil pH more than MCP, but APP application decreased soil pH more than MCP and MAP together.

Increased MAP, MCP and APP levels decreased soil pH linearily (Fig. 1). The small differences in soil pH depression among the different P sources were mainly caused by the differences in acidification power of P sources due to the release of $H_3PO_4^o$ and the reaction of MCP with basic cations in soil and the amount of ammonium in MAP and APP (Lindsay, 1979; Lindsay and Stephenson, 1959; and Tisdale and Nelson, 1975). This also attributed to linear and cubic interactions in pH values that were observed.

A significant increase in Bray and Kurtz No. 1 P was observed with the application of all P sources. MAP increased Bray and Kurtz No. 1 P more than MCP treatments. Since P rates were the same, different reactions and products were formed from the P sources applied to soil. The increase of Bray and Kurtz No. 1 P by APP more than observed with MCP plus MAP treatments suggested the formation of $CaHPO_4.2H_2O$ crystals or colloidal ferric aluminum phosphate by monocalcium phosphate. However, the formation of $CaHPO_4.2H_2O$, which depends on exchangeable Ca and carbonate forms, or the precipitation of P as tarankite can account for P fixation with MAP (Bell and Black, 1970; and Lindsay et al., 1962). All P sources induced a linear increase in Bray and Kurtz No. 1 P (Fig. 1), which was good indication of the identical retention of different P sources by this soil. However, the quadratic effect of MCP application on Bray and Kurtz No. 1 P suggested high retention of P at low MCP rates which might be related to the formation of OCP (Havlin and Westfall, 1984) and the change in the chemical properties of the soil system. A quadratic interaction in Bray and Kurtz No. 1 P among P sources and levels was caused by different behavior of P sources in soil.

Application of P decreased extractable Fe, Mn and Cu (Mandal and Haldar, 1980; Kim et al., 1983). MCP treatments decreased extractable Fe, Mn and Cu more than MAP, which was good indication of the dissociation and precipitation of Fe, Mn, and Cu or the formation of colloidal ferric aluminum phosphate by both MCP and MAP (Lindsay and Stephenson, 1959; Haseman et al., 1950a, 1950b; Lindsay et al., 1962). MAP decreased soil pH more than MCP.

The increase of extractable Fe, Mn, and Cu by APP over MCP plus MAP was mainly caused by the sequestration effect of APP and the solubilization of soil organic matter by either the formed ortho or the original polyphosphates (Philen and Lehr, 1967; and Khasawneh et al., 1974).

Increased MCP levels induced a cubic and linear increase in extractable Zn and Cu, respectively (Table 3, Fig. 2). Increased levels of MAP induced a linear increase in extractable Fe, Mn, and cubic increase in extractable Fe and Cu (Table 3, Fig. 2 and 3), which might be related to the uniform soil pH decrease and the effect of soil organic matter. However, the linear and cubic increase in extractable Fe, Mn and Cu and quadratic increase in extractable Cu by APP might be related to the APP level and the time required for APP transformation and sequestration of Fe and Mn in soil. In addition it could be related to the limited ability of APP to solubilize soil organic matter and decrease extractable Cu after P application (Philen and Lehr, 1967; Mortvedt and Obsorn, 1977).

The similarity between MCP and APP and the nonsimilarity between MAP and the other source effects on extractable Cu suggested solubilization of soil organic matter may have occurred. In addition to the decrease in pH by MAP application and the sequestration influence of APP.

A linear cubic and quadratic interaction in extractable Fe, Mn, and Cu, respectively, was observed and was caused by different reactions of P sources and levels in soil.

## Nutrient Ratios

A higher P/Fe ratio was obtained in P treated soil than nontreated soil, and in MCP than MAP treatments (Tables 2 and 3), due to the decrease of extractable Fe and the increase of Bray and Kurtz No. 1 P. The lower P/Fe ratio with APP than MCP plus MAP treatments was caused by the increase in extractable Fe by APP application. Increased MCP levels caused a linear increase in P/Fe ratio, while increasing APP Levels caused a linear and cubic decrease in P/Fe ratio. Linear interaction in P/Fe ratio was observed with different sources and levels of P.

Phosphorus application caused lower Mn/Fe ratios in the treated than the nontreated soils due to the decrease in extractable Mn. The higher Mn/Fe ratio with APP treatments than MCP plus MAP treatments was caused by the increase of the extractable Mn with APP application. A linear and cubic increase and interaction in Mn/Fe ratio was caused by increased APP levels and different P sources, respectively.

Application of P caused an increase in Zn/Fe ratios due to the decrease in extractable Fe. A decrease in Zn/Fe ratio was caused by MAP and APP over MCP treatments and MCP plus MAP treatments, respectively, due to the lower decrease in Bray and Kurtz No. 1 P by MAP over MCP and the increase of extractable Fe by APP application. A linear decrease in Zn/Fe ratios was caused by MAP and APP application due to the increase in extractable Fe with increasing MAP and APP levels. The cubic increase and the linear and cubic interaction in Zn/Fe ratios was caused by increased MCP levels and P sources, respectively.

Cu/Fe ratios were lower in P treated soils than nontreated soils due to the decrease of extractable Cu by P application. Increased MAP levels induced a linear decrease in Cu/Fe ratios, while increasing APP levels induced both linear and quadratic decreases in Cu/Fe ratios which were mainly due to the increase of extractable Fe with increasing MAP and APP levels. Different P sources and levels induced a linear and cubic interaction in Cu/Fe ratios.

Table 2. Influence of P sources and rates on soil pH, P, and micronutrient concentrations and ratios in McLain soil.

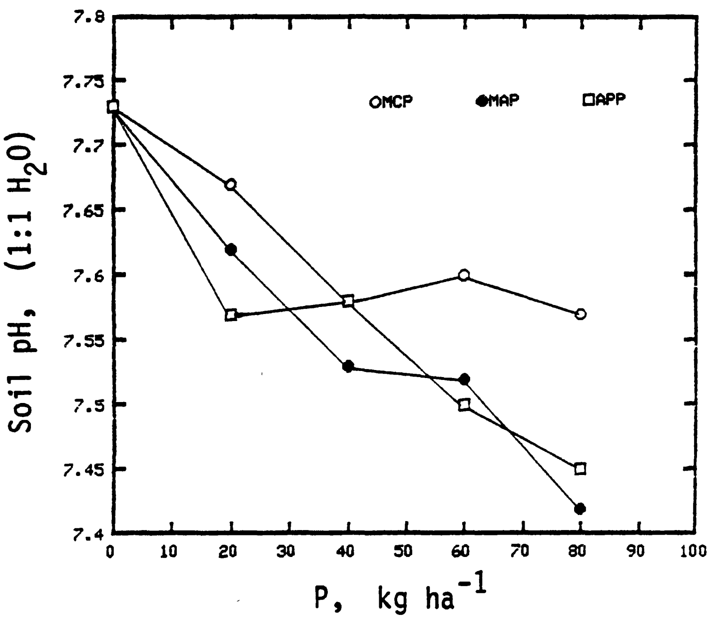
| Sources | P Rate | pH | P | Fe | Mn | Zn | Cu | P/Fe | Mn/Fe | Zn/Fe | Cu/Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | kg ha$^{-1}$ | | mg kg$^{-1}$ | | | | | | | | |
| Check | 0 | 7.73 | 113 | 8.4 | 7.5 | 0.85 | 1.06 | 13.5 | 0.89 | 0.10 | 0.13 |
| MCP | 20 | 7.67 | 119 | 7.5 | 4.3 | 0.85 | 0.89 | 15.8 | 0.58 | 0.11 | 0.12 |
| MCP | 40 | 7.58 | 119 | 7.5 | 4.3 | 0.87 | 0.90 | 15.9 | 0.58 | 0.12 | 0.12 |
| MCP | 60 | 7.60 | 128 | 7.5 | 4.4 | 0.85 | 0.92 | 17.0 | 0.59 | 0.11 | 0.12 |
| MCP | 80 | 7.57 | 137 | 7.7 | 4.6 | 0.88 | 0.93 | 17.8 | 0.59 | 0.11 | 0.12 |
| MCP $\bar{x}$ | | 7.61 | 126 | 7.56 | 4.4 | 0.86 | 0.91 | 16.3 | 0.59 | 0.11 | 0.12 |
| MAP | 20 | 7.62 | 118 | 7.5 | 4.5 | 0.83 | 0.94 | 15.7 | 0.60 | 0.11 | 0.13 |
| MAP | 40 | 7.53 | 123 | 7.8 | 4.6 | 0.84 | 0.93 | 15.8 | 0.60 | 0.11 | 0.12 |
| MAP | 60 | 7.52 | 131 | 8.3 | 4.8 | 0.85 | 0.98 | 15.7 | 0.57 | 0.10 | 0.12 |
| MAP | 80 | 7.42 | 137 | 8.4 | 4.9 | 0.86 | 0.96 | 16.4 | 0.58 | 0.10 | 0.11 |
| MAP $\bar{x}$ | | 7.52 | 127 | 8.0 | 4.7 | 0.85 | 0.95 | 15.9 | 0.59 | 0.11 | 0.12 |
| APP | 20 | 7.57 | 121 | 7.8 | 4.9 | 0.87 | 0.96 | 15.4 | 0.63 | 0.11 | 0.12 |
| APP | 40 | 7.58 | 125 | 8.2 | 5.0 | 0.85 | 0.99 | 15.3 | 0.61 | 0.10 | 0.12 |
| APP | 60 | 7.50 | 129 | 9.3 | 7.3 | 0.87 | 1.08 | 13.9 | 0.78 | 0.10 | 0.11 |
| APP | 80 | 7.45 | 137 | 9.6 | 7.3 | 0.87 | 1.03 | 14.3 | 0.76 | 0.09 | 0.10 |
| APP $\bar{x}$ | | 7.53 | 128 | 8.7 | 6.1 | 0.87 | 1.02 | 14.7 | 0.70 | 0.10 | 0.13 |

Table 3. Analysis of variance and orthogonal contrasts of the effects of P sources and rates on soil pH, P, and micronutrient concentrations and ratios in McLain soil.

| Sources[+] | df | F-Value | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | P | Fe | Mn | Zn | Cu | P/Fe | Mn/Fe | Zn/Fe | Cu/Fe |
| Block | 2 | 1.21 | 2.30 | 0.08 | 1.71 | 0.70 | 0.88 | 1.03 | 1.07 | 0.58 | 0.16 |
| Treatment | 12 | 21.30*** | 66.66*** | 69.71*** | 144.53*** | 1.34 | 22.74*** | 29.74*** | 57.94*** | 15.03*** | 4.55*** |
| Orthogonal Contrasts | | | | | | | | | | | |
| Check vs. others | 1 | 92.19*** | 171.99*** | 12.63** | 518.97*** | 0.03 | 63.64*** | 99.61*** | 382.43*** | 9.29** | 9.47** |
| MCP vs. MAP | 1 | 41.27*** | 4.53* | 57.71*** | 16.53*** | 1.69 | 23.68*** | 22.94*** | 0.20 | 31.45*** | 0.25 |
| MCP + MAP vs. APP | 1 | 11.14** | 6.72* | 357.1*** | 641.01*** | 2.39 | 118.81*** | 137.47*** | 176.31*** | 60.39*** | 6.84 |
| MCP linear | 1 | 11.93** | 214.65*** | 4.19 | 3.58 | 1.13 | 6.06* | 50.42*** | 0.72 | 1.13 | 0.00 |
| MAP linear | 1 | 56.50*** | 219.05*** | 73.87*** | 6.69* | 1.97 | 2.97 | 3.79 | 2.51 | 15.22*** | 8.21** |
| APP linear | 1 | 27.90*** | 150.28*** | 299.19*** | 442.74*** | 0.06 | 29.34*** | 22.69*** | 90.41*** | 50.32*** | 19.85*** |
| MCP quadratic | 1 | 1.86 | 21.90*** | 2.45 | 0.54 | 1.17 | 0.08 | 2.21 | 0.02 | 0.63 | 0.00 |
| MAP quadratic | 1 | 0.21 | 1.01 | 1.60 | 0.02 | 0.01 | 0.08 | 2.16 | 0.26 | 0.63 | 0.51 |
| APP quadratic | 1 | 3.30 | 4.02 | 0.20 | 0.05 | 0.29 | 12.80** | 1.82 | 0.06 | 0.00 | 8.10** |
| MCP cubic | 1 | 3.34 | 4.38* | 0.00 | 0.01 | 6.83* | 0.00 | 1.84 | 0.08 | 10.19** | 0.00 |
| MAP cubic | 1 | 3.34 | 1.10 | 5.08* | 0.14 | 0.02 | 4.38* | 1.10 | 0.63 | 1.13 | 0.91 |
| APP cubic | 1 | 2.64 | 0.36 | 22.49*** | 104.12*** | 0.53 | 11.05** | 10.82** | 41.63*** | 0.00 | 0.41 |
| P Source * levels | 6 | 3.55* | 2.50 | 22.13*** | 50.43*** | 1.20 | 3.66** | 13.60*** | 16.46*** | 3.98** | 3.10* |
| Orthogonal Contrasts | | | | | | | | | | | |
| Interaction linear | 2 | 4.14* | 2.03 | 58.52*** | 117.95*** | 0.36 | 3.82** | 35.39*** | 33.99*** | 9.10** | 5.10* |
| Interaction quadratic | 2 | 2.54 | 3.61* | 2.12 | 0.20 | 0.24 | 4.34** | 0.01 | 0.10 | 0.21 | 3.55* |
| Interaction cubic | 2 | 3.98* | 1.84 | 5.75** | 33.15*** | 3.0 | 2.82 | 5.40 | 15.28*** | 2.64* | 0.64 |
| Error mean square | 24 | 0.0010 | 2.9829 | 0.02066 | 0.03 | 0.0007 | 0.0004 | 0.1419 | 0.00052 | 0.0000133 | 0.000016 |
| C.V.% | | 0.42 | 1.37 | 1.77 | 3.29 | 3.12 | 2.17 | 2.42 | 3.55 | 3.43 | 3.39 |

*, **, ***, Significant at .05 or 0.01 or 0.001 probability levels, respectively.

[+] MCP, MAP, APP refers to monocalcium phosphate, monoammonium phosphate and ammonium polyphospahte, respectively.



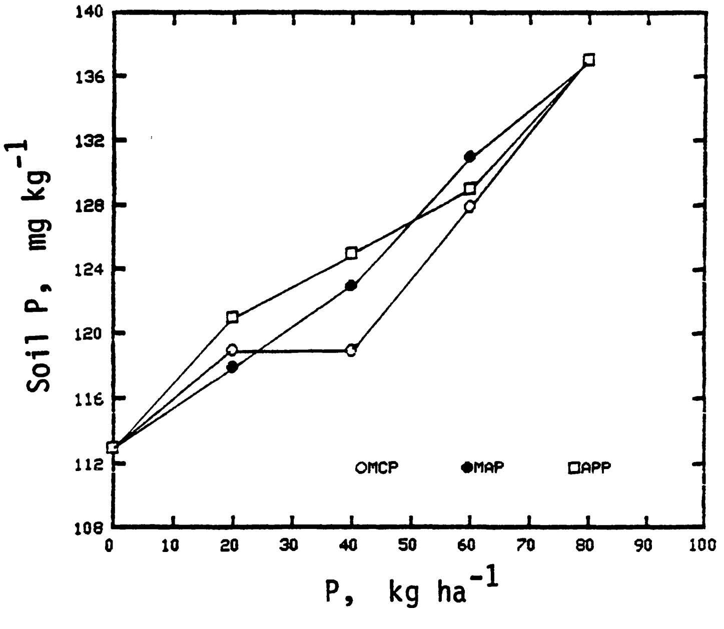


Fig. 1. Influence of P sources and rates on soil pH and Bray and Kurtz No. 1 P in McLain soil.

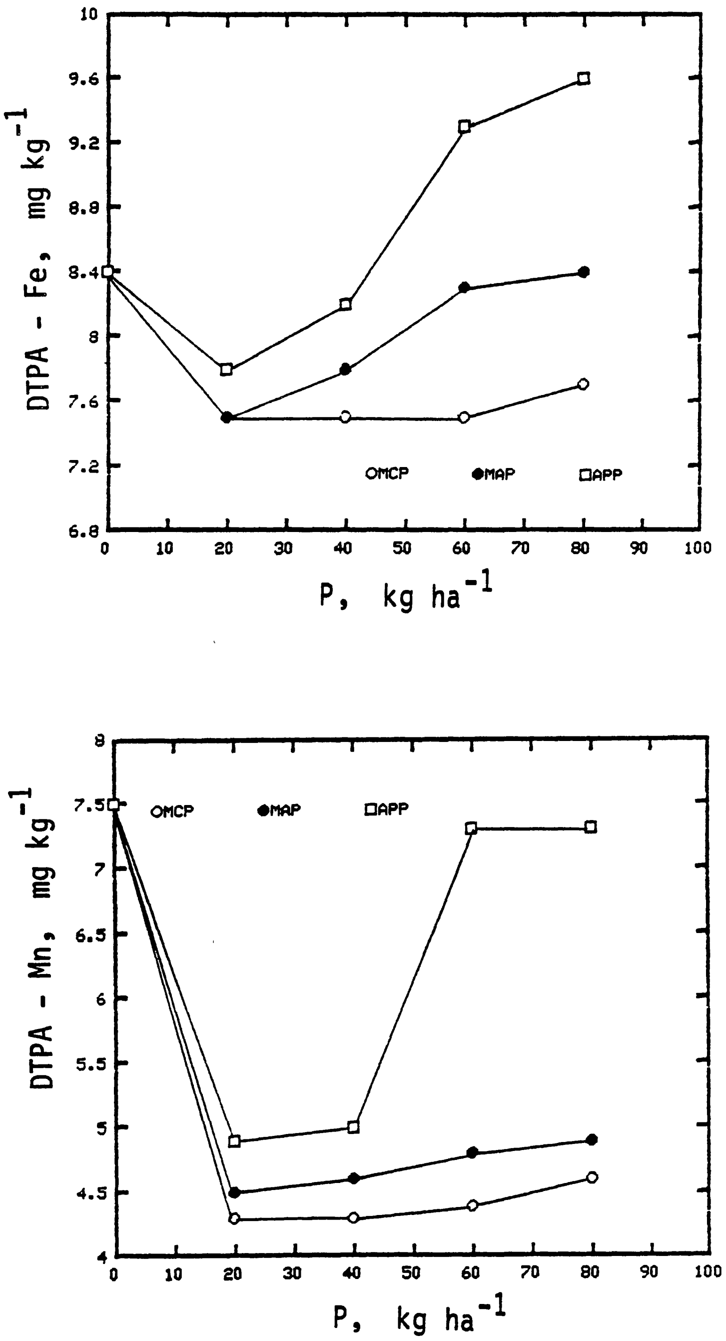


Fig. 2. Influence of P sources and rates on DTPA extractable iron and manganese in McLain soil.

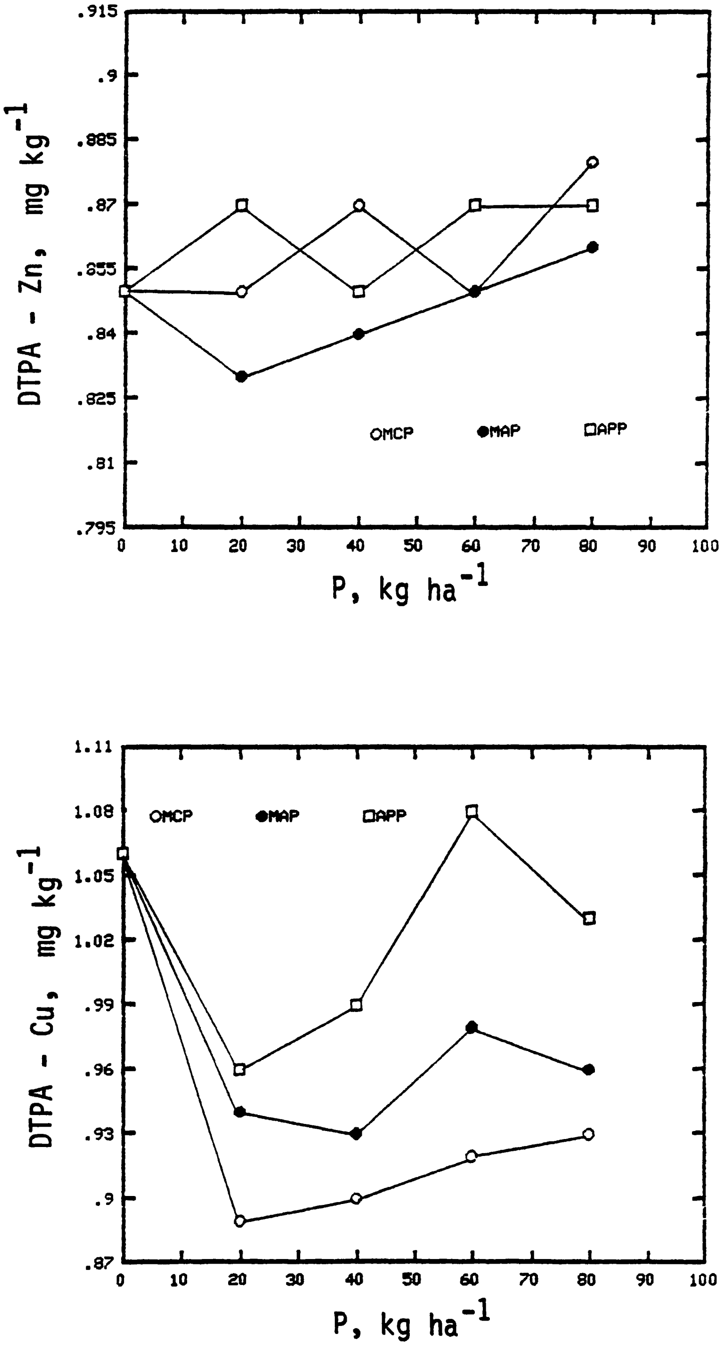


Fig. 3. Influence of P sources and rates on DTPA extractable zinc and copper in McLain soil.

## Quinlan Soil

### pH, and P and micronutrient concentrations

Phosphorus application decreased soil pH (Tables 4 and 5). MAP application induced lower pH than MCP, and APP application induced lower pH than MCP plus MAP treatments. A linear decrease in soil pH was caused by increased MAP and APP levels (Fig. 4). The nature of the chemical reaction and proton donation of P sources in soil was the reason for different pH depression by the different P sources (Lindsay and Stephenson, 1959; and Tisdale and Nelson, 1975). Linear interaction in soil pH was caused by different P sources and levels, due to the different reactions and products of P sources in soil.

Increased Bray and Kurtz No. 1 P in P treated soils compared to the untreated soils was induced by all P sources (Tables 4 and 5). MAP induced higher Bray and Kurtz No. 1 P than MCP treatments; this finding suggested the precipitation of P as DCPD, DCP, OCP and TCP with MCP and as $Ca(NH_4)_2P_2O_7.2H_2O$ with APP (Lindsay, 1979; Bell and Black, 1970; Havlin and Westfall, 1984; and Subbarao and Ellis, 1975). All P sources induced a linear increase in Bray and Kurtz No. 1 P with increasing P levels (Fig. 4). High $CaCO_3$ content of soil is the main reason for P fixation or retention (Murphy et al., 1981).

The nonsignificant effect of MCP and MAP application on DTPA extractable Zn, and Cu (Table 5) suggested that high $CaCO_3$ concentration and high soil pH are the main causative factors (Mortvedt and Osborn, 1977). APP application induced higher extractable Fe than MCP plus MAP treatments, due to the sequestration effect of APP (Philen and Lehr, 1967; Khasawneh et al., 1974). Increased levels of APP caused a linear increase in extractable Fe, and increased levels of MAP caused a cubic decrease in extractable Fe (Fig. 5), which might be caused by the Fe sequestration and solubilization of O.M. by APP and the precipitation of Fe by MAP application (Philen and Lehr, 1967; Lindsay et al. 1962; Bell and Black, 1970). A linear and cubic interaction in extractable Fe was observed between P sources and levels and was caused by the same factors.

All P sources decreased extractable Mn (Tables 4 and 5). The higher extractable Mn by MAP than MCP treatments suggested MAP had a greater effect than MCP on soil pH and organic matter. However, the nonsignificant changes in extractable Fe, Zn and Cu, and the significant decrease in extractable Mn suggested the precipitation of Mn as Mn phosphate by MCP and MAP (Mandal and Halder, 1980; and Lindsay and Stephenson, 1959). The higher extractable Mn by APP application over MCP plus MAP suggested the sequestration effect of high levels of APP (Philen and Laher, 1967). Increased MCP and MAP levels caused a linear and cubic decrease and a linear and cubic increase in extractable Mn, respectively (Fig. 5), which may be due to the dissociation and precipitation of Mn by MCP (Lindsay and Stephenson, 1959) and to the influence on organic matter and the decrease in soil pH by MAP. A linear, quadratic, and cubic interaction in extractable Mn was induced by different P sources and levels due to the different chemical reactions of P sources in soil.

## Nutrient ratios

P/Fe ratios were higher in P treated soils than nontreated soils (Tables 4 and 5) due to the increase of Bray and Kurtz No. 1 P with the addition of P to soil. A higher P/Fe ratio was caused by MAP than MCP treatments, which was mainly caused by more extractable Bray and Kurtz No. 1 P from MAP than MCP treatments. APP induced lower P/Fe ratio than MCP plus MAP treatments which was caused by the increase of extractable Fe specifically with the highest two levels of APP. Linear increase in P/Fe ratio was caused by all P sources due to the increase in Bray and Kurtz No. 1 P with increasing P levels. A linear interaction in P/Fe ratios was caused by different P sources and levels due to the changes of Bray and Kurtz No. 1 P, and DTPA extractable Fe concentrations.

Mn/Fe ratios were lower in P treated soils than nontreated soils, mainly due to the decrease in extractable Mn. The higher Mn/Fe ratios with MAP and APP treatments over MCP and MCP plus MAP treatments, respectively, were caused by lower decrease in extractable Mn with MAP than MCP treatments and the small decrease of extractable Fe and Mn by APP application. Increased MCP levels caused a cubic change in Mn/Fe ratios, while increased MAP and APP levels cuased a linear and quadratic increase and linear decrease in Mn/Fe ratios, respectively. This was due to the increase in extractable Mn with MAP and the increase of extractable Mn and Fe wIth APP application, respectively. Linear and quadratic interaction in Mn/Fe ratios was caused by P sources and levels.

Zn/Fe and Cu/Fe ratios were lower in APP than MCP plus MAP treatments (Tables 4 and 5), due to the increase of extractable Fe with APP treatments. A cubic interaction in Zn/Fe ratios was induced by increasing MCP levels and different P sources, respectively.

Phosphorus sources and rates had no significant effect on Zn and Cu concentration in Quinlan soil.

Table 4. Influence of P sources and rates on soil pH, P, and micronutrient concentrations and ratios in Quinlan soil.

| Sources | P Rate | pH | P | Fe | Mn | Zn | Cu | P/Fe | Mn/Fe | Zn/Fe | Cu/Fe |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $kg\ ha^{-1}$ | | $mg\ kg^{-1}$ | | | | | | | | |
| Check | 0 | 8.30 | 16.3 | 0.75 | 7.9 | 0.63 | 0.34 | 21.8 | 10.5 | 0.85 | 0.46 |
| MCP | 20 | 8.32 | 22.0 | 0.74 | 5.8 | 0.65 | 0.33 | 29.6 | 7.8 | 0.87 | 0.44 |
| MCP | 40 | 8.27 | 28.7 | 0.73 | 5.9 | 0.67 | 0.33 | 39.3 | 8.1 | 0.91 | 0.45 |
| MCP | 60 | 8.25 | 34.7 | 0.76 | 5.5 | 0.63 | 0.33 | 45.7 | 7.3 | 0.83 | 0.44 |
| MCP | 80 | 8.27 | 40.0 | 0.67 | 5.6 | 0.68 | 0.34 | 59.6 | 8.3 | 1.02 | 0.51 |
| MCP $\bar{x}$ | | 8.28 | 33.6 | 0.73 | 5.7 | 0.66 | 0.33 | 43.6 | 7.98 | 0.91 | 0.46 |
| MAP | 20 | 8.23 | 22.7 | 0.66 | 5.8 | 0.67 | 0.33 | 34.5 | 8.8 | 1.02 | 0.50 |
| MAP | 40 | 8.22 | 30.0 | 0.70 | 7.2 | 0.62 | 0.32 | 41.5 | 9.9 | 0.86 | 0.44 |
| MAP | 60 | 8.15 | 35.3 | 0.68 | 7.0 | 0.68 | 0.34 | 52.2 | 10.3 | 1.00 | 0.50 |
| MAP | 80 | 8.08 | 42.0 | 0.73 | 7.0 | 0.67 | 0.34 | 57.8 | 9.7 | 0.92 | 0.47 |
| MAP $\bar{x}$ | | 8.17 | 32.5 | 0.69 | 6.8 | 0.66 | 0.33 | 46.5 | 9.7 | 0.95 | 0.48 |
| APP | 20 | 8.22 | 24.0 | 0.73 | 7.7 | 0.63 | 0.32 | 32.8 | 10.5 | 0.87 | 0.43 |
| APP | 40 | 8.20 | 30.0 | 0.77 | 7.8 | 0.63 | 0.32 | 38.8 | 10.1 | 0.82 | 0.41 |
| APP | 60 | 8.10 | 35.3 | 0.80 | 7.8 | 0.65 | 0.34 | 44.0 | 9.7 | 0.81 | 0.42 |
| APP | 80 | 8.10 | 40.7 | 0.82 | 7.8 | 0.68 | 0.34 | 49.4 | 9.4 | 0.82 | 0.42 |
| APP $\bar{x}$ | | 8.16 | 32.5 | 0.78 | 7.8 | 0.65 | 0.33 | 41.3 | 9.9 | 0.83 | 0.42 |

Table 5. Analysis of variance and orthogonal contrasts of the effects of P sources and rates on soil pH, P, and micronutrient concentrations and ratios in Quinlan soil.

| Sources$^+$ | df | F-Value | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | pH | P | Fe | Mn | Zn | Cu | P/Fe | Mn/Fe | Zn/Fe | Cu/Fe |
| Block | 2 | 0.61 | 0.11 | 0.51 | 1.03 | 0.26 | 0.89 | 0.36 | 0.18 | 0.42 | 0.23 |
| Treatment | 12 | 14.34*** | 114.4*** | 4.46*** | 96.30*** | 0.62 | 0.75 | 48.53*** | 13.74*** | 2.14 | 1.65 |
| Orthogonal Contrasts | | | | | | | | | | | |
| Check vs. others | 1 | 22.06*** | 410.5*** | 0.30 | 133.7*** | 0.55 | 1.18 | 178.36*** | 20.41*** | 0.85 | 0.07 |
| MCP vs. MAP | 1 | 51.86*** | 4.86* | 2.50 | 225.1*** | 0.01 | 0.05 | 7.00* | 74.83*** | 1.13 | 0.95 |
| MCP + MAP vs. APP | 1 | 30.12*** | 1.62 | 25.47*** | 660.3*** | 0.19 | 0.14 | 15.06*** | 41.26*** | 9.58** | 9.19** |
| MCP linear | 1 | 3.32 | 321.5*** | 3.23 | 5.59* | 0.28 | 1.31 | 185.13*** | 0.30 | 2.39 | 3.54 |
| MAP linear | 1 | 31.90*** | 358.2*** | 1.77 | 60.54*** | 0.23 | 1.31 | 129.93*** | 4.57* | 0.38 | 0.10 |
| APP linear | 1 | 24.20*** | 273.5*** | 8.99** | 0.06 | 1.76 | 3.82 | 60.90*** | 7.87** | 0.22 | 0.09 |
| MCP quadratic | 1 | 2.66 | 0.79 | 2.68 | 0.23 | 0.35 | 0.20 | 1.75 | 1.35 | 1.98 | 1.73 |
| MAP quadratic | 1 | 1.49 | 0.20 | 0.35 | 47.49*** | 0.51 | 0.20 | 0.19 | 8.45** | 0.54 | 0.35 |
| APP quadratic | 1 | 0.17 | 0.20 | 0.20 | 0.08 | 0.35 | 0.02 | 0.04 | 0.15 | 0.54 | 0.16 |
| MCP cubic | 1 | 0.00 | 0.00 | 2.56 | 5.59* | 1.13 | 0.00 | 2.33 | 5.54* | 2.75 | 0.68 |
| MAP cubic | 1 | 0.30 | 0.99 | 5.44* | 16.97*** | 2.06 | 0.55 | 1.63 | 0.11 | 5.30* | 2.81 |
| APP cubic | 1 | 4.02 | 0.04 | 0.00 | 0.02 | 0.00 | 0.22 | 0.02 | 0.00 | 0.00 | 0.09 |
| P source * levels | 6 | 2.42 | 0.60 | 3.42* | 15.30*** | 0.60 | 0.12 | 3.82** | 4.39** | 1.86 | 1.13 |
| Orthogonal Contrast | | | | | | | | | | | |
| Interaction linear | 2 | 4.13* | 1.44 | 5.93** | 27.77*** | 0.23 | 0.22 | 8.58** | 6.37** | 1.46 | 1.60 |
| Interaction quadratic | 2 | 2.05 | 0.07 | 0.42 | 14.12*** | 0.00 | 0.03 | 0.91 | 4.67* | 0.15 | 0.23 |
| Interaction cubic | 2 | 1.07 | 0.28 | 3.91* | 4.00* | 1.57 | 0.11 | 1.96 | 2.12 | 3.96* | 1.57 |
| Error mean square | 24 | 0.00126 | 1.6795 | 0.0015 | 0.0286 | 0.00236 | 0.00037 | 7.5008 | 0.2615 | 0.00814 | 0.00193 |
| C.V.% | | 0.43 | 4.19 | 5.25 | 2.48 | 7.44 | 5.78 | 6.51 | 5.52 | 10.11 | 9.68 |

*, **, *** Significant at 0.05 or 0.01 or 0.001 probability levels, respectively.

$^+$MCP, MAP, APP refers to monocalcium phosphate, monoammonium phosphate and ammonium polyphosphate, respectively.

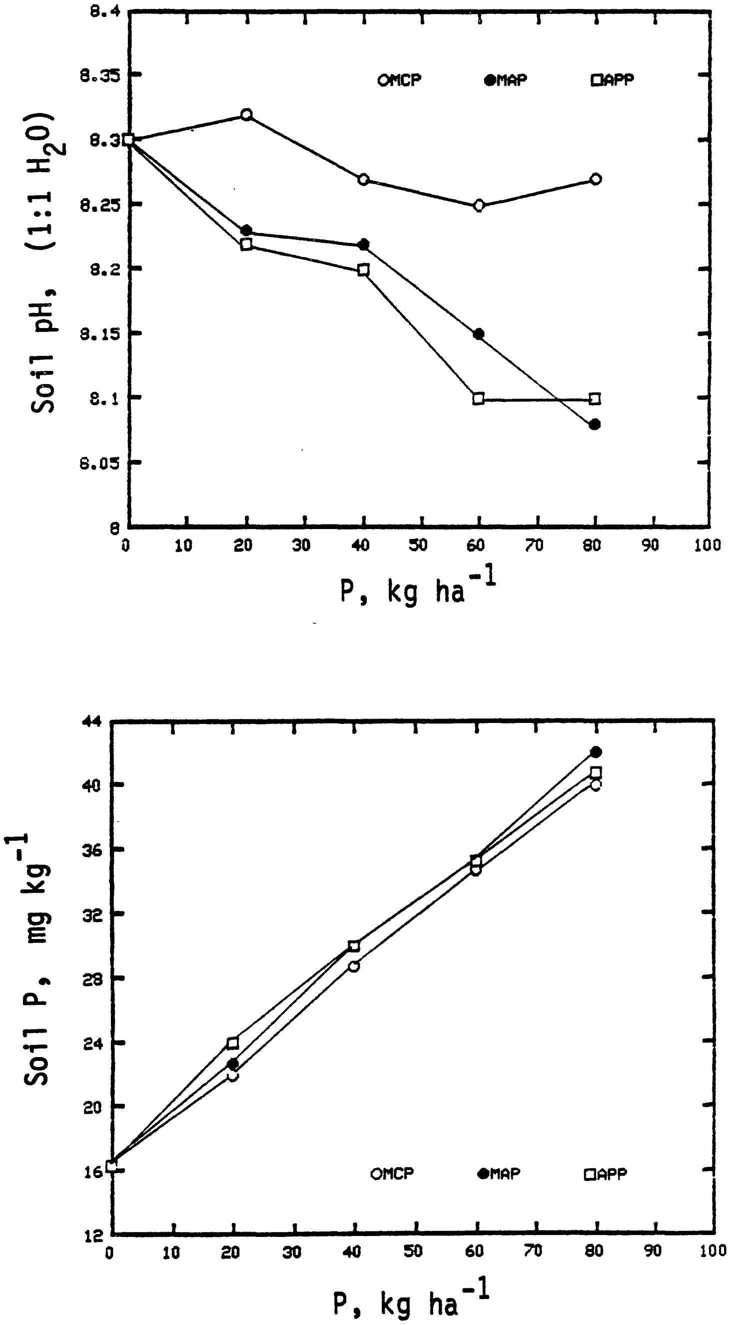


Fig. 4. Influence of P sources and rates on soil pH and Bray and Kurtz No. 1 P in Quinlan soil.

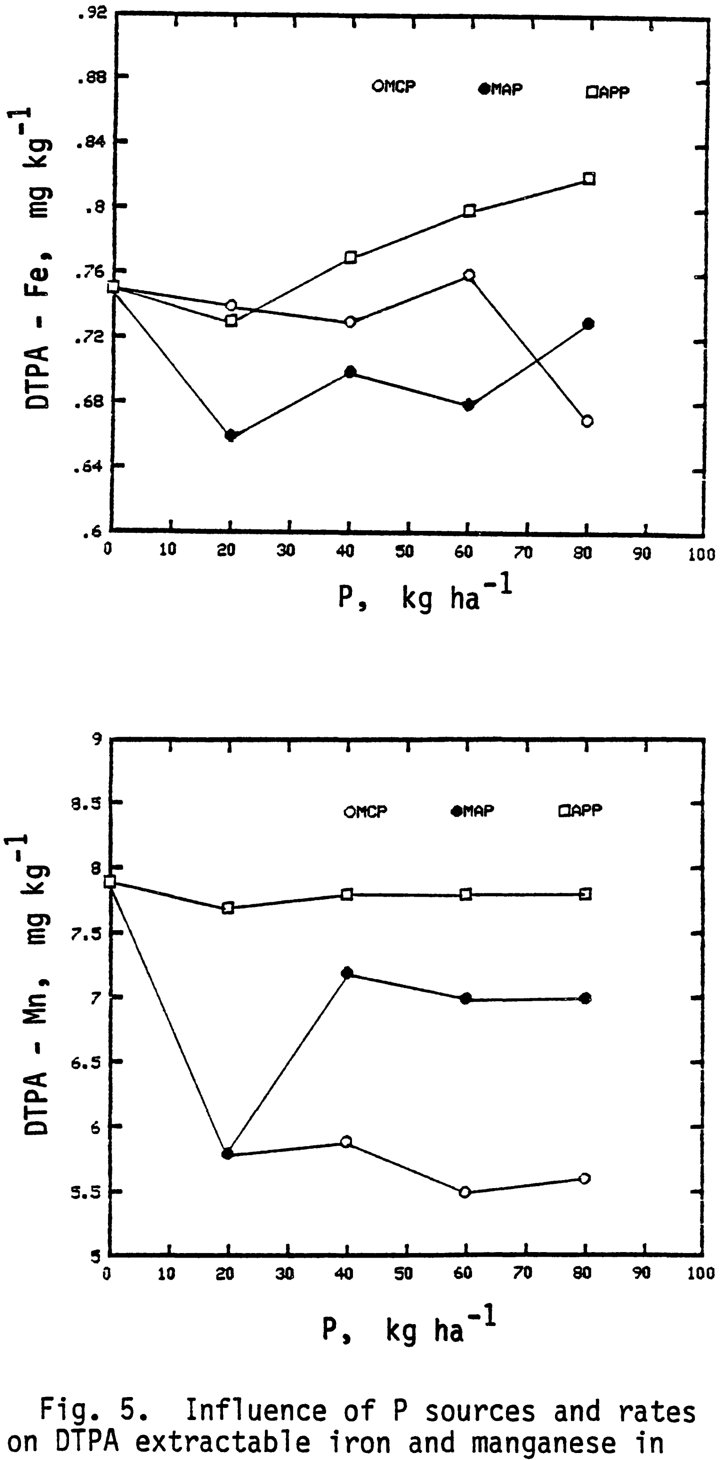


Fig. 5. Influence of P sources and rates on DTPA extractable iron and manganese in Quinlan soil.

# CONCLUSIONS

Since the application of P sources caused many changes in the chemical properties of the two soils, it is possible to state the following:

a. In both soils, P application decreased soil pH, however, MAP or APP application induced greater reduction in soil pH than MCP application.

b. Bray and Kurtz No. 1 extractable P was increased by P application in both soils.

c. MCP and MAP application in McLain soil decreased DTPA extractable Fe, Mn, and Cu, but high levels of APP application increased DTPA extractable Fe, Mn, and Cu.

d. Phosphorus application in Quinlan soil did not affect DTPA extractable Zn and Cu. However, high levels of APP application increased DTPA extractable Fe; and MCP or MAP application decreased DTPA extractable Mn.

e. Application of MAP and MCP to McLain soil decreased DTPA extactable Fe and increased P/Fe ratio, but application of high levels of APP to the same soil increased DTPA extractable Fe and decreased P/Fe ratio. Furthermore, P fertilization caused different changes in Zn/Fe, Mn/Fe, and Cu/Fe ratios with respect to each soil.

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# APPENDIX

## pH, P, AND, MICRONUTRIENT CONCENTRATIONS AND RATIOS

Key:
MCP = monocalcium phosphate
MAP = monoammonium phosphate
APP = ammonium polyphosphate

Treatment
" 0 = control
" 1 = MCP 20 kg P $ha^{-1}$
" 2 = MCP 40 kg P $ha^{-1}$
" 3 = MCP 60 kg P $ha^{-1}$
" 4 = MCP 80 kg P $ha^{-1}$
" 5 = MAP 20 kg P $ha^{-1}$
" 6 = MAP 40 kg P $ha^{-1}$
" 7 = MAP 60 kg P $ha^{-1}$
" 8 = MAP 80 kg P $ha^{-1}$
" 9 = APP 20 kg P $ha^{-1}$
" 10 = APP 40 kg P $ha^{-1}$
" 11 = APP 60 kg P $ha^{-1}$
" 12 = APP 80 kg P $ha^{-1}$

Soil Type 1 = McLain sicl
Soil Type 2 = Quinlan cl

| OBS | BLOCK | TREATMNT | SOILTYPE | PH | P_PPM | FE_PPM | MN_PPM | ZN_PPM | CU_PPM | P_FE | MN_FE | ZN_FE | CU_FE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 1 | 7 75 | 114 | 8 45 | 7 48 | 0 85 | 1 05 | 13 49 | 0 89 | 0 10 | 0 12 |
| 2 | 2 | 0 | 1 | 7 70 | 114 | 8 37 | 7 33 | 0 83 | 1 05 | 13 62 | 0 88 | 0 10 | 0 13 |
| 3 | 3 | 0 | 1 | 7 75 | 112 | 8 37 | 7 55 | 0 88 | 1 08 | 13 38 | 0 90 | 0 10 | 0 13 |
| 4 | 1 | 0 | 2 | 8 30 | 16 | 0 75 | 7 95 | 0 65 | 0 35 | 21 33 | 10 60 | 0 87 | 0 47 |
| 5 | 2 | 0 | 2 | 8 30 | 16 | 0 75 | 7 93 | 0 65 | 0 33 | 21 33 | 10 57 | 0 87 | 0 44 |
| 6 | 3 | 0 | 2 | 8 30 | 17 | 0 75 | 7 85 | 0 60 | 0 35 | 22 67 | 10 47 | 0 80 | 0 47 |
| 7 | 1 | 1 | 1 | 7 65 | 120 | 7 43 | 4 25 | 0 88 | 0 90 | 16.15 | 0 57 | 0 12 | 0 12 |
| 8 | 2 | 1 | 1 | 7 65 | 120 | 7 38 | 4 50 | 0 83 | 0 88 | 16 26 | 0 61 | 0 11 | 0 12 |
| 9 | 3 | 1 | 1 | 7 70 | 116 | 7 68 | 4 25 | 0 83 | 0 90 | 15 10 | 0.55 | 0 11 | 0 12 |
| 10 | 1 | 1 | 2 | 8 30 | 22 | 0 73 | 5 60 | 0 60 | 0 33 | 30.14 | 7 67 | 0 82 | 0 45 |
| 11 | 2 | 1 | 2 | 8 35 | 24 | 0 75 | 5 65 | 0 65 | 0 33 | 32 00 | 7 53 | 0 87 | 0 44 |
| 12 | 3 | 1 | 2 | 8 30 | 20 | 0 75 | 6 10 | 0 70 | 0 32 | 26 67 | 8 13 | 0 93 | 0 43 |
| 13 | 1 | 2 | 1 | 7 50 | 120 | 7 33 | 4 28 | 0 85 | 0 88 | 16 37 | 0 58 | 0 12 | 0.12 |
| 14 | 2 | 2 | 1 | 7 60 | 120 | 7 45 | 4 33 | 0 90 | 0 93 | 16 11 | 0 58 | 0.12 | 0 12 |
| 15 | 3 | 2 | 1 | 7 65 | 116 | 7 56 | 4 40 | 0 87 | 0 90 | 15 34 | 0 58 | 0.12 | 0 12 |
| 16 | 1 | 2 | 2 | 8 25 | 30 | 0 72 | 5 90 | 0 65 | 0 33 | 41 67 | 8 19 | 0 90 | 0 46 |
| 17 | 2 | 2 | 2 | 8 25 | 28 | 0 73 | 5 80 | 0 65 | 0 33 | 38 36 | 7.95 | 0 89 | 0 45 |
| 18 | 3 | 2 | 2 | 8 30 | 28 | 0 74 | 6 10 | 0 70 | 0 32 | 37 84 | 8 24 | 0 95 | 0 43 |
| 19 | 1 | 3 | 1 | 7 60 | 128 | 7 45 | 4 30 | 0.83 | 0 90 | 17 18 | 0 58 | 0 11 | 0 12 |
| 20 | 2 | 3 | 1 | 7 60 | 128 | 7 55 | 4 45 | 0 83 | 0 92 | 16 95 | 0 59 | 0 11 | 0.12 |
| 21 | 3 | 3 | 1 | 7 60 | 128 | 7 55 | 4 55 | 0 82 | 0 93 | 16.95 | 0 60 | 0 11 | 0 12 |
| 22 | 1 | 3 | 2 | 8 25 | 36 | 0 75 | 5 68 | 0 60 | 0 32 | 48 00 | 7 57 | 0 80 | 0 43 |
| 23 | 2 | 3 | 2 | 8 25 | 32 | 0 78 | 5 30 | 0 65 | 0 33 | 41 03 | 6 79 | 0 83 | 0 42 |
| 24 | 3 | 3 | 2 | 8 25 | 36 | 0 75 | 5 58 | 0 65 | 0 35 | 48 00 | 7.44 | 0 87 | 0 47 |
| 25 | 1 | 4 | 1 | 7 55 | 140 | 7 90 | 4 70 | 0 90 | 0 93 | 17 72 | 0.59 | 0 11 | 0.12 |
| 26 | 2 | 4 | 1 | 7 55 | 136 | 7 78 | 4 45 | 0 88 | 0 95 | 17 48 | 0 57 | 0 11 | 0 12 |
| 27 | 3 | 4 | 1 | 7 60 | 136 | 7 50 | 4 60 | 0 88 | 0 92 | 18 13 | 0 61 | 0.12 | 0 12 |
| 28 | 1 | 4 | 2 | 8 30 | 40 | 0 72 | 5 50 | 0 60 | 0 35 | 55 56 | 7 64 | 0.83 | 0.49 |
| 29 | 2 | 4 | 2 | 8 25 | 40 | 0.65 | 5 80 | 0 75 | 0 33 | 61.54 | 8 92 | 1 15 | 0 51 |
| 30 | 3 | 4 | 2 | 8 25 | 40 | 0 65 | 5 43 | 0 70 | 0 35 | 61 54 | 8 35 | 1.08 | 0 54 |
| 31 | 1 | 5 | 1 | 7.60 | 118 | 7 30 | 4 50 | 0 83 | 0 93 | 16 16 | 0 62 | 0 11 | 0 13 |
| 32 | 2 | 5 | 1 | 7 65 | 118 | 7 63 | 4 68 | 0 81 | 0 95 | 15.47 | 0 61 | 0 11 | 0 12 |
| 33 | 3 | 5 | 1 | 7 60 | 118 | 7 58 | 4 43 | 0 85 | 0 95 | 15 57 | 0 58 | 0 11 | 0 13 |
| 34 | 1 | 5 | 2 | 8 20 | 22 | 0 63 | 5 55 | 0 65 | 0 33 | 35.20 | 8 88 | 1 04 | 0 53 |
| 35 | 2 | 5 | 2 | 8 30 | 22 | 0 63 | 5 83 | 0 65 | 0 33 | 35.20 | 9 33 | 1 04 | 0 53 |
| 36 | 3 | 5 | 2 | 8 20 | 24 | 0 73 | 6 03 | 0 70 | 0 32 | 33 10 | 8 32 | 0.97 | 0 44 |
| 37 | 1 | 6 | 1 | 7 55 | 124 | 7 78 | 4 70 | 0 83 | 0 93 | 15 94 | 0 60 | 0.11 | 0 12 |
| 38 | 2 | 6 | 1 | 7 50 | 124 | 7 75 | 4 55 | 0 82 | 0 95 | 16 00 | 0.59 | 0 11 | 0 12 |
| 39 | 3 | 6 | 1 | 7 55 | 120 | 7 75 | 4 65 | 0 87 | 0 92 | 15 48 | 0 60 | 0 11 | 0 12 |
| 40 | 1 | 6 | 2 | 8 25 | 30 | 0 83 | 7 43 | 0 60 | 0 30 | 36.36 | 9 01 | 0.73 | 0 36 |
| 41 | 2 | 6 | 2 | 8 20 | 30 | 0 63 | 7 05 | 0 65 | 0 35 | 48 00 | 11 28 | 1 04 | 0 56 |
| 42 | 3 | 6 | 2 | 8 20 | 30 | 0 75 | 7 05 | 0 60 | 0 31 | 40.00 | 9 40 | 0.80 | 0 41 |
| 43 | 1 | 7 | 1 | 7 55 | 132 | 8 23 | 4 40 | 0 83 | 0 95 | 16 04 | 0 53 | 0.10 | 0 12 |
| 44 | 2 | 7 | 1 | 7.50 | 132 | 8 48 | 4 95 | 0 83 | 1 00 | 15 57 | 0 58 | 0.10 | 0 12 |
| 45 | 3 | 7 | 1 | 7 50 | 128 | 8 28 | 5 05 | 0 88 | 0 98 | 15 46 | 0 61 | 0 11 | 0 12 |
| 46 | 1 | 7 | 2 | 8 20 | 34 | 0 68 | 6 95 | 0 65 | 0 35 | 50 00 | 10.22 | 0 96 | 0 51 |
| 47 | 2 | 7 | 2 | 8 15 | 36 | 0 68 | 6 80 | 0 68 | 0 31 | 53 33 | 10 07 | 1 01 | 0 46 |
| 48 | 3 | 7 | 2 | 8 10 | 36 | 0 68 | 7 18 | 0 70 | 0 35 | 53 33 | 10 64 | 1 04 | 0 52 |
| 49 | 1 | 8 | 1 | 7 45 | 136 | 8 55 | 4 90 | 0 88 | 0 95 | 15 91 | 0 57 | 0 10 | 0 11 |
| 50 | 2 | 8 | 1 | 7 40 | 136 | 8 35 | 4 70 | 0 85 | 0 98 | 16 29 | 0 56 | 0 10 | 0 12 |
| 51 | 3 | 8 | 1 | 7 40 | 140 | 8 23 | 5 00 | 0 85 | 0 95 | 17 01 | 0 61 | 0.10 | 0 12 |
| 52 | 1 | 8 | 2 | 8 05 | 40 | 0 70 | 7 03 | 0 75 | 0 35 | 57 14 | 10 04 | 1 07 | 0 50 |
| 53 | 2 | 8 | 2 | 8 10 | 44 | 0 75 | 6 98 | 0 60 | 0 32 | 58 67 | 9 31 | 0 80 | 0 43 |
| 54 | 3 | 8 | 2 | 8 10 | 42 | 0 73 | 7 00 | 0 65 | 0 35 | 57 53 | 9 59 | 0 89 | 0 48 |
| 55 | 1 | 9 | 1 | 7 60 | 118 | 7 83 | 4 70 | 0 83 | 0 93 | 15 07 | 0 60 | 0 11 | 0 12 |
| 56 | 2 | 9 | 1 | 7 55 | 122 | 7 85 | 5 08 | 0 88 | 0 97 | 15 54 | 0 65 | 0 11 | 0 12 |

| OBS | BLOCK | TREATMNT | SOILTYPE | PH | P_PPM | FE_PPM | MN_PPM | ZN_PPM | CU_PPM | P_FE | MN_FE | ZN_FE | CU_FE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 57 | 3 | 9 | 1 | 7 55 | 122 | 7 83 | 5 05 | 0 90 | 0 97 | 15 58 | 0 64 | 0 11 | 0 12 |
| 58 | 1 | 9 | 2 | 8 20 | 24 | 0 70 | 7 60 | 0 65 | 0 31 | 34.29 | 10.86 | 0 93 | 0 44 |
| 59 | 2 | 9 | 2 | 8.25 | 24 | 0 75 | 7 83 | 0 60 | 0 29 | 32 00 | 10.44 | 0.80 | 0 39 |
| 60 | 3 | 9 | 2 | 8 20 | 24 | 0 75 | 7 75 | 0 65 | 0 35 | 32.00 | 10 33 | 0 87 | 0 47 |
| 61 | 1 | 10 | 1 | 7 60 | 126 | 7.98 | 5 05 | 0 90 | 1 00 | 15.79 | 0 63 | 0 11 | 0 13 |
| 62 | 2 | 10 | 1 | 7 55 | 124 | 8 38 | 5 00 | 0 83 | 1 00 | 14.80 | 0.60 | 0.10 | 0 12 |
| 63 | 3 | 10 | 1 | 7 60 | 124 | 8 13 | 4 80 | 0 83 | 0 98 | 15 25 | 0 59 | 0 10 | 0 12 |
| 64 | 1 | 10 | 2 | 8 20 | 30 | 0 75 | 7 88 | 0 60 | 0 35 | 40.00 | 10 51 | 0 80 | 0.47 |
| 65 | 2 | 10 | 2 | 8 25 | 30 | 0 78 | 7 75 | 0 65 | 0 30 | 38 46 | 9 94 | 0 83 | 0 38 |
| 66 | 3 | 10 | 2 | 8 15 | 30 | 0 79 | 7 70 | 0 65 | 0 31 | 37 97 | 9 75 | 0.82 | 0 39 |
| 67 | 1 | 11 | 1 | 7 50 | 130 | 9 45 | 7 30 | 0 83 | 1.08 | 13 76 | 0.77 | 0.09 | 0.11 |
| 68 | 2 | 11 | 1 | 7 50 | 130 | 9 25 | 6 95 | 0 88 | 1 07 | 14 05 | 0 75 | 0.10 | 0 12 |
| 69 | 3 | 11 | 1 | 7 50 | 128 | 9 30 | 7 53 | 0 90 | 1.08 | 13 76 | 0 81 | 0 10 | 0 12 |
| 70 | 1 | 11 | 2 | 8.10 | 36 | 0 83 | 7 60 | 0.70 | 0 35 | 43 37 | 9.16 | 0 84 | 0 42 |
| 71 | 2 | 11 | 2 | 8 10 | 34 | 0 80 | 7 88 | 0 65 | 0 35 | 42.50 | 9 85 | 0 81 | 0 44 |
| 72 | 3 | 11 | 2 | 8 10 | 36 | 0 78 | 7 83 | 0 60 | 0 31 | 46.15 | 10 04 | 0 77 | 0.40 |
| 73 | 1 | 12 | 1 | 7 45 | 138 | 9 63 | 7 13 | 0 88 | 1 08 | 14.33 | 0 74 | 0 09 | 0 11 |
| 74 | 2 | 12 | 1 | 7.45 | 136 | 9.38 | 7 35 | 0 88 | 1 00 | 14.50 | 0 78 | 0 09 | 0.11 |
| 75 | 3 | 12 | 1 | 7.45 | 138 | 9 75 | 7 45 | 0 85 | 1.00 | 14 15 | 0 76 | 0 09 | 0 10 |
| 76 | 1 | 12 | 2 | 8.10 | 40 | 0 80 | 7 78 | 0.70 | 0 36 | 50 00 | 9 73 | 0.88 | 0.45 |
| 77 | 2 | 12 | 2 | 8 05 | 42 | 0 82 | 7 68 | 0 75 | 0 35 | 51 22 | 9 37 | 0 91 | 0 43 |
| 78 | 3 | 12 | 2 | 8.15 | 40 | 0 85 | 7 83 | 0 60 | 0 32 | 47 06 | 9 21 | 0 71 | 0 38 |

# PART III

# INFLUENCE OF P SOURCES AND RATES ON SELECTED CHEMICAL SPECIES AND P COMPLEXES IN SOIL SOLUTION

# ABSTRACT

Previous workers have reported on the complexation and precipitation of applied P in soil. Therefore, the objectives of this study were to determine the influence of three P sources on the ion and the ion pair activities of selected chemical species and P complexes in soil solution. A factorial arrangement of treatments (2 x 3 x 4 + 2 checks) in a randomized complete block design with three replications was used in a laboratory experiment. Factors were soils (McLain sicl - Pachic Argiustolls and Quinlan cl - Typic Ustocrept); P sources (monocalcium phosphate, MCP, monoammonium phosphate, MAP and ammonium polyphosphate, APP); and rates (0, 20, 40, 60, and 80 kg P $ha^{-1}$). Rates of P using the three sources were applied to 1 kg of soil and incubated aerobically at room temperature and 0.033 MPa moisture for two months. Soil solution was obtained by immiscible displacement after packing 800 g of soil in 60 cm long by 5 cm diameter glass columns. Results of this study indicated that in both soils $Ca^{2+}$, $Mg^{2+}$, and $NO_3^-$ activities were increased by P application. Activity of $Mg^{2+}$ was not affected by MCP application in Quinlan soil, but the highest level of P as APP caused higher $NO_3^-$ activity than the same level of P as MCP. Phosphorus application increased $SO_4^{2-}$ activity in McLain soil and decreased activity in Quinlan soil. All P sources decreased pH of soil solution extracted from Quinlan soil, while only MAP and APP decreased the pH of soil solution extracted from McLain

soil. Phosphorus application in both soils increased $HPO_4^{2-}$, $H_2PO_4^-$, $CaHPO_4^0$, and $MgHPO_4^0$ activities. However, no differences in $HPO_4^{-2}$ activity were observed among the same levels of all P sources. Higher $H_2PO_4^-$ activities were observed with MAP and APP than with MCP. All P sources increased $CaPO_4^-$ and $MgPO_4^-$ activities in Quinlan soil, but in McLain soil, activities of $CaPO_4^-$ and $MgPO_4^-$ were not affected by MAP application, and APP had no effect on $MgPO_4^-$ activity. No specific patterns were observed in the changes of $CaPO_4^-$ and $MgPO_4^-$ activities due to P sources. Analysis of the soil solution with respect to ion and ion pair activities was shown to be bery useful in describing P complexations and compound formations due to P fertilizer sources.

# INTRODUCTION

Analysis of the composition of soil solution can be used as an effective tool by determining actual ionic concentrations and activities because there is chemical equilibrium between the soil solution electrolytes and their ionic species in the soil system. Soil solution composition can be useful to help define the effect of P fertilizers on: ionic strength, activity coefficients, ion pair concentrations and ion and/or ion-pair activities by solving the related equations simultaneously by successive approximation (Adams, 1971).

Several methods have been used to obtain the actual soil solution. Parker (1921) displaced soil solution with ethyl alcohol after packing a moist soil in an appropriate cylinder. Whelan and Barrow (1980) displaced soil solution by centrifugation at 170,000 $ms^{-2}$ for 30 minutes. Howard and Adams (1965) proposed an effective method for displacing soil solution from fine textured soils at field capacity by wetting the soil to 0.033 MPa, sieving through a 5 to 10 mm screen, packing in a glass column and displacing with a saturated $CaSO_4$ solution containing 0.4% KCNS. Adams et al. (1980); and Mubarak et al. (1976) reported that the ionic composition of the soil solution obtained by column displacement, simple centrifugation, and immiscible displacement with $CCl_4$ was the same. Adams (1971) described a procedure for correcting soil solution ionic concentrations to actual ionic concentrations and ionic activities.

White and Ross (1936) reported different fertilizers increased the effective concentration of the soil solution in the following order: $NaNO_3$ > $(NH_4)_2SO_4$ > KCl > $K_2SO_4$ > $NH_4H_2PO_4$. Eaton and Sokoloff (1935) observed the displaced soil solution contained lower amounts of $Na^+$ than the aqueous extract, but $Ca^{2+}$ was higher in the displaced than the extract. This was related to an increase in the water-soil ratio and occasionally $Ca^{2+}$ entered the absorbing complex and liberated $Na^+$ as well as $Mg^{2+}$ and P. Sample et al. (1979) reported that the $NH_4^+$ ion derived from ammonium polyphosphate (APP) fertilizer displaced the exchangeable $Ca^{2+}$ in soil. Adding $CaCO_3$ to the miscible displacement of the soil solution quickly caused a large increase in soil solution pH, $Ca^{2+}$, $HCO_3^-$, $NO_3^-$ and O.M. and a reduction in $K^+$ and $Si^{4+}$ content. The activities of $Ca^{2+}$, $Mg^{2+}$, $K^+$, $Na^+$, and $NO_3^-$ increased substantially, whereas pH decreased during incubation (Curtin and Smillie, 1983). Adams et al. (1982) found that concentrated superphosphate (TSP) application at the rates of 0, 24, 98, 196, and 392 kg P $ha^{-1}$ had different effects on soil solution components. Soil solution $Ca^{2+}$, $Mg^{2+}$, and $K^+$ concentrations were not affected by P rates, but soil solution $SO_4^{2-}$ was increased and pH was decreased by P application. Petrie and Jackson (1984) observed that banded application of P as $Ca(H_2PO_4)_2$ at the rate of 19 kg P $ha^{-1}$ with or without N fertilizer decreased the soil solution pH after 7, 14, and 28 days and decreased $Mn^{2+}$ concentration after 28 days. Greb (1984) reported that there were no differences in the activity of $H_2PO_4^-$ among rates of 20, 30, 60, 120, 300 kg P $ha^{-1}$ application, but when the rate was increased to 600 kg P $ha^{-1}$, activity increased. Also, he found no significant difference in the activity of $HPO_4^{2-}$ over all P rates, but ion pairing of $H_2PO_4^-$ with $Ca^{2+}$ and $Mg^{2+}$ was reported, and $Ca^{+2}$ and $NO_3^-$ activities were increased significantly at higher rates of P application.

Tisdale and Nelson (1975) reported the increase of N mineralization by the addition of N fertilizers, and the immobilization of $SO_4^{2-}$ with low rates of S in soil. Monocalcium phosphate (MCP) application released $H_3PO_4^0$ and precipitated P as dicalcium phosphate dihydrate (DCPD) and dicalcium phosphate (DCP) (Lindsay, 1979). Bell and Black (1970) reported that crystalline $CaHPO_4.2H_2O$ and trace amounts of $CaHPO_4^0$ were formed by $Ca(H_2PO_4)_2.\ H_2O$ application. $CaHPO_4.2H_2O$ was formed by the application of $NH_4H_2PO_4$ and the presence of $Ca^{2+}$ in the exchangeable and the carbonate forms; but $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ application in a high $Mg^{2+}$ exchangeable soil formed $Mg_3(PO_4)_2.22H_2O$ and $Mg\ NH_4PO_4.6H_2O$, respectively. Reaction of monoammonium phosphate (MAP) with calcareous soils caused the precipitation of $CaHPO_4.2H_2O$ and $MgNH_4PO_4.6H_2O$ struvite, (Lindsay et al., 1962). Havlin and Westfall (1984) reported the accumulation of octacalcium phosphate (OCP) at a $NaHCO_3$ extractable P level 32 mg $kg^{-1}$. Phosphorus solubility was controlled by β- tricalcium phosphate (TCP) below this level after the application of triple superphosphate (TSP) fertilizer to a calcareous soils. Fixen et al. (1983) found that OCP controlled solution P if the $NaHCO_3$ extractable P was 35 mg $kg^{-1}$ or greater, while TCP dominated P intensity in the range of 10 to 25 mg $kg^{-1}$ $NaHCO_3$ extractable P when TSP was applied to calcareous soils. Subbarao and Ellis (1975) reported the formation of $Ca(NH_4)_2P_2O_7.H_2O$ by the addition of ammonium polyphosphate (APP) to alkaline calcareous soils. Racz and Soper (1967) reported the application of orthophosphates caused the formation of DCPD ($CaHPO_4.2H_2O$) in soils with water soluble Ca/Mg ratios of approximately 1.5 or greater, and the formation DCPD and/or dimagnesium phosphate trihydrate ($MgHPO_4.3H_2O$) in soils with water soluble Ca/Mg ratios of less than 1.5.

In order to better understand the influence of different P sources on the soil solution chemistry, objectives of this study were to determine the effects of P rates of MCP, MAP, and APP on (a) ionic activities and (b) ion pair activities of selected P species and P complexes in soil solution.

# MATERIALS AND METHODS

Samples of two soils, McLain sicl (Pachic Argiustolls) and Quinlan cl (Typic Ustocrept) were collected at the depth of 0 to 15 cm from western Oklahoma for the experiment. Basic characteristics of these soils are reported in Table 1.

Soil samples were passed through a 5 to 10 mesh screen to remove any large rocks or clods, and 2 kg of each soil was placed in polyethylene bags in the laboratory. Treatments consisted of five P rates (0, 20, 40, 60, and 80 kg $ha^{-1}$) of moncalcium phosphate (MCP) 0-56-0 (chemical grade), monoammonium phosphate (MAP) 12-62-0 (chemical grade), and four P rates (0, 40, 60, and 80 kg $ha^{-1}$) of ammonium polyphosphate (APP) 11-55-0 (commercial grade). Due to an error in the laboratory, the 20 kg P $ha^{-1}$ rate of APP was omitted.

Treatments were arranged in a randomized complete block design with three replications. Phosphorus sources were dissolved in deionized water and mixed uniformly with soils. Moisture content was maintained at approximately 0.033 MPa by the addition of deionized water throughout the experimental period.

After two months of aerobic incubation at room temperature, soils were air dried, ground, and passed through a 5 to 10 mesh screen. Soil solution was obtained by immiscible displacement techniques (Howard and Adams, 1965), which involved moistening 800 g soil samples to approximately 10% moisture and packing into glass columns (5 cm diameter by 60

Table 1. Initial soil characteristics.

| Soil type | Classification | pH | P* | O.M. | $CaCO_3$ |
|---|---|---|---|---|---|
| | | 1:1 ($H_2O$) | ug/g | mg/g | |
| McLain<br>silt clay loam | Pachic<br>Argiustolls | 7.7 | 110 | 22.5 | 19.5 |
| Quinlan<br>clay loam | Typic<br>Ustocrept | 8.3 | 16.2 | 11.3 | 127.2 |

*Bray and Kurtz No. 1 (1:20) P

cm long). A plug of glass wool was placed into the nipple in the bottom of each column and filled with soil to a depth of about 50 cm. Deionized water was used to readjust the soil in the columns to approximately 0.033 MPa and were equilibrated for 24 hr. Saturated $CaSO_4.2H_2O$ containing 4 g KCNS per liter was slowly and carefully added without disturbing the soil surface until the columns were filled. The first 5 ml of the displaced soil solution was discarded. Contamination of the soil solution by the displaced solution was determined after each 10 ml displacement by catching a drop of soil solution on a spot plate containing one drop of $FeCl_3$. When the red color of 125:1 contamination was observed, the extraction was terminated.

The displaced soil solution was collected in test tubes and closed to prevent the influence of $CO_2$ in the air. The solutions were analyzed during collection for pH and after collection for cations and anions by the following methods: Ammonium and $NO_3^-$ by technicon autoanalyzer, (Henriksen and Selner-Olsen, 1970), $HCO_3^-$ by dilute $H_2SO_4$ titration (Bower, 1965), $Cl^-$ by titration with $AgN_3$ (Bower, 1965), $SO_4^{2-}$ turbidimetrically with $BaCl_2$ (Bardsley and Lancaster, 1960), P colorimetrically (Murphy and Riley, 1962), $Ca^{2+}$, $Mg^{2+}$, $Na^+$, and $K^+$ by atomic absorption spectroscopy with air-acetylene flame (Issac et al., 1972). Soil solution activities were determined by successive iterations using the GEOCHEM program (Sposito and Mattigod, 1979), and Davis equation for estimating activity coefficient (Davis, 1962).

Significant differences among treatments were determined using the least significant test outlined by Steel and Torrie (1960).

# RESULTS AND DISCUSSION

## McLain Soil

### $Ca^{2+}$ and $Mg^{2+}$ activities

All P sources increased $Ca^{2+}$ and $Mg^{2+}$ activities (Fig. 1). This finding suggested the displacement of exchangeable $Ca^{2+}$ and $Mg^{2+}$ by $NH_4^+$ ions derived from MAP and APP application (Sample et al., 1979), or the effect of $Ca^{2+}$ due to MCP application. No changes in $Ca^{2+}$ and $Mg^{2+}$ activities among the rates of 20, 40, 60, and 80 kg P $ha^{-1}$ of MAP or MCP, or the rates of 40, 60, and 80 kg P $ha^{-1}$ of APP were observed. Also, no difference in $Mg^{2+}$ activities was observed between the control and the 20 kg P $ha^{-1}$ of MCP. However, all P rates except the MCP rate of 20 kg P $ha^{-1}$ induced higher $Ca^{2+}$ and $Mg^{2+}$ activities than the control. The stable $Ca^{2+}$ and $Mg^{2+}$ activities could be caused by the adsorption of $Ca^{2+}$ and $Mg^{2+}$ on the exchangeable sites. However, formation of DCPD and DCP might be considered as other factors for the above changes (Lindsay, 1979; Bell and Black, 1970; Racz and Soper, 1967).

No differences in $Ca^{2+}$ and $Mg^{2+}$ activities were observed between similar rates of P from different sources except, that the APP rate of 80 kg P $ha^{-1}$ induced higher $Ca^{2+}$ activity than the similar rates of MCP.

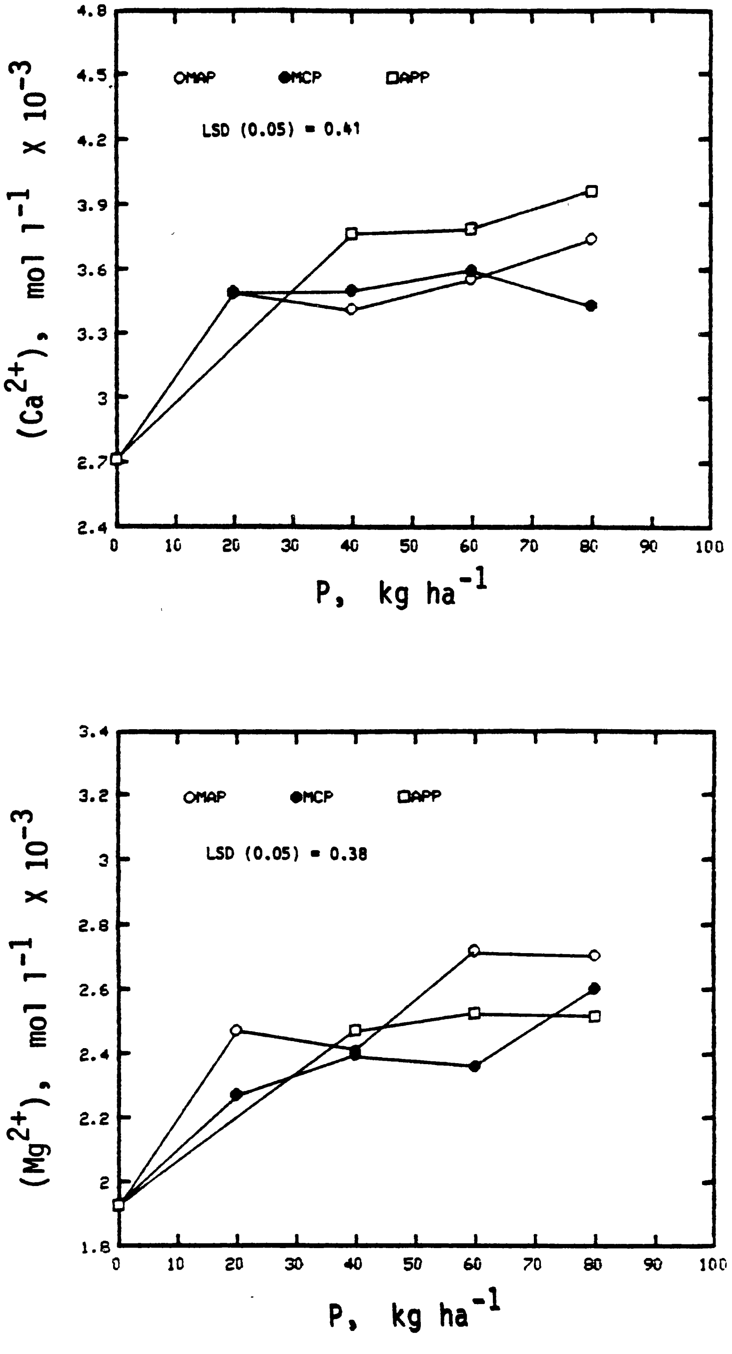


Fig. 1-Effect of P sources and rates on $Ca^{2+}$ and $Mg^{2+}$ activities in McLain soil solution.

## $NO_3^-$ Activity

Nitrate-N activities were increased by all P sources (Fig. 2), due to the behavior of MAP and APP as N and P sources, and the increase of the N mineralization process by P sources containing N (Tisdale and Nelson, 1975).

No differences in $NO_3^-$ activities between MAP rates of 20 and 40, or 40 and 60, or 60 and 80 kg P $ha^{-1}$ were observed. This finding suggested there was little effect due to 20 kg P $ha^{-1}$ increment of MAP on the N mineralization process. However, all MAP rates induced higher $NO_3^-$ activities than the control. Also MAP rates of 60 and 80 kg P $ha^{-1}$ caused greater $NO_3^-$ activities than MAP rates of 20, or 20 and 40 kg P $ha^{-1}$, respectively.

No differences in $NO_3^-$ activities among the rates of 0, 20, 40, and 60 or 60 and 80 kg P $ha^{-1}$ of MCP or 40, 60, and 80 kg P $ha^{-1}$ of APP were observed. But 80 kg P $ha^{-1}$ of MCP caused greater $No_3^-$ activities than MCP rates of 0, 20, and 40 kg P $ha^{-1}$. All APP rates induced higher $NO_3^-$ activities than the control.

Ammonium polyphosphate rates of 40, 60, and 80 kg P $ha^{-1}$ induced higher $NO_3^-$ activities than similar rates of MCP. Also, 60 kg P $ha^{-1}$ as APP and MAP caused higher $NO_3^-$ activities than the corresponding rate of MCP. This finding suggested that the $NH_4^+$ content of the P sources had a marked effect on $NO_3^-$ activities.

## $SO_4^{2-}$ Activity

Sulfate activity was increased by all P source applications (Fig. 2) (Adams et al., 1982; C. R. Greb, 1984), due to the increase of the microbial activity, and the S mineralization process.

No differences in $SO_4^{2-}$ activities were observed among rates of 0, 20, and 40 or 60 and 80 kg P $ha^{-1}$ of MAP. However, MAP rates of 60 and 80 kg P $ha^{-1}$ increased $SO_4^{2-}$ activity more than all other levels. No differences in $SO_4^{2-}$ activities between MCP rates of 20 and 40, or 40 and 60, or 60 and 80 kg P $ha^{-1}$ were observed. However, all MCP rates caused higher $SO_4^{2-}$ activities than observed in the control. Also, MCP rates of 60 and 80 kg P $ha^{-1}$ increased $SO_4^{2-}$ activities more than MCP rates of 20, or 20 and 40 kg P $ha^{-1}$, respectively. The stable $SO_4^{2-}$ activities observed with MCP application suggested 20 kg P $ha^{-1}$ increments of MCP had no effect on S mineralization. Moreover, the stability of $SO_4^{2-}$ activities by other levels of P sources suggested pairing of $SO_4^{2-}$ with $Ca^{2+}$ and $Mg^{2+}$ and the increase in $CaSO_4^0$ and $MgSO_4^0$ activities (Fig. 3) and/or complexation of $SO_4^{2-}$ with other species. No differences in $SO_4^{2-}$ activities were observed between APP rates of 60 and 80 kg P $ha^{-1}$. But all APP rates induced higher $SO_4^{2-}$ activities than the control. Also, APP rates of 60 and 80 kg P $ha^{-1}$ caused greater $SO_4^{2-}$ activities than the APP rate of 40 kg P $ha^{-1}$.

No differences in $SO_4^{2-}$ activities were observed among similar rates of MCP and APP, but all MCP and APP rates induced higher $SO_4^{2-}$ activities than corresponding rates of MAP.

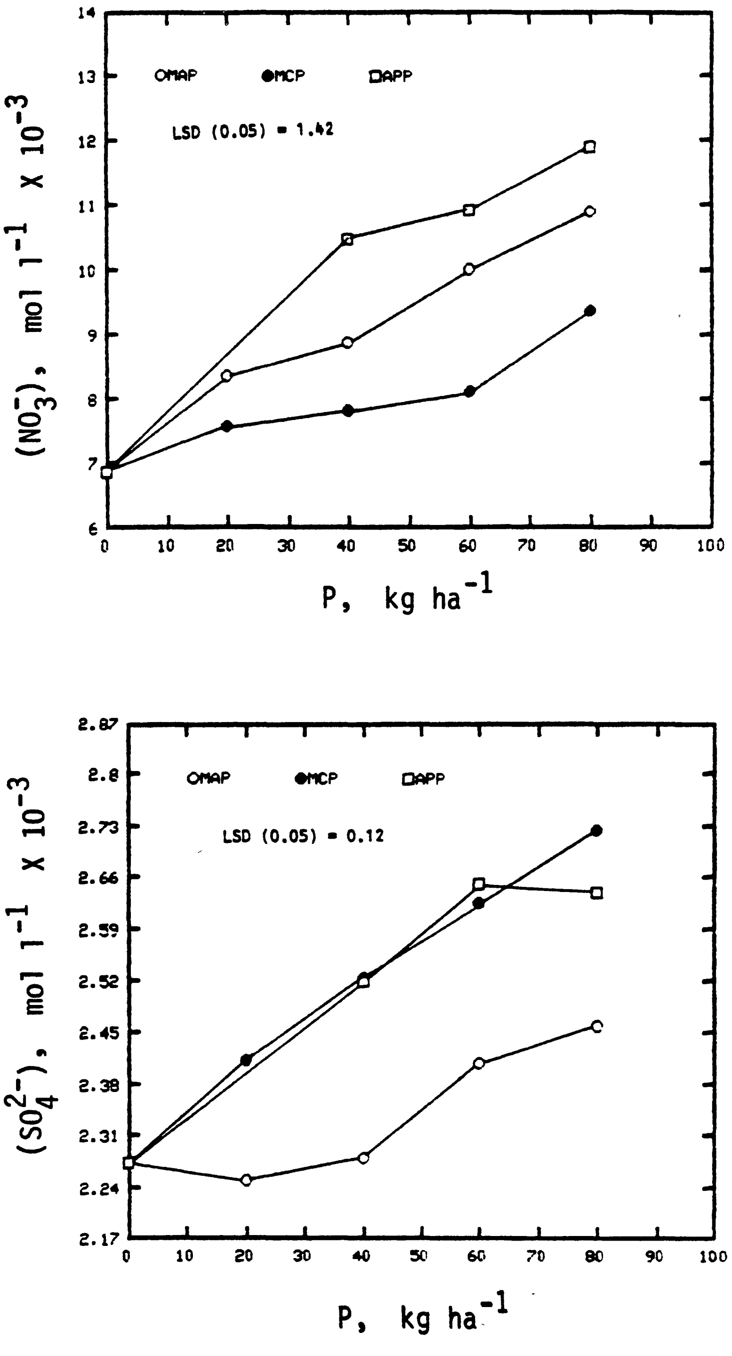


Fig. 2-Effect of P sources and rates on $NO_3^-$ and $SO_4^{2-}$ activities in McLain soil solution.

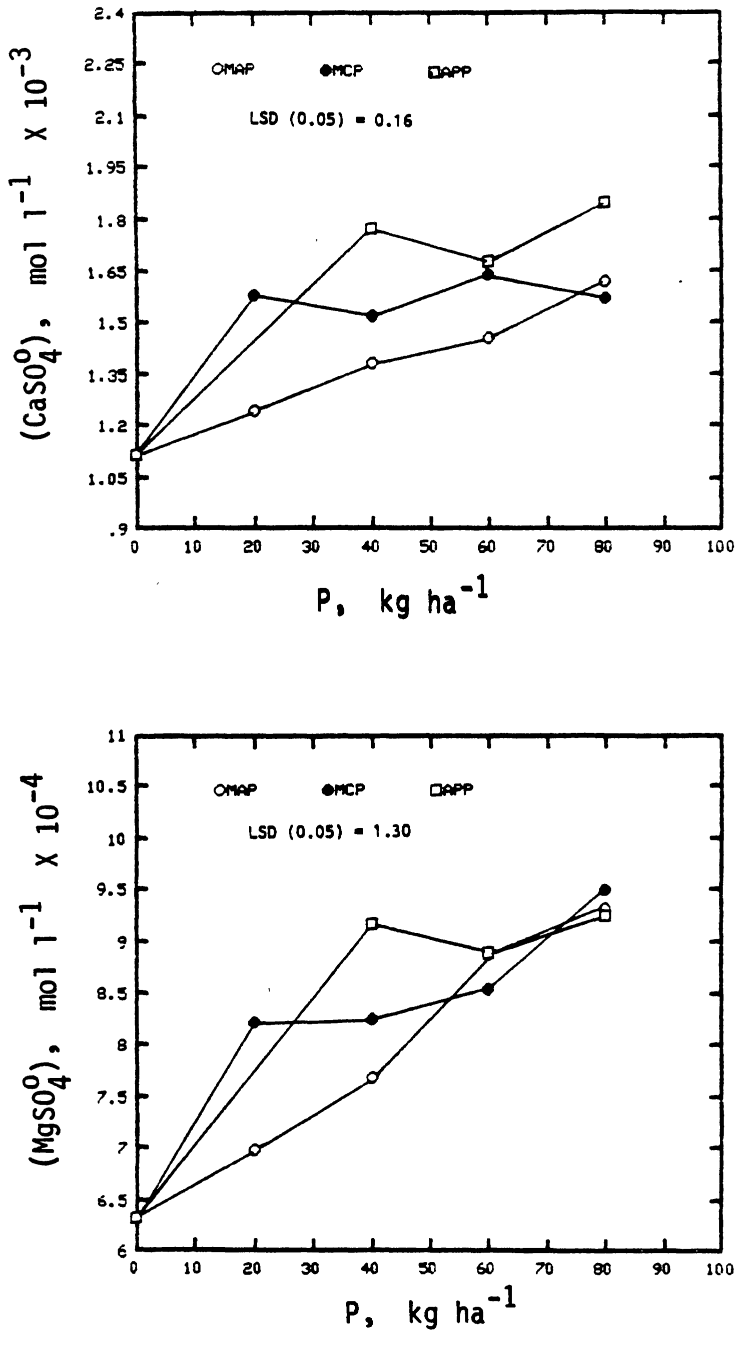


Fig. 3-Effect of P sources and rates on $CaSO_4^0$ and $MgSO_4^0$ activities in McLain soil solution.

## pH and $HCO_3^-$ Activity

Soil solution pH was decreased (Fig. 4) with MAP and APP application, due to the donation of protons in the nitrification process (Tisdale and Nelson, 1975) and/or the result of a decrease in $HCO_3^-$ activity (Fig. 4). There were no differences in soil solution pH among rates of 20, 40, and 60 or 40, 60, and 80 kg P $ha^{-1}$ of MAP. However, all rates of MAP induced lower soil solution pH than the control and the 80 kg P $ha^{-1}$ induced lower soil solution pH than 20 kg P $ha^{-1}$.

No changes in soil solution pH among APP rates of 0 and 40, or 40 and 60, or 60 and 80 kg $ha^{-1}$ P were observed, however, 60 and 80 kg P $ha^{-1}$ of APP caused lower soil solution pH than observed in the control. Also 80 kg P $ha^{-1}$ caused lower soil solution pH than 40 kg P $ha^{-1}$. The stability of soil solution pH might have been caused by the lack of effect of the 40 kg P $ha^{-1}$ of APP on the buffer capacity of the soil and/or the stability of $HCO_3^-$ activities between the rates of 40 and 60 kg P $ha^{-1}$ of APP.

Soil solution pH did not change with MCP application, consequently, there was no change in $HCO_3^-$ activities among the rates of 20, 40, 60 and 80 kg P $ha^{-1}$. Rates of 20, 40, 60, and 80 kg P $ha^{-1}$ of MAP caused lower soil solution pH than the corresponding rates of MCP. Also, the rate of 80 kg P $ha^{-1}$ of APP induced lower soil solution pH than the similar rate of MCP. Furthermore, the rates of 40 and 60 kg P $ha^{-1}$ of MAP caused lower soil solution pH than the corresponding rates of APP. No changes in $HCO_3^-$ activities were observed among similar rates of P sources. This finding indicated the $NH_4^+$ content of MAP and APP influenced the depression of the soil solution pH.

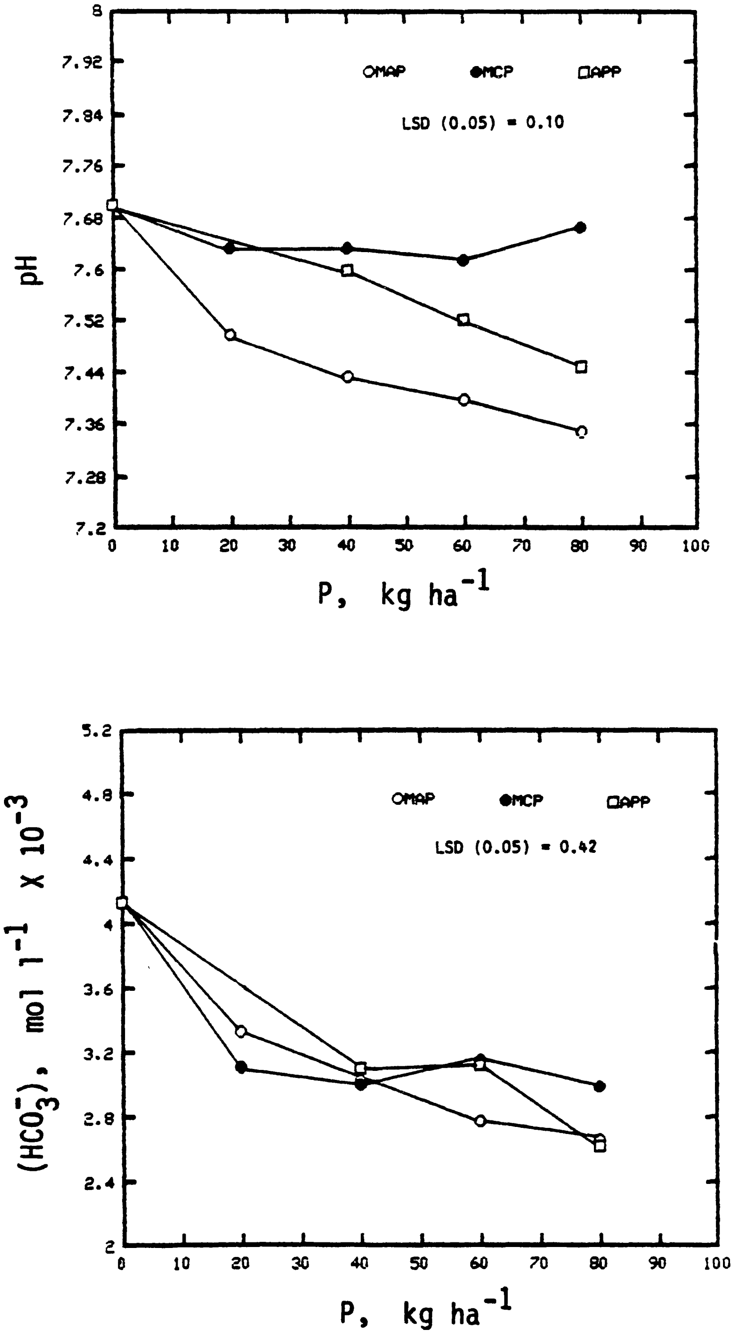


Fig. 4-Effect of P sources and rates on pH and $HCO_3^-$ activity in McLain soil solution.

## $HPO_4^{2-}$ and $H_2PO_4^-$ Activities

Phosphorus application increased (Fig. 5) both $HPO_4^{2-}$ and $H_2PO_4^-$ activities and concentrations in soil solution. No differences in $HPO_4^{2-}$ activities among the rates of 0 and 20, or 20 and 40 kg P ha$^{-1}$ of MAP or MCP were observed. Also, no changes in $HPO_4^{2-}$ activities between MAP rates of 40 and 60 kg P ha$^{-1}$ or MCP rates of 60 and 80 kg P ha$^{-1}$ were found. However, MAP and MCP rates of 40, 60, and 80 kg P ha$^{-1}$ caused higher $HPO_4^{2-}$ activities than observed in the control. Also 80 kg P ha$^{-1}$ of MAP induced higher $HPO_4^{2-}$ activities than all other P levels; and 60 kg P ha$^{-1}$ caused higher $HPO_4^{2-}$ activity than 20 kg P ha$^{-1}$. Moreover, 60 kg P ha$^{-1}$ of MCP caused higher $HPO_4^{2-}$ activities than MCP 20 and 40 kg P ha$^{-1}$. The lack of changes in $HPO_4^{2-}$ activities between MAP rates of 0 and 20 kg P ha$^{-1}$ might be caused by the decrease in the soil soluton pH between the same rates of MAP (Fig. 4). However, according to Lindsay, 1979; and Bell and Black, 1970; formation of DCPD, DCP and $Mg_3(PO_4)_2.22H_2O$ by other levels of MAP or MCP could be considered as reasons for the above changes in $HPO_4^{2-}$ activities.

No changes in $HPO_4^{2-}$ activities among APP rates of 40 and 60, or 60 and 80 kg P ha$^{-1}$ were noted. However, all APP rates induced higher $HPO_4^{2-}$ activities than the control. Also 80 kg P ha$^{-1}$ as APP induced higher $HPO_4^{2-}$ activity than 40 kg P ha$^{-1}$. The stability of $HPO_4^{2-}$ activity might be caused by the formation of DCPD and $MgHPO_4.3H_2O$ (Racz and Soper, 1967), or the decrease of soil solution pH between APP rates of 40 and 80 kg ha$^{-1}$.

No differences in $H_2PO_4^-$ activities between MAP rates of 0 and 20, or 20 and 40, or 40 and 60 kg P $ha^{-1}$ were observed. However, 80 kg P $ha^{-1}$ as MAP induced higher $H_2PO_4^-$ activity than all other rates. Also 40 and 60 kg P $ha^{-1}$ induced higher $H_2PO_4^-$ activities than the control or 0 and 20 kg P $ha^{-1}$, respectively. There were no changes in $H_2PO_4^-$ activities among the rates of 0, 20, and 40, or 20, 40, 60, and 80 kg P $ha^{-1}$ of MCP or 0 and 40 kg P $ha^{-1}$ of APP. However, MCP rates of 60 and 80 kg P $ha^{-1}$ increased $H_2PO_4^-$ activity higher than observed in the control. Also, 60 and 80 kg P $ha^{-1}$ as MCP caused higher $H_2PO_4^-$ activities than rates of 20, or 20 and 40 kg P $ha^{-1}$, respectively. Furthermore, 80 kg P $ha^{-1}$ as APP caused greater $H_2PO_4^-$ activity than 60 kg P $ha^{-1}$. Also, APP rates of 60 and 80 kg P $ha^{-1}$ induced higher $H_2PO_4^-$ activities than 0 and 40 kg P $ha^{-1}$. The stability of $H_2PO_4^-$ activities was the result of the lack of change in soil solution pH within these levels (Fig. 4); or the formation of DCPD, DCP and $MgHPO_4.3H_2O$ (Lindsay, 1979; Racz and Soper, 1967).

No differences in $HPO_4^{2-}$ activities between the similar rates of P sources were observed. However, over all P rates, MAP induced higher $H_2PO_4^-$ activites than the other P sources. Also the rates of 40, 60, and 80 kg P $ha^{-1}$ of MAP caused higher $H_2PO_4^-$ activity than the corresponding rates of MCP. Similarly, 80 kg P $ha^{-1}$ of MAP and APP induced higher $H_2PO_4^-$ activity than the similar rates of APP and MCP. This finding shows that a good trend exists between P source effects on soil solution pH and $H_2PO_4^-$ activities.

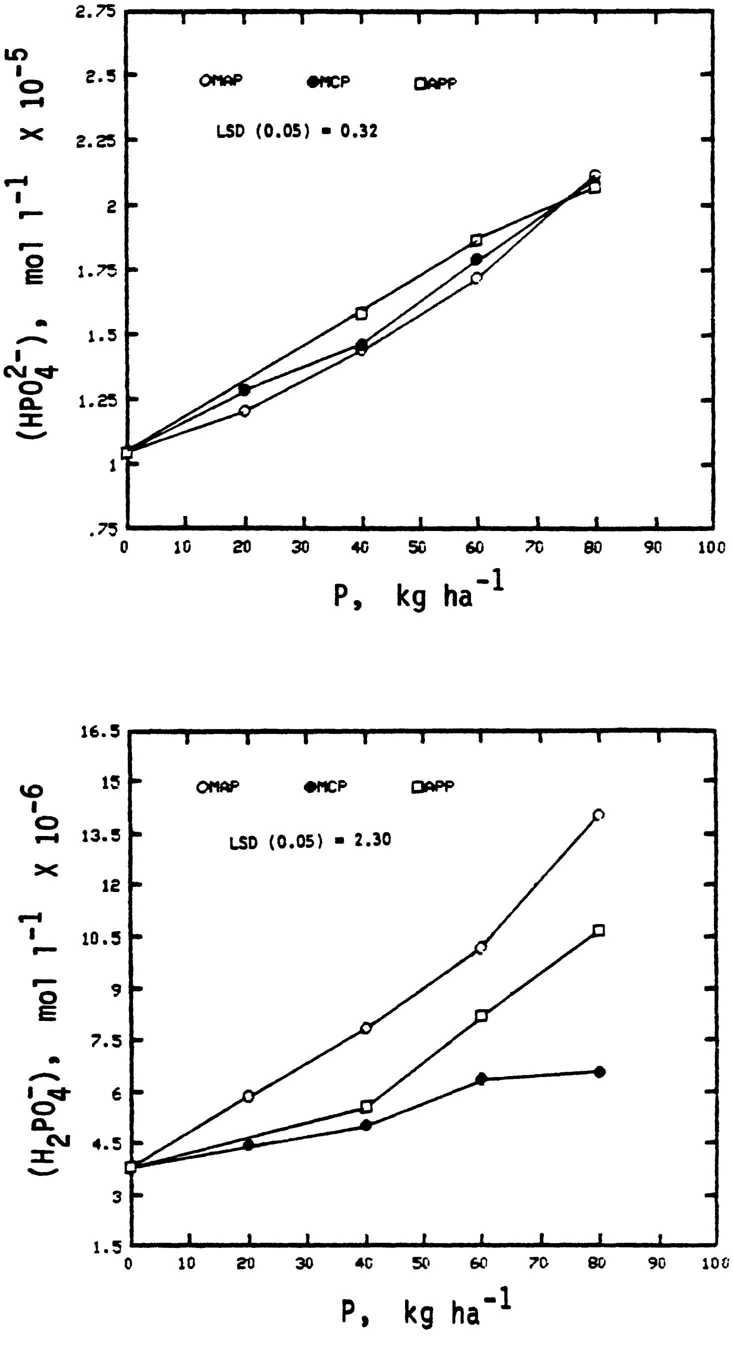
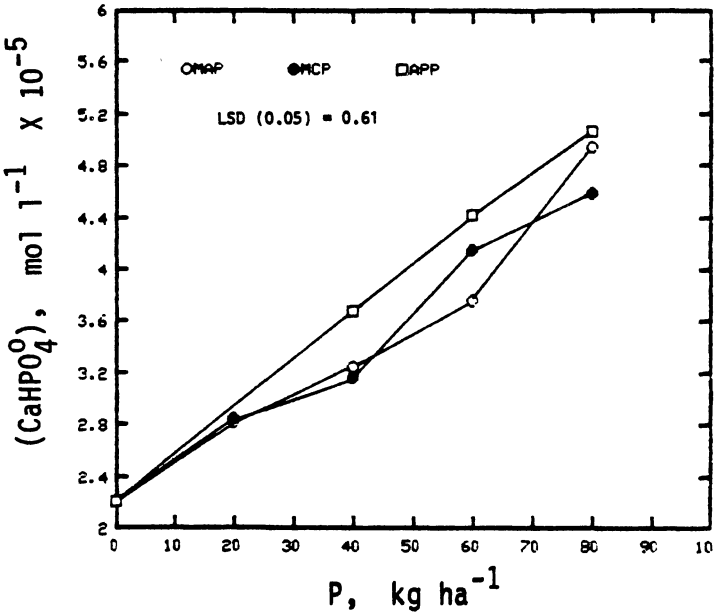


Fig. 5-Effect of P sources and rates on $HPO_4^{2-}$ and $H_2PO_4^-$ activities in McLain soil solution.

## $CaHPO_4^o$ and $MgHPO_4^o$ Activities

All P sources increased $CaHPO_4^o$ and $MgHPO_4^o$ activities (Fig. 6). Increases in $CaHPO_4^o$ activities were observed among all APP levels. No changes in $CaHPO_4^o$ activities among MAP rates of 20 and 40, or 40 and 60 kg P $ha^{-1}$ were observed. Also there were no differences in $CaHPO_4^o$ activities among MCP rates of 20 and 40, or 60 and 80 kg P $ha^{-1}$. But all MAP and MCP rates induced higher $CaHPO_4^o$ activities than the control. However, 80 kg P $ha^{-1}$ as MAP caused higher $CaHPO_4^o$ activity than all other rates; and 60 kg P $ha^{-1}$ caused greater $CaHPO_4^o$ activity than 20 kg P $ha^{-1}$. Furthermore, MCP rates of 60 and 80 kg P $ha^{-1}$ induced higher $CaHPO_4^o$ activities than 20 and 40 kg P $ha^{-1}$.

No differences in $MgHPO_4^o$ activities between the rates of 0 and 20, or 20 and 40 kg P $ha^{-1}$ of MAP or MCP were observed. Also there were no changes in $MgHPO_4^o$ activity observed among APP rates of 40 and 60, or 60 and 80 kg P $ha^{-1}$. However, MAP and MCP rates of 60 and 80 kg P $ha^{-1}$ caused higher $MgHPO_4^o$ activites than the other P levels. Rates of 40 kg P $ha^{-1}$ as MAP and MCP caused greater $MgHPO_4^o$ activity than observed in the control. All rates of APP induced higher $MgHPO_4^o$ activities than the control and 80 kg P $ha^{-1}$ caused greater $MgHPO_4^o$ activity than 40 kg P $ha^{-1}$. The increase in $CaHPO_4^o$ and $MgHPO_4^o$ activities suggested soil solution pH depression had little effect on the activities of these complexes within this range of soil solution pH. Formation of DCPD, DCP, $Mg_3(PO_4)_2.22H_2O$ and $MgHPO_4.3H_2O$ by P sources may also be considered as a contributing factor (Lindsay, 1979; Bell and Black, 1970; Racz and Soper, 1967) for the observed changes. This finding suggested



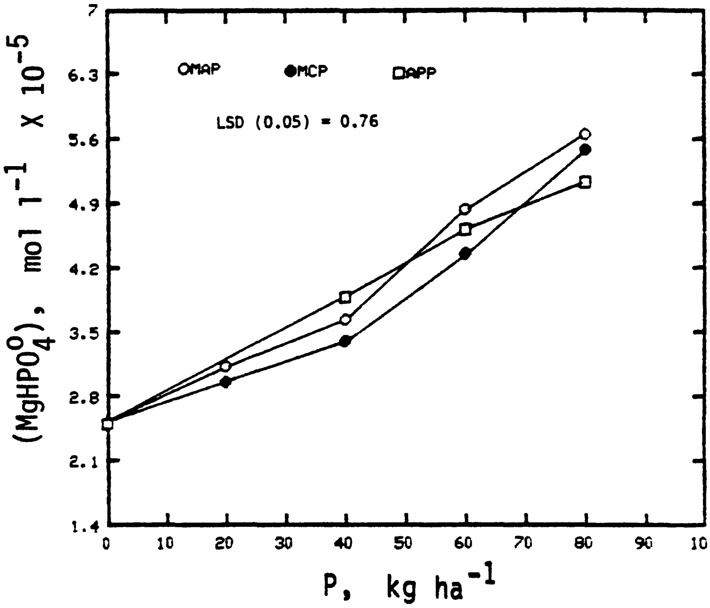


Fig. 6-Effect of P sources and rates on $CaHPO_4^0$ and $MgHPO_4^0$ activities in McLain soil solution.

that in many cases an increment of 20 kg P $ha^{-1}$ is not sufficient to increase $CaHPO_4^o$ and $MgHPO_4^o$ activities.

No differences in $CaHPO_4^o$ and $MgHPO_4^o$ activities were found between similar levels of P sources, except that the rate of 80 kg P $ha^{-1}$ of APP caused higher $CaHPO_4^o$ activity than the similar rates of MCP.

## $CaPO_4^-$ and $MgPO_4^-$ Activities

$CaPO_4^-$ activity was not affected by MAP application (Fig. 7). Both MCP and APP applications increased $CaPO_4^-$ activity. But no differences in $CaPO_4^-$ activity were observed among rates of 0, 20, and 40 or 40, 60, and 80 kg P $ha^{-1}$ of MCP and APP, respectively. However, MCP rates of 60 and 80 kg P $ha^{-1}$ induced higher $CaPO_4^-$ activities than all other rates. Similarly, APP rates of 40, 60, and 80 kg P $ha^{-1}$ induced greater $CaPO_4^-$ activities than the control.

$MgPO_4^-$ activity (Fig. 7) was not affected by MAP or APP application. However, MCP application increased $MgPO_4^-$ activities. But no changes in $MgPO_4^-$ activities among the rates of 0, 20, and 40 or 40 and 60 kg P $ha^{-1}$ were observed. Furthermore, 80 kg P $ha^{-1}$ caused higher $MgPO_4^-$ activities than all other levels and 60 kg P $ha^{-1}$ caused higher $MgPO_4^-$ activities than 0 and 20 kg P $ha^{-1}$. The stable $CaPO_4^-$ and $MgPO_4^-$ activities by MAP and APP application was caused by soil solution pH depression. However, increased $CaPO_4^-$ activity by MCP application was caused by the lack of change in soil solution pH (Fig. 4). Also the stability of $CaPO_4^-$ and $MgPO_4^-$ activities was probably caused by the formation of DCPD, DCP, $Mg_3(PO_4)_2.22H_2O$ and $MgHPO_4.3H_2O$ (Lindzay, 1979; Bill and Black, 1970; Racz and Soper, 1967).

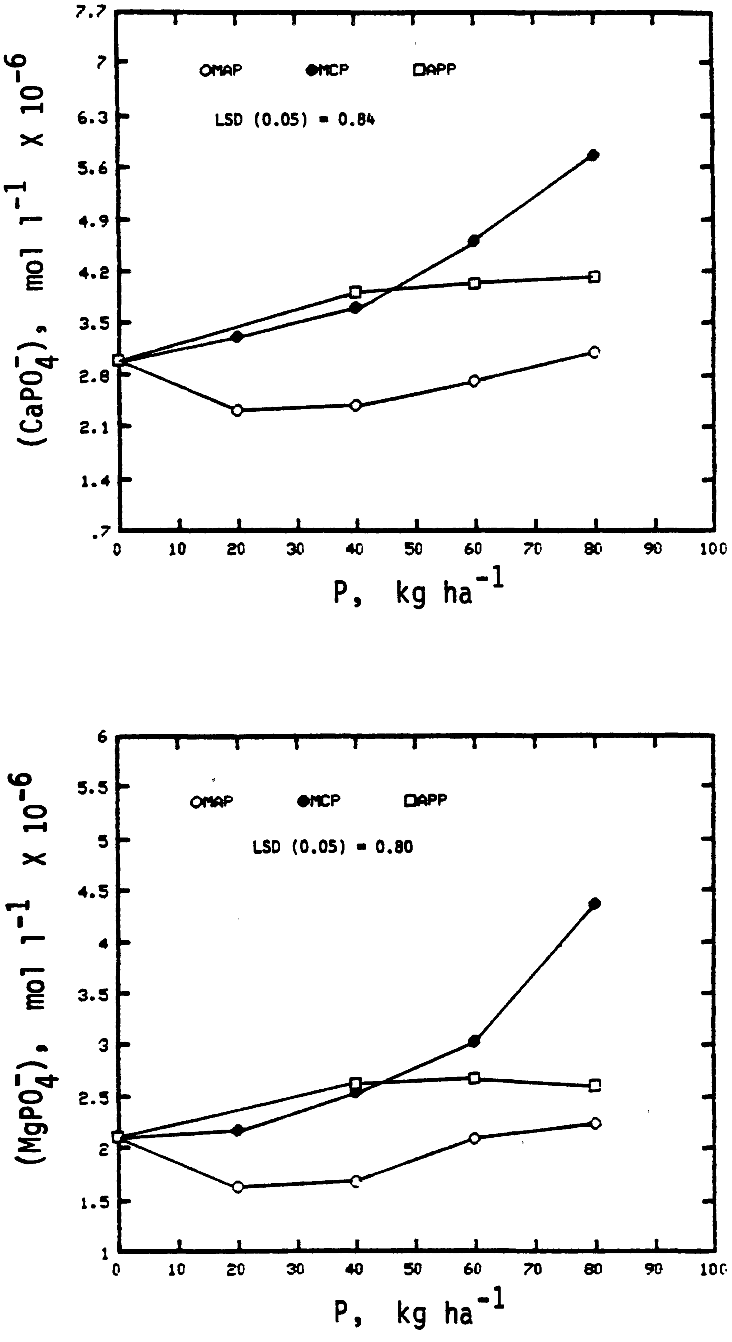


Fig. 7-Effect of P sources and rates on $CaPO_4^-$ and $MgPO_4^-$ activities in McLain soil solution.

All MAP rates lowered $CaPO_4^-$ activities more than corresponding rates of APP and MCP due to the greater decrease of soil solution pH by MAP than APP and MCP (Fig. 4). The rate of 80 kg P $ha^{-1}$ of MCP increased $CaPO_4^-$ and $MgPO_4^-$ activities more than the similar rate of APP. Furthermore, MAP rates of 40, 60, and 80 kg P $ha^{-1}$ caused lower $MgPO_4^-$ activities than similar rates of MCP. Also, MAP rates of 40, and 60 kg P $ha^{-1}$ induced lower $MgPO_4^-$ activities than the corresponding rates of APP. This finding suggested different effects of P sources on $CaPO_4^-$ and $MgPO_4^-$ activities.

## Quinlan Soil

### $Ca^{2+}$ and $Mg^{2+}$ Activities

All P sources increased $Ca^{2+}$ and $Mg^{2+}$ activities except MCP which had no effect on $Mg^{2+}$ activity (Fig. 8). The increase in $Ca^{2+}$ and $Mg^{2+}$ activities was caused by the displacement of the exchangeable $Ca^{2+}$ and $Mg^{2+}$ by $NH_4^+$ derived from APP (Sample et al., 1979), or the influence of $Ca^{2+}$ from MCP application. No changes in $Ca^{2+}$ activities among the rates of 20, 40, 60, and 80 kg P $ha^{-1}$ of MAP and MCP, or 40, 60, and 80 kg P $ha^{-1}$ of APP were observed. However, all P rates induced higher $Ca^{2+}$ activities than the control.

No differences in $Mg^{2+}$ activities among the rates of 20, 40, and 60 or 40, 60, and 80 kg P $ha^{-1}$ of MAP, or 40, 60, and 80 kg P $ha^{-1}$ of APP were observed. However, all MAP and APP rates caused higher $Mg^{2+}$ activities than the control. Also 80 kg P $ha^{-1}$ as MAP induced higher $Mg^{2+}$ activity than 20 kg P $ha^{-1}$. The lack of changes in $Ca^{2+}$ and $Mg^{2+}$ activities might be caused by the adsorption of these cations on the

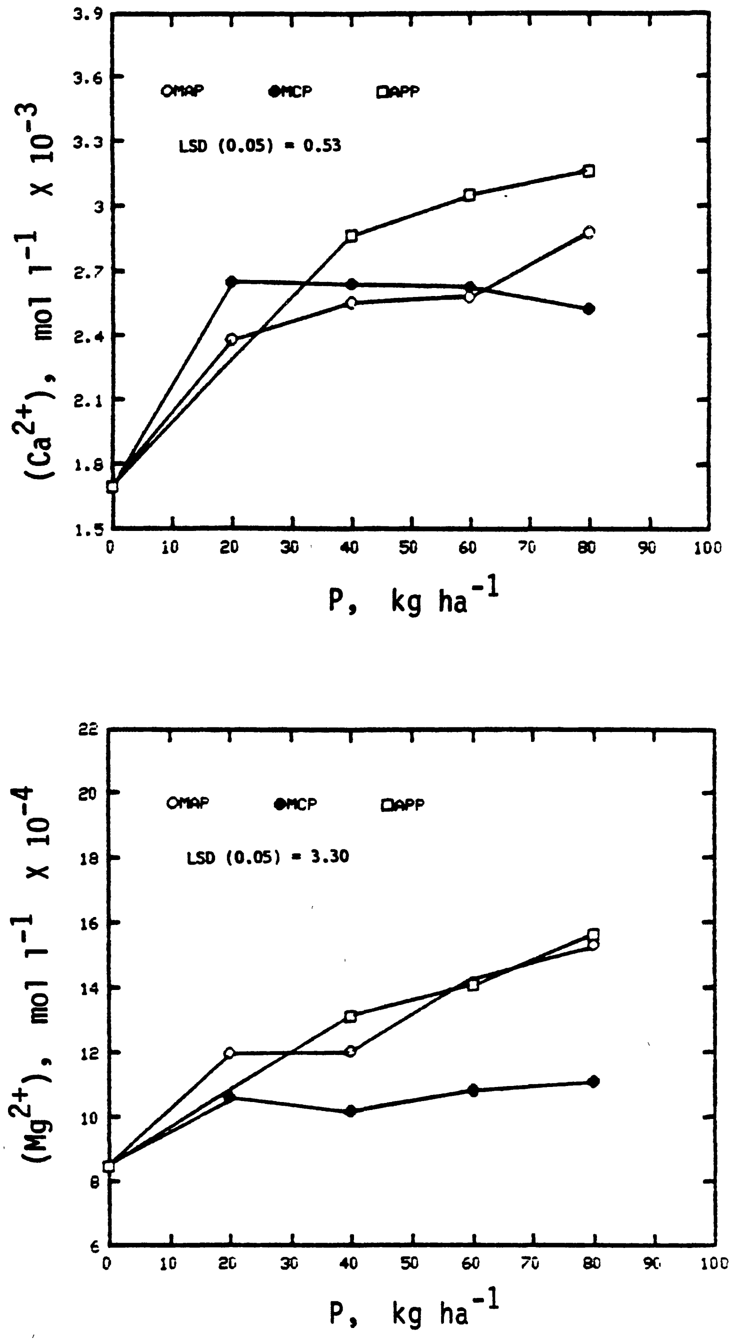


Fig. 8-Effect of P sources and rates on $Ca^{2+}$ and $Mg^{2+}$ activities in Quinlan soil solution.

exchangeable sites. Formation of DCPD, DCP, OCP, TCP and $MgNH_4PO_4.6H_2O$ by MCP and MAP might be considered as other factors for the above changes (Lindsay, 1979; Havlin and Westfall, 1984; Fixen et al., 1983; Lindsay et al., 1962; Bell and Black, 1970).

No changes in $Ca^{2+}$ and $Mg^{2+}$ activities were observed between the similar rates of P sources. But 80 kg P $ha^{-1}$ of APP caused higher $Ca^{2+}$ activity than the similar rate of MCP. Also, 60 and 80 kg P $ha^{-1}$ of MCP induced lower $Mg^{2+}$ activities than the corresponding rates of MAP and APP. This was good indication for the displacement of the exchangeable cations by $NH_4^+$ ions derived from MAP and APP.

## $NO_3^-$ Activity

Nitrate-N activities (Fig. 9) were increased by all P sources due to the influence of MAP and APP as P and N sources, and the increase of the N mineralization process by P sources application (Tisdale and Nelson, 1975). No changes in $NO_3^-$ activities between the rates of 0 and 20, or 20 and 40, or 40 and 60, or 60 and 80 kg P $ha^{-1}$ of MAP were observed. This finding suggested 20 kg P $ha^{-1}$ increments of MAP had little effect on N mineralization. However, MAP rates of 40, 60, and 80 kg P $ha^{-1}$ induced greater $NO_3^-$ activities than was observed in the control. Also, 60 and 80 kg P $ha^{-1}$ of MAP caused greater $NO_3^-$ activities than MAP rates of 20 or 20 and 40 kg P $ha^{-1}$, respectively.

No differences in $NO_3^-$ activities among the APP rates of 40 and 60 or 60 and 80 kg P $ha^{-1}$ were observed. But all APP rates caused greater $NO_3^-$ activity than the control. Also 80 kg P $ha^{-1}$ as APP induced higher $NO_3^-$ activity than 40 kg P $ha^{-1}$. The lack of change in $NO_3^-$ activities by 20 kg P $ha^{-1}$ increments of APP was due to insignificant changes in the N mineralization process.

There were no differences in $NO_3^-$ activities among the rates of 0, 20, 40, and 80 kg P $ha^{-1}$ or the rates of 20, 40, 60, and 80 kg P $ha^{-1}$ of MCP. However, 60 kg P $ha^{-1}$ induced higher $NO_3$ activity than the control. The stable $NO_3^-$ activities with increasing rates of MCP was caused by the lack of influence of MCP on organic matter decomposition and N mineralization processes. This finding suggested similar influences of MAP and APP application on $NO_3^-$ activities, and different influences of P sources on the N mineralization process and $NO_3^-$ activities in soil solution.

No changes in $NO_3^-$ activities were induced by the similar rates of P sources. But the rates of 60, and 80 kg P $ha^{-1}$ of MAP and APP caused higher $NO_3^-$ activities than the corresponding rates of MCP, which might be related to the increase of the microbial activity by the addition of the N sources.

## $SO_4^{2-}$ Activity

All P sources decreased $SO_4^{2-}$ activities (Fig. 9) due to the low S content and the immobilization of $SO_4^{2-}$ by soil microorganisms (Tisdale and Nelson, 1975) or, perhaps, by complexation of $SO_4^{2-}$ by $Ca^{2+}$ and $Mg^{2+}$.

No differences in $SO_4^{2-}$ activities between MAP rates of 20 and 40, or 20 and 60, or 60 and 80 kg P $ha^{-1}$ were observed. But all MAP rates induced lower $SO_4^{2-}$ activities than the control. Also MAP rates of 60 and 80 kg P $ha^{-1}$ caused lower $SO_4^{2-}$ activities than MAP rates of 40 or

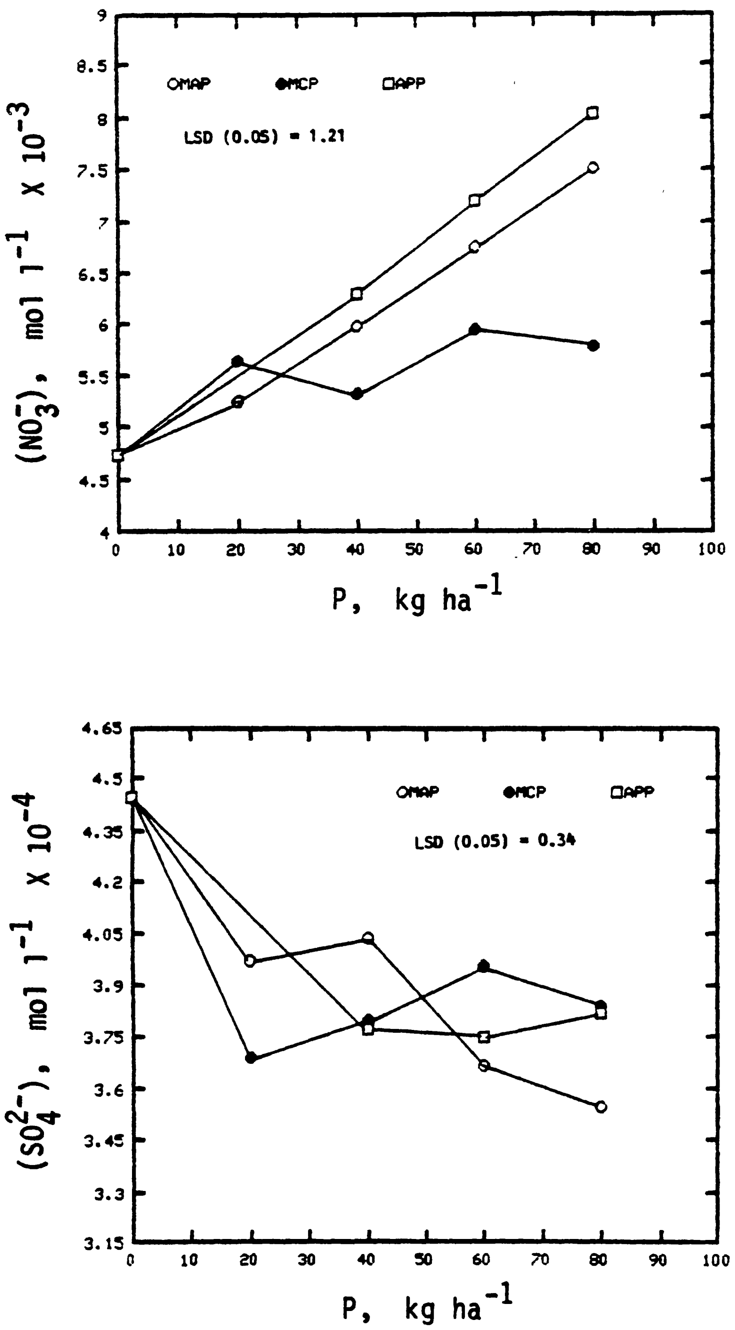
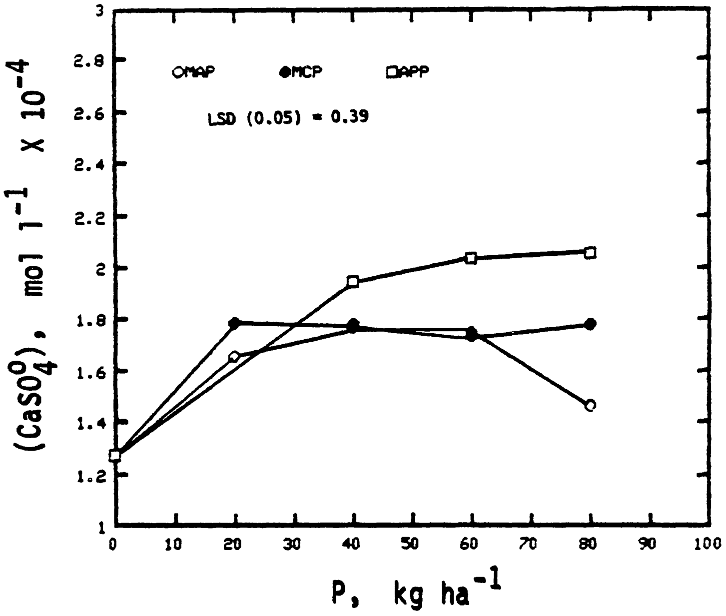


Fig. 9-Effect of P sources and rates on $NO_3^-$ and $SO_4^{2-}$ activities in Quinlan soil solution.



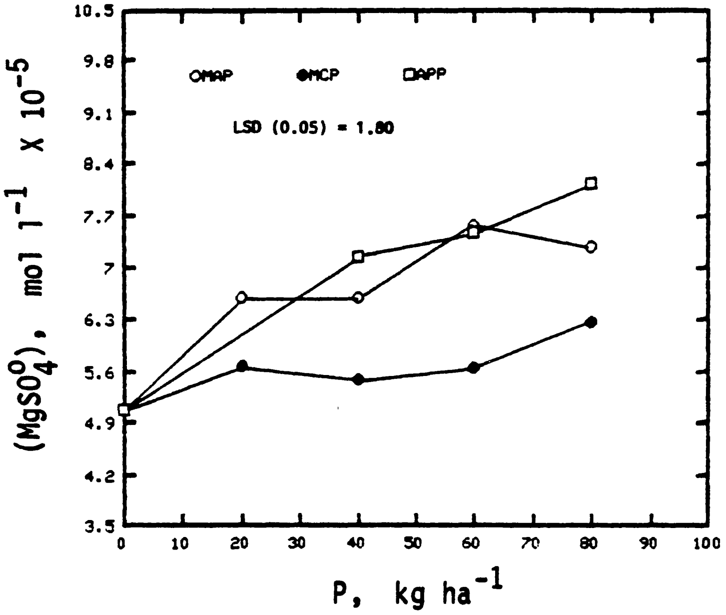


Fig. 10-Effect of P sources and rates on $CaSO_4^0$ and $MgSO_4^0$ activities in Quinlan soil solution.

20 and 40 kg P ha$^{-1}$, respectively. The lack of changes in $SO_4^{2-}$ activities occurred because MAP had no influence on $SO_4^{2-}$ fixation, or the inhibition of $SO_4^{2-}$ immobilization. No differences in $SO_4^{2-}$ activities among the rates of 20, 40, 60, and 80 or 40, 60, and 80 kg P ha$^{-1}$ of MCP and APP, respectively were observed. However, all MCP or APP rates induced lower $SO_4^{2-}$ activities than the control. Furthermore, the stability of $CaSO_4^o$ and $MgSO_4^o$ activities between the rates of 20, 40, 60, and 80 kg P ha$^{-1}$ of MAP and MCP (Fig. 10) was good indication for high $SO_4^{2-}$ immobilization or fixation within these rates. Also the increase in $CaSO_4^o$ and $MgSO_4^o$ activities by APP rates of 40, 60, and 80 kg P ha$^{-1}$ might be considered as another reason for the above changes in $SO_4^{2-}$ activities.

No changes in $SO_4^{2-}$ activities among the similar rates of P sources were observed, except that MAP rate of 60 kg P ha$^{-1}$ induced lower $SO_4^{2-}$ activity than the similar rate of MCP.

## pH and $HCO_3^-$ Activity

All P sources decreased soil solution pH (Fig. 11) which can be attributed to nitrification and donation of protons by MAP and APP, or the increase in the microbial activity and $CO_2$ pressure by all P sources (Curtin and Smille 1983; Petri and Jackson, 1984). No differences in soil solution pH between the rates of 40 and 60 kg P ha$^{-1}$ of MAP or APP were observed. However, all MAP and APP rates induced lower soil solution pH than the control. Also MAP or APP rates of 80 kg P

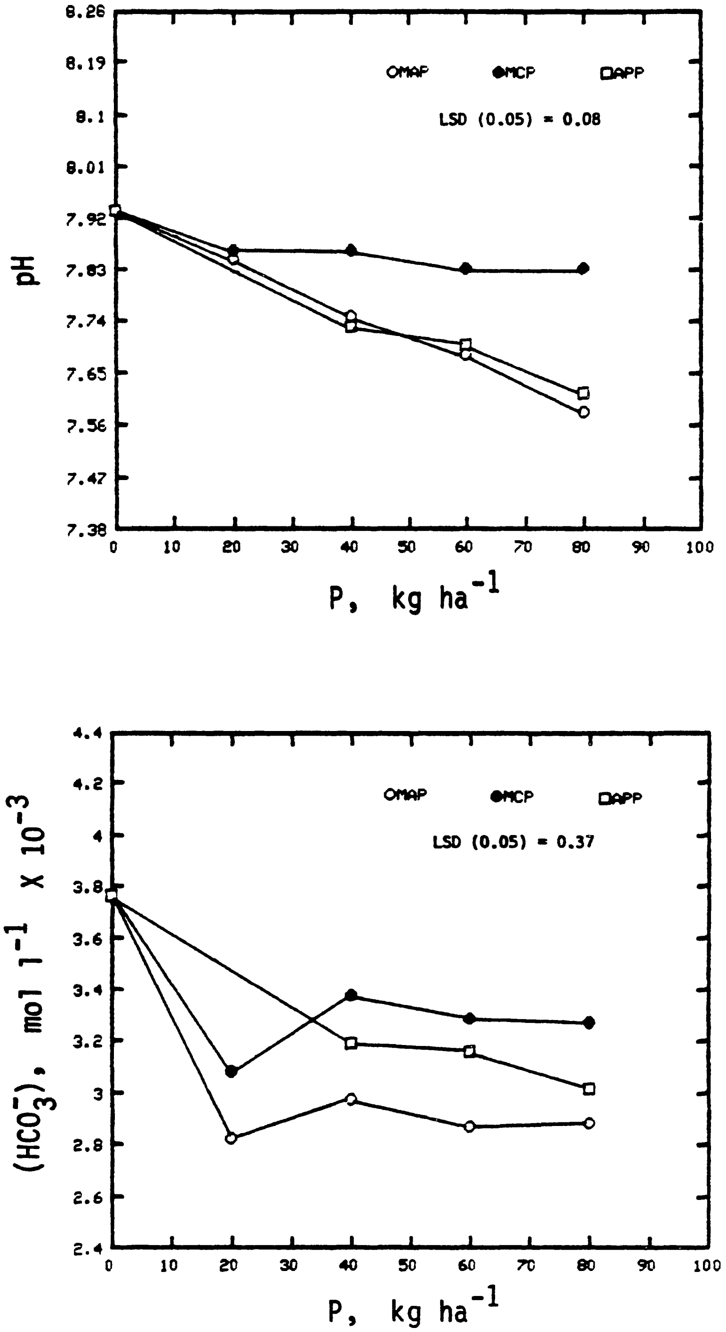


Fig. 11-Effect of P sources and rates on pH and $HCO_3^-$ activities in Quinlan soil solution.

ha$^{-1}$ caused lower soil solution pH than all other rates. Similarly 60 kg P ha$^{-1}$ as MAP caused lower soil solution pH than 20 kg P ha$^{-1}$. The stable $HCO_3^-$ activity among the rates of 20, 40, 60, and 80 or 40, 60, and 80 kg P ha$^{-1}$ of MAP and APP, respectively, (Fig. 11) might be considered as one reason for the lack of change in soil solution pH. However, the decrease of soil solution pH by other MAP and APP rates was mainly caused by the nitrification and donation of protons. No changes in soil solution pH among MCP rates of 0, 20, and 40 or 20, 40, 60, and 80 kg P ha$^{-1}$ were observed. However, MCP rates of 60 and 80 kg P ha$^{-1}$ induced lower soil solution pH than the control. The lack of changes in $HCO_3^-$ activities among the rates of 20, 40, 60, and 80 kg P ha$^{-1}$ of MCP can be related to the above changes in soil solution pH.

No differences in soil solution pH or $HCO_3^-$ activities were observed between the similar levels of MAP and APP. But the rates of 40, 60, and 80 kg P ha$^{-1}$ of MAP and APP caused lower soil soluton pH than the corresponding rates of MCP. Also the rates of 40, 60, and 80 kg P ha$^{-1}$ of MAP induced lower $HCO_3^-$ activities than the corresponding levels of MCP. This finding suggested the $NH_4^+$ group from MAP and APP had a marked effect on soil solution pH and $HCO_3^-$ activities.

## $HPO_4^{2-}$ and $H_2PO_4^-$ Activities

All P sources increased $HPO_4^{2-}$ and $H_2PO_4^-$ activities (Fig. 12) due to the increase of the free P concentration. No differences in $HPO_4^{2-}$ activities between the rates of 0 and 20 kg P ha$^{-1}$ of MAP or MCP were observed. However, an increase in $HPO_4^{2-}$ activity was observed between the rates of 20, 40, 60, and 80 kg P ha$^{-1}$ of MCP and MAP, or all APP

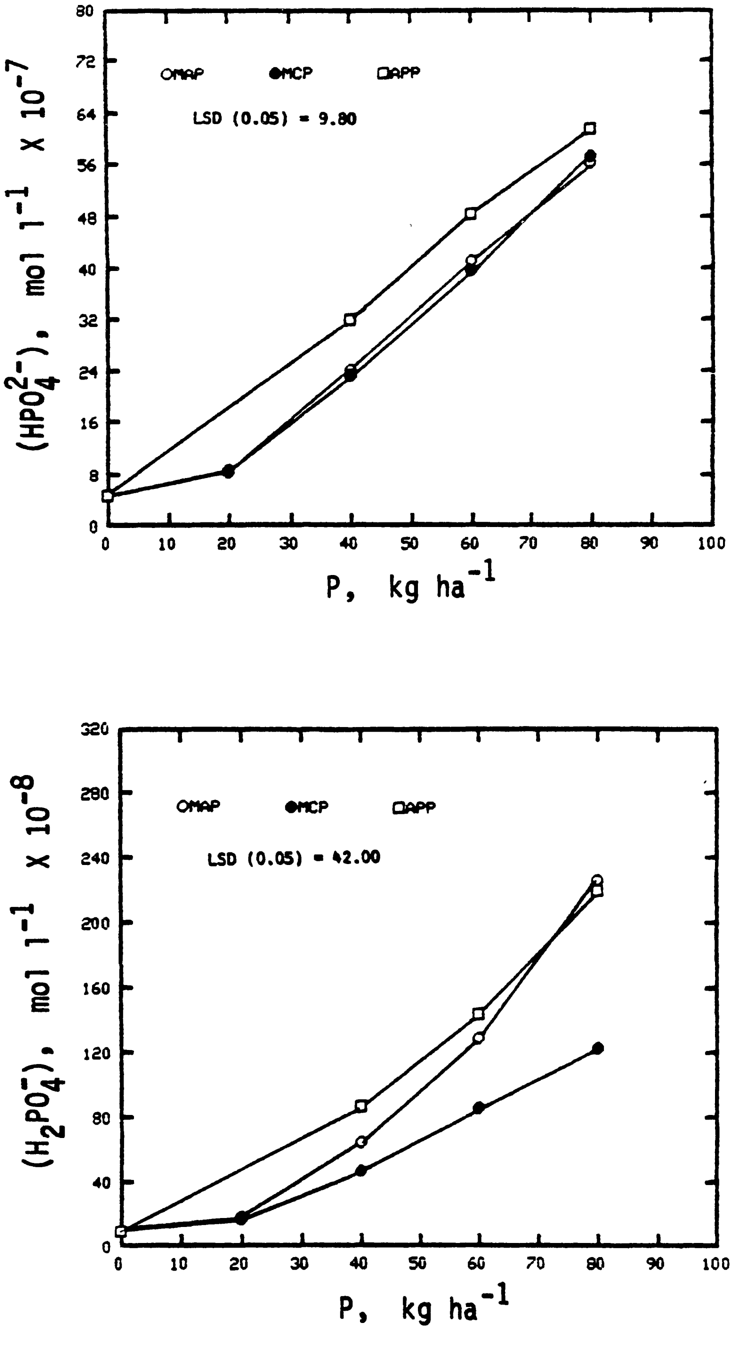


Fig. 12-Effect of P sources and rates on $HPO_4^{2-}$ and $H_2PO_4^-$ activities in Quinlan soil solution

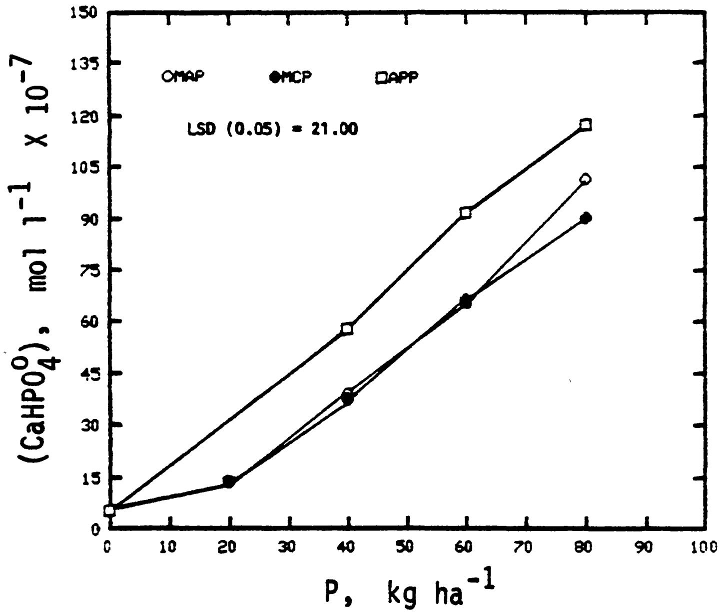
rates. Also MAP and MCP rates of 40, 60, and 80 kg P $ha^{-1}$ had higher $HPO_4^{2-}$ activities than the control. The increase in $HPO_4^{2-}$ activities among all MCP levels except the rate of 20 kg P $ha^{-1}$ might be caused by the high soil solution pH, the little decrease in that pH (Fig. 11) and the increase of the free P concentration.

No changes in $H_2PO_4^-$ activities among the rates of 0, 20, and 40, or 40 and 60, or 60 and 80 kg P $ha^{-1}$ of MCP were observed. But 80 kg P $ha^{-1}$ as MCP caused higher $H_2PO_4^-$ activities than the rates of 0, 20, and 40 kg P $ha^{-1}$. Also 60 kg P $ha^{-1}$ induced higher $H_2PO_4^-$ activities than 0 and 20 kg P $ha^{-1}$. However, increases in $H_2PO_4^-$ activities were observed between all MAP and APP levels. The stable $H_2PO_4^-$ activities by MCP application might be caused by lack of change of soil soluton pH by 20, 40, 60, and 80 kg P $ha^{-1}$ of MCP. Formation of TCP, DCPD, and DCP could be considered as another reason for the above changes in $HPO_4^{2-}$ and $H_2PO_4^-$ activities (Lindsay, 1979; Havlin and Westfall, 1984).

No differences in $HPO_4^{2-}$ and $H_2PO_4^-$ activities were observed among the similar rates of P sources. However, 60 and 80 kg P $ha^{-1}$ of MAP and APP induced higher $H_2PO_4^-$ activities than the corresponding rates of MCP. The differences in $H_2PO_4^-$ activities by P sources are associated with the depression of the soil solution pH.

### $CaHPO_4^o$ and $MgHPO_4^o$ Activities

All P sources increased $CaHPO_4^o$ and $MgHPO_4^o$ activities (Fig. 13). No differences in $CaHPO_4^o$ and $MgHPO_4^o$ activities between the rates of 0 and 20 kg P $ha^{-1}$ of MAP or MCP were observed. However, increases in $CaHPO_4^o$ activities were observed between 40, 60, and 80 kg P $ha^{-1}$ of



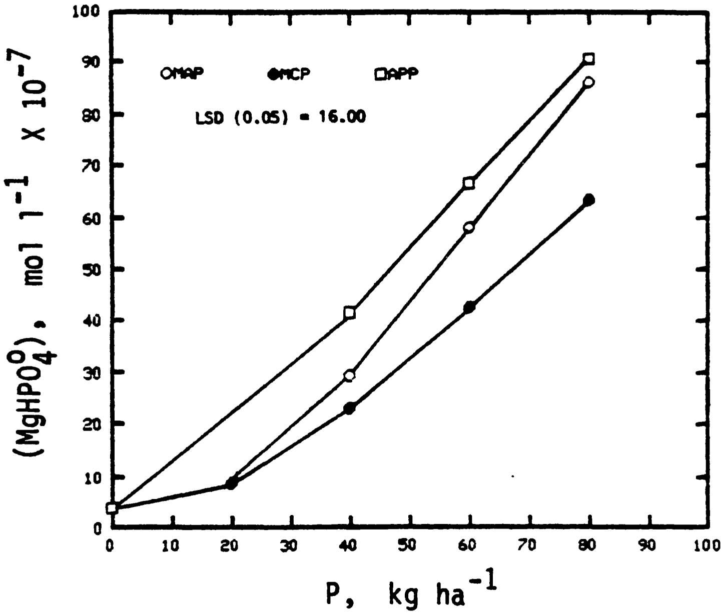


Fig. 13-Effect of P sources and rates on $CaHPO_4^0$ and $MgHPO_4^0$ activities in Quinlan soil solution.

both MAP and MCP and all APP rates. Also 40, 60, and 80 kg P ha$^{-1}$ as MAP and MCP induced higher $CaHPO_4^o$ activities than all other levels. Furthermore, no differences in $MgHPO_4^o$ activities between MCP rates of 20 and 40 kg P ha$^{-1}$ were observed. Increases of $MgHPO_4^o$ activities were observed between 20, 40, 60, and 80 kg P ha$^{-1}$ and 40, 60 and 80 kg P ha$^{-1}$ of MAP and MCP, respectively, and all APP rates. Moreover, MAP and MCP rates of 40, 60, and 80 kg P ha$^{-1}$ caused higher $MgHPO_4^o$ activities than the control. This finding suggested soil solution pH depression had little effect on $CaHPO_4^o$ and $MgHPO_4^o$ activities, and the high complexation of $Ca^{2+}$ and $Mg^{2+}$ with $H_2PO_4^-$.

The increase of $CaHPO_4^o$ and $MgHPO_4^o$ activities by all APP rates, and the lack of effect of APP on the activities of most of the other complexes was good indication of the high affinity of $Ca^{2+}$, $Mg^{2+}$, and $H_2PO_4^-$ to form $CaHPO_4^o$ and $MgHPO_4^o$ within these ranges of soil solution pH. Higher $CaHPO_4^o$ and $MgHPO_4^o$ activities were observed with 80 kg P ha$^{-1}$ as APP than in the corresponding rate of MCP and 60 kg P ha$^{-1}$ as APP caused higher $CaHPO_4^o$ activities than the similar rates of MAP and MCP. Also 80 kg P ha$^{-1}$ as MAP induced higher $MgHPO_4^o$ activity than the similar rate of MCP.

## $CaPO_4^-$ and $MgPO_4^-$ Activities

All P sources increased $CaPO_4^-$ and $MgPO_4^-$ activities (Fig. 14). No changes in $CaPO_4^-$ activities between the rates of 0 and 20, or 20 and 40, or 40 and 60, or 60 and 80 kg P ha$^{-1}$ of MAP were observed. However, MAP rates of 40, 60, and 80 kg P ha$^{-1}$ induced higher $CaPO_4^-$ activities than the control. Also MAP rates of 60 and 80 kg P ha$^{-1}$

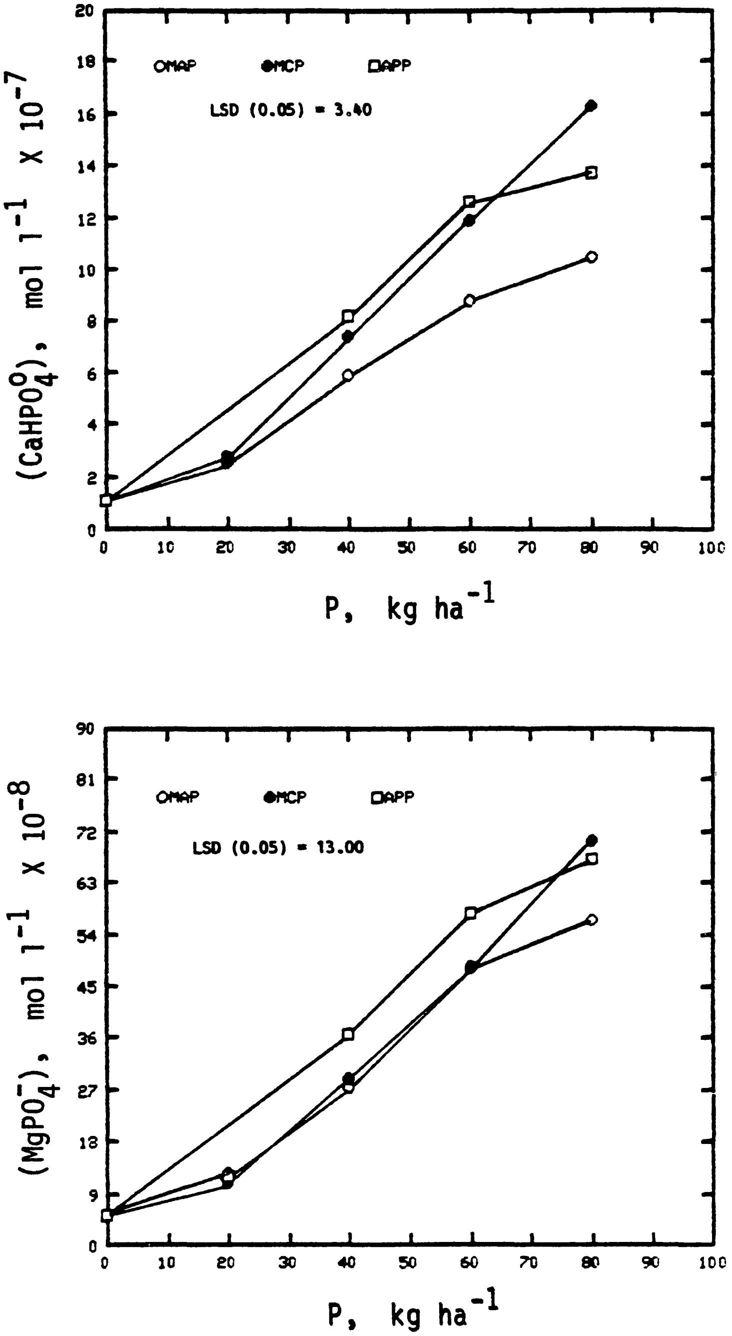


Fig. 14-Effect of P sources and rates on CaPO$_4^-$ and MgPO$_4^-$ activities in Quinlan soil solution.

caused higher $CaPO_4^-$ activity than MAP rates of 20, or 20 and 40 kg P $ha^{-1}$, respectively. No differences in $MgPO_4^-$ activities between MAP rates of 0 and 20 or 60 and 80 kg P $ha^{-1}$ were observed. But MAP rates of 60 and 80 kg P $ha^{-1}$ caused higher $MgPO_4^-$ activities than all other rates. Also 60 kg P $ha^{-1}$ as MAP caused higher $MgPO_4^-$ activities than 0 and 20 kg P $ha^{-1}$. Formation of DCPD and $MgNH_4PO_4.6H_2O$ might be considered as a reason for the above changes (Lindsay et al., 1962; Bell and Black, 1970).

No changes in $CaPO_4^-$ and $MgPO_4^-$ activities by the rate of 20 kg P $ha^{-1}$ of MCP was observed. However, an increase in $CaPO_4^-$ and $MgPO_4^-$ activities between MCP rates of 40, 60, and 80 kg P $ha^{-1}$ were found. Similarly, MCP rates of 40, 60, and 80 kg P $ha^{-1}$ induced higher $CaPO_4^-$ and $MgPO_4^-$ activities than the control. The stability of $CaPO_4^-$ and $MgPO_4^-$ activities could be caused by the formation of DCP and TCP (Havlin and Westfall, 1984; Fixen et al., 1983).

No changes in $CaPO_4^-$ and $MgPO_4^-$ activiteis between the rates of 60 and 80 kg P $ha^{-1}$ of APP were observed. However, APP rates of 60 and 80 kg P $ha^{-1}$ caused higher $CaPO_4^-$ and $MgPO_4^-$ activities than all other rates. The stability of $CaPO_4^-$ activity might be caused by the formation of $Ca(NH_4)_2P_2O_7.H_2O$ (Subbarao and Ellis 1975). APP applied at the rate of 80 kg P $ha^{-1}$ caused higher $CaPO_4^-$ activity than the similar rate of MAP. Also 80 kg P $ha^{-1}$ as MAP induced lower $CaPO_4^-$ and $MgPO_4^-$ activities than the corresponding rate of MCP.

# CONCLUSIONS

a. Phosphorus fertilization affects most chemical species and P complex activities in soil solution.

b. APP and MAP caused greater effects on chemical species and complex activities than MCP.

c. Application of P increased $SO_4^{2-}$ activity in McLain soil and decreased it in Quinlan soil.

d. The main reasons for decreasing the activity of P species were speculated to be the formation of DCPD, DCP, and OTC.

e. Activities of many chemical species and complexes exhibited no specific pattern due to P fertilization.

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# APPENDIX A

## ION AND ION COMPLEXES ACTIVITIES

Key:
MAP = monoammonium phosphate
MCP = monocalcium phosphate
APP = ammonium polyphosphate

Treatment
" 0 = control
" 1 = MAP 20 kg P $ha^{-1}$
" 2 = MAP 40 kg P $ha^{-1}$
" 3 = MAP 60 kg P $ha^{-1}$
" 4 = MAP 80 kg P $ha^{-1}$
" 5 = MCP 20 kg P $ha^{-1}$
" 6 = MCP 40 kg P $ha^{-1}$
" 7 = MCP 60 kg P $ha^{-1}$
" 8 = MCP 80 kg P $ha^{-1}$
" 9 = APP 20 kg P $ha^{-1}$
" 10 = APP 40 kg P $ha^{-1}$
" 11 = APP 60 kg P $ha^{-1}$
" 12 = APP 80 kg P $ha^{-1}$

M = molar

Soil Type 1 = McLain Sicl
Soil Type 2 = Quinlain cl

Note: All chemical species are present in ionic forms.

| OBS | BLOCK | TREATMNT | SOILTYPE | M_CA | M_MG | M_NO3 | M_SO4 | M_CASO4 | M_MGSO4 |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0 | 1 | 0 002405 | 0 001665 | 0 006168 | 0 002331 | 0 00105541 | 0 00057962 |
| 2 | 1 | 0 | 2 | 0 001903 | 0 000998 | 0 004010 | 0 000431 | 0 00014177 | 0 00005910 |
| 3 | 1 | 1 | 1 | 0 003241 | 0 002134 | 0 007800 | 0 002262 | 0 00118685 | 0 00069884 |
| 4 | 1 | 1 | 2 | 0 002168 | 0 001386 | 0 005185 | 0 000430 | 0 00014512 | 0 00007275 |
| 5 | 1 | 2 | 1 | 0 003477 | 0 002409 | 0 008636 | 0 002254 | 0 00139505 | 0 00076669 |
| 6 | 1 | 2 | 2 | 0.002859 | 0 001138 | 0 005986 | 0 000405 | 0 00020048 | 0.00006340 |
| 7 | 1 | 3 | 1 | 0 003382 | 0 002906 | 0 009394 | 0 002454 | 0 00133360 | 0 00092262 |
| 8 | 1 | 3 | 2 | 0 002566 | 0 001377 | 0 007065 | 0 000372 | 0 00017868 | 0 00007623 |
| 9 | 1 | 4 | 1 | 0 003557 | 0 002903 | 0 010372 | 0 002461 | 0 00153149 | 0 00098880 |
| 10 | 1 | 4 | 2 | 0 003000 | 0 001483 | 0 006968 | 0 000362 | 0 00010527 | 0 00007284 |
| 11 | 1 | 5 | 1 | 0 003389 | 0 002131 | 0 006618 | 0 002500 | 0 00160073 | 0 00080224 |
| 12 | 1 | 5 | 2 | 0 002549 | 0 001209 | 0 004398 | 0 000367 | 0 00017055 | 0 00006485 |
| 13 | 1 | 6 | 1 | 0 003687 | 0 002425 | 0 009218 | 0 002508 | 0 00164022 | 0.00084121 |
| 14 | 1 | 6 | 2 | 0 002446 | 0 001133 | 0 004691 | 0 000402 | 0 00015917 | 0 00005914 |
| 15 | 1 | 7 | 1 | 0 003737 | 0 002426 | 0 009518 | 0 002605 | 0 00171759 | 0 00088101 |
| 16 | 1 | 7 | 2 | 0 002779 | 0 001263 | 0 006692 | 0 000361 | 0 00017066 | 0 00006197 |
| 17 | 1 | 8 | 1 | 0 003301 | 0 002716 | 0 009933 | 0 002773 | 0 00146255 | 0.00096629 |
| 18 | 1 | 8 | 2 | 0 002232 | 0 001221 | 0 004994 | 0 000397 | 0 00016288 | 0.00007109 |
| 19 | 1 | 10 | 1 | 0 003995 | 0 002447 | 0 010478 | 0 002484 | 0 00188413 | 0 00090180 |
| 20 | 1 | 10 | 2 | 0 002692 | 0 001589 | 0 005979 | 0 000388 | 0 00019150 | 0 00008947 |
| 21 | 1 | 11 | 1 | 0 003945 | 0 002788 | 0 011916 | 0 002564 | 0 00171973 | 0.00096721 |
| 22 | 1 | 11 | 2 | 0 003076 | 0 001317 | 0 006176 | 0 000396 | 0 00019595 | 0 00006641 |
| 23 | 1 | 12 | 1 | 0 003991 | 0 002364 | 0 011549 | 0 002647 | 0 00188260 | 0.00088057 |
| 24 | 1 | 12 | 2 | 0.003130 | 0 001363 | 0 007746 | 0 000358 | 0 00019108 | 0 00006638 |
| 25 | 2 | 0 | 1 | 0 002774 | 0 002125 | 0 006583 | 0 002119 | 0 00105634 | 0 00065141 |
| 26 | 2 | 0 | 2 | 0 001565 | 0 000745 | 0 005304 | 0 000460 | 0 00012059 | 0 00004585 |

| OBS | PH | M_HCO3 | M_HPO4 | M_H2PO4 | M_CAHPO4 | M_MGHPO4 | M_CAPO4 | M_MGPO4 |
|---|---|---|---|---|---|---|---|---|
| 1 | 7.75 | 0 00412257 | 0 00001380 | 0.00000367 | 0 00002106 | 0 00002308 | 0.0000032 | 0.00000221 |
| 2 | 7 95 | 0 00367606 | 0 00000034 | 0 00000006 | 0 00000043 | 0 00000035 | 1.00000E-07 | 5.00000E-08 |
| 3 | 7 55 | 0 00370095 | 0.00001105 | 0 00000476 | 0 00002368 | 0 00002778 | 0 00000218 | 0.00000162 |
| 4 | 7 90 | 0 00252075 | 0.00000084 | 0 00000017 | 0 00000121 | 0 00000121 | 2.50000E-07 | 1.60000E-07 |
| 5 | 7 45 | 0 00321260 | 0 00001310 | 0 00000687 | 0 00003052 | 0 00003347 | 0 00000233 | 0.00000161 |
| 6 | 7.75 | 0 00294069 | 0 00000242 | 0 00000064 | 0 00000439 | 0 00000276 | 6.60000E-07 | 2.60000E-07 |
| 7 | 7 45 | 0.00298045 | 0 00001893 | 0 00001010 | 0 00004217 | 0 00005688 | 0 00000319 | 0.00000272 |
| 8 | 7 65 | 0 00274202 | 0 00000439 | 0 00000147 | 0 00000711 | 0 00000605 | 8.70000E-07 | 4.70000E-07 |
| 9 | 7 30 | 0 00283991 | 0 00002066 | 0 00001527 | 0 00004624 | 0 00005958 | 0.00000259 | 0.00000211 |
| 10 | 7 60 | 0 00260379 | 0 00000481 | 0.00000184 | 0 00000895 | 0 00000712 | 9.70000E-07 | 4.80000E-07 |
| 11 | 7 70 | 0 00274701 | 0 00001217 | 0 00000354 | 0 00002596 | 0 00002596 | 0.00000354 | 0.00000223 |
| 12 | 7.85 | 0 00339474 | 0 00000098 | 0 00000020 | 0 00000156 | 0 00000118 | 2.90000E-07 | 1.40000E-07 |
| 13 | 7 65 | 0 00278635 | 0 00001349 | 0.00000442 | 0 00003054 | 0 00003196 | 0.00000367 | 0.00000243 |
| 14 | 7 85 | 0 00355746 | 0 00000248 | 0 00000051 | 0 00000362 | 0 00000264 | 6.80000E-07 | 3. 10000E-07 |
| 15 | 7 70 | 0 00319562 | 0 00001615 | 0 00000462 | 0 00003846 | 0 00004026 | 0 00000518 | 0 00000342 |
| 16 | 7 80 | 0 00329275 | 0 00000372 | 0 00000087 | 0 00000649 | 0 00000470 | 0 00000109 | 5.00000E-07 |
| 17 | •7 60 | 0 00290927 | 0.00002214 | 0 00000801 | 0 00004625 | 0 00005958 | 0 00000194 | 0.00000402 |
| 18 | 7 75 | 0 00356111 | 0 00000570 | 0 00000148 | 0 00000816 | 0 00000695 | 0 00000121 | 6.50000E-07 |
| 19 | 7 55 | 0 00297695 | 0 00001604 | 0 00000636 | 0 00004027 | 0 00004027 | 0 00000383 | 0 00000236 |
| 20 | 7 70 | 0 00328620 | 0 00000360 | 0 00000104 | 0 00000606 | 0 00000563 | 7.90000E-07 | 4.60000E-07 |
| 21 | 7 55 | 0 00347862 | 0 00001680 | 0 00000678 | 0 00004222 | 0 00004629 | 0 00000409 | 0.00000283 |
| 22 | 7 75 | 0 00306235 | 0 00000555 | 0 00000150 | 0 00001053 | 0 00000712 | 0 00000161 | 6 90000E-07 |
| 23 | 7 35 | 0 00236041 | 0 00002099 | 0 00001327 | 0 00005162 | 0 00004838 | 0 00000326 | 0.00000192 |
| 24 | 7 60 | 0 00291443 | 0 00000721 | 0 00000266 | 0 00001358 | 0 00000935 | 0 00000153 | 6 70000E-07 |
| 25 | 7 65 | 0 00382098 | 0 00001226 | 0 00000409 | 0 00002157 | 0 00002653 | 0.00000264 | 0 00000201 |
| 26 | 7 90 | 0 00329478 | 0 00000066 | 0 00000013 | 0 00000066 | 0 00000050 | 1 30000E-07 | 6 00000E-08 |

```
OBS   BLOCK   TREATMNT   SOILTYPE      M_CA        M_MG        M_NO3       M_SO4        M_CASO4       M_MGSO4

27      2         1          1       0 003793    0 002633    0 008902    0.002181    0 00130234    0.00071578
28      2         1          2       0 002978    0 000995    0 005095    0.000356    0 00020042    0 00005272
29      2         2          1       0 003214    0 002652    0 009207    0 002272    0 00130161    0 00084055
30      2         2          2       0 002619    0 001109    0 005853    0 000409    0 00018273    0.00006188
31      2         3          1       0 003650    0 002752    0 010486    0.002379    0 00139639    0.00084141
32      2         3          2       0 002780    0 001274    0 006575    0 000371    0 00019144    0.00006952
33      2         4          1       0 003981    0 002449    0 011100    0 002499    0 00175842    0 00086124
34      2         4          2       0 002506    0 001829    0 008440    0 000349    0 00014873    0 00008559
35      2         5          1       0 003282    0 002362    0 007977    0 002377    0.00146041    0 00084032
36      2         5          2       0 002774    0 001055    0 005889    0 000353    0.00017862    0 00005395
37      2         6          1       0 003204    0 002041    0 006763    0 002592    0 00142639    0.00073152
38      2         6          2       0 003042    0 000813    0 005385    0 000360    0 00020511    0 00004385
39      2         7          1       0 003518    0 002417    0 006555    0 002648    0 00160178    0 00088024
40      2         7          2       0 002172    0 001228    0 004828    0 000401    0.00014510    0 00006483
41      2         8          1       0 003734    0 002364    0 009292    0.002746    0 00160287    0 00080338
42      2         8          2       0 002988    0 000981    0 006831    0.000370    0 00020519    0 00005397
43      2        10          1       0 003405    0 002680    0 011113    0 002563    0.00164069    0 00101165
44      2        10          2       0 003325    0.001069    0 006807    0.000357    0 00021494    0 00005399
45      2        11          1       0 003454    0 002326    0 010234    0 002753    0 00160272    0 00086076
46      2        11          2       0 002987    0 001560    0 007258    0 000349    0 00019600    0 00008176
47      2        12          1       0 003683    0 002772    0 011879    0.002670    0 00171887    0.00103254
48      2        12          2       0 003160    0 001564    0 007246    0 000383    0.00020519    0 00008178
49      3         0          1       0 002968    0 002011    0 007890    0 002368    0.00124203    0.00066704
50      3         0          2       0 001618    0 000804    0 004856    0.000444    0 00012064    0 00004797
51      3         1          1       0 003434    0 002360    0 008418    0 002310    0 00124313    0.00068307
52      3         1          2       0 002012    0 001216    0 005213    0 000406    0 00015197    0 00007269

OBS    PH      M_HCO3        M_HPO4        M_H2PO4       M_CAHPO4      M_MGHPO4        M_CAPO4        M_MGPO4

27    7 45   0.00285491   0 00001155   0 000006250   0 00002912   0.00003195     0.00000217      0.0000015
28    7 80   0 00262934   0 00000095   0 000000220   0 00000183   0 00000096    3.10000E-07    1.00000E-07
29    7 40   0 00273655   0 00001441   0 000008460   0 00003052   0 00004022     0.00000208     0 00000173
30    7 80   0 00269216   0 00000229   0 000000550   0 00000391   0 00000264    6.50000E-07    2.80000E-07
31    7 35   0 00236813   0 00001540   0 000010340   0 00003065   0 00004416     0 00000221     0 00000168
32    7 75   0.00250152   0 00000391   0 000001040   0 00000679   0 00000491     0.00000104    4.80000E-07
33    7 35   0 00236433   0 00002316   0.000015260   0 00005690   0 00005560     0 00000358     0.00000221
34    7.60   0 00285137   0 00000562   0 000002160   0 00000895   0 00001053    9.70000E-07    7.20000E-07
35    7 65   0 00344975   0 00001322   0 000004340   0 00002783   0 00003195     0.00000337     0.00000244
36    7 85   0.00269308   0 00000079   0 000000170   0 00000139   0.00000084    2.60000E-07    1.00000E-07
37    7.55   0 00294670   0 00001575   0 000006450   0 00003120   0 00003120     0.00000295     0.00000186
38    7.85   0 00295068   0 00000234   0 000000490   0 00000449   0 00000191    8.50000E-07    2.30000E-07
39    7 55   0 00293044   0 00001940   0 000007890   0 00004412   0 00004837     0 00000414     0.00000286
40    7.85   0.00303749   0 00000389   0 000000820   0 00000539   0 00000481     0.00000101    5.70000E-07
41    7 65   0 00278558   0 00001994   0 000006530   0 00004841   0 00004841     0.00000582     0 00000367
42    7 90   0 00293712   0 00000480   0 000000870   0 00000915   0 00000470      0 0000019     6 10000E-07
43    7 65   0 00304982   0 00001611   0 000005060   0 00003350   0 00004217     0 00000402     0 00000319
44    7.75   0 00292393   0 00000371   0 000000970   0 00000780   0 00000400     0 00000114    3.70000E-07
45    7 50   0 00272380   0 00002092   0 000009660   0 00004516   0 00004840     0 00000394     0.00000266
46    7.65   0.00308216   0 00000477   0 000001570   0 00000875   0 00000724     0.00000106    5 60000E-07
47    7 45   0 00241344   0.00002138   0 000010780   0 00004859   0 00005821     0.00000383      0.0000029
48    7 60   0.00304678   0 00000593   0 000002210   0 00001157   0 00000895      0 0000013    6.40000E-07
49    7 70   0 00446684   0.00000537   0 000003720   0.00002367   0 00002535     0 00000316     0 00000214
50    7 95   0 00433205   0 00000046   0 000000080   0 00000048   0 00000038    1.10000E-07    5.00000E-08
51    7 50   0 00344752   0 00001380   0 000006720   0 00003193   0 00003423     0 00000268     0 00000181
52    7 85   0 00333341   0 00000085   0 000000180   0 00000109   0 00000105    2 10000E-07    1 20000E-07
```

| OBS | BLOCK | TREATMNT | SOILTYPE | M_CA | M_MG | M_NO3 | M_SO4 | M_CASO4 | M_MGSO4 |
|---|---|---|---|---|---|---|---|---|---|
| 53 | 3 | 2 | 1 | 0 003576 | 0 002172 | 0 008854 | 0.002318 | 0 00146042 | 0 00069899 |
| 54 | 3 | 2 | 2 | 0 002203 | 0 001372 | 0 006140 | 0 000397 | 0 00014857 | 0 00007273 |
| 55 | 3 | 3 | 1 | 0 003651 | 0 002505 | 0 010191 | 0 002393 | 0.00164012 | 0 00090132 |
| 56 | 3 | 3 | 2 | 0 002387 | 0 001593 | 0 006627 | 0 000357 | 0 00015565 | 0.00008169 |
| 57 | 3 | 4 | 1 | 0.003707 | 0 002763 | 0 011240 | 0 002424 | 0.00156719 | 0 00094433 |
| 58 | 3 | 4 | 2 | 0 003137 | 0 001281 | 0 007159 | 0 000354 | 0.00018703 | 0 00006058 |
| 59 | 3 | 5 | 1 | 0 003811 | 0 002325 | 0 008103 | 0 002369 | 0.00167750 | 0 00082158 |
| 60 | 3 | 5 | 2 | 0 002627 | 0 000923 | 0 006630 | 0 000388 | 0 00018705 | 0 00005152 |
| 61 | 3 | 6 | 1 | 0 003634 | 0 002727 | 0 007569 | 0 002471 | 0 00149571 | 0 00090132 |
| 62 | 3 | 6 | 2 | 0 002444 | 0 001118 | 0 005898 | 0 000379 | 0 00017057 | 0.00006194 |
| 63 | 3 | 7 | 1 | 0 003555 | 0 002239 | 0 008293 | 0 002626 | 0 00160226 | 0 00080302 |
| 64 | 3 | 7 | 2 | 0 002938 | 0 000757 | 0 006369 | 0 000425 | 0.00020515 | 0 00004286 |
| 65 | 3 | 8 | 1 | 0 003280 | 0 002736 | 0 008848 | 0 002653 | 0 00164016 | 0 00108363 |
| 66 | 3 | 8 | 2 | 0 002351 | 0 001126 | 0 005545 | 0 000385 | 0 00016668 | 0 00006337 |
| 67 | 3 | 10 | 1 | 0 003892 | 0 002296 | 0 009854 | 0 002509 | 0 00179834 | 0 00084127 |
| 68 | 3 | 10 | 2 | 0 002581 | 0 001281 | 0 006110 | 0 000388 | 0 00017866 | 0 00007113 |
| 69 | 3 | 11 | 1 | 0 003975 | 0 002460 | 0 010571 | 0 002638 | 0 00171859 | 0.00084179 |
| 70 | 3 | 11 | 2 | 0 003099 | 0 001357 | 0 008206 | 0 000381 | 0 00022027 | 0 00007624 |
| 71 | 3 | 12 | 1 | 0 004212 | 0 002406 | 0 012250 | 0 002600 | 0 00193417 | 0 00086187 |
| 72 | 3 | 12 | 2 | 0 003212 | 0 001765 | 0 009125 | 0 000405 | 0 00022042 | 0 00009612 |

| OBS | PH | M_HCO3 | M_HPO4 | M_H2PO4 | M_CAHPO4 | M_MGHPO4 | M_CAPO4 | M_MGPO4 |
|---|---|---|---|---|---|---|---|---|
| 53 | 7.45 | 0 00314554 | 0 00001588 | 0 000008270 | 0 00003644 | 0 00003585 | 0.0000028 | 0.00000173 |
| 54 | 7.70 | 0 00331310 | 0 00000252 | 0 000000760 | 0.00000356 | 0 00000348 | 4.70000E-07 | 2.90000E-07 |
| 55 | 7 40 | 0 00298670 | 0 00001741 | 0 000010120 | 0 00004025 | 0 00004414 | 0.00000279 | 0 00000193 |
| 56 | 7 65 | 0 00337189 | 0 00000409 | 0 000001370 | 0 00000606 | 0 00000649 | 7.40000E-07 | 5 00000E-07 |
| 57 | 7.40 | 0 00277770 | 0 00001971 | 0 000011580 | 0 00004520 | 0 00005434 | 0 00000319 | 0.00000242 |
| 58 | 7 55 | 0 00320141 | 0 00000648 | 0 000002790 | 0 00001265 | 0 00000817 | 0 00000122 | 5 00000E-07 |
| 59 | 7 55 | 0 00313716 | 0 00001337 | 0 000005450 | 0 00003194 | 0 00003123 | 0.00000307 | 0.00000189 |
| 60 | 7 90 | 0 00316257 | 0 00000078 | 0 000000140 | 0 00000126 | 0 00000069 | 2.60000E-07 | 9.00000E-08 |
| 61 | 7.70 | 0 00327492 | 0.00001481 | 0 000004320 | 0 00003348 | 0 00003934 | 0.00000452 | 0.00000335 |
| 62 | 7 90 | 0 00363347 | 0 00000219 | 0 000000410 | 0 00000333 | 0 00000247 | 7.10000E-07 | 3.30000E-07 |
| 63 | 7 60 | 0 00335827 | 0 00001838 | 0 000006700 | 0 00004214 | 0 00004214 | 0 00000453 | 0.00000286 |
| 64 | 7 85 | 0 00353993 | 0 00000432 | 0 000000890 | 0 00000798 | 0 00000333 | 0 00000148 | 3.90000E-07 |
| 65 | 7 75 | 0 00327348 | 0 00002044 | 0 000005190 | 0 00004314 | 0 00005687 | 0 00000653 | 0.00000543 |
| 66 | 7 85 | 0 00332021 | 0 00000668 | 0 000001353 | 0 00000981 | 0 00000744 | 0 00000178 | 8 50000E-07 |
| 67 | 7 60 | 0 00327204 | 0 00001546 | 0 000005430 | 0 00003672 | 0 00003429 | 0.00000393 | 0.00000232 |
| 68 | 7 75 | 0 00337811 | 0 00000231 | 0 000000600 | 0 00000365 | 0 00000289 | 5 40000E-07 | 2 70000E-07 |
| 69 | 7.52 | 0 00318447 | 0 00001827 | 0 000008190 | 0 00004512 | 0 00004418 | 0 0000041 | 0.00000253 |
| 70 | 7 70 | 0 00334307 | 0 00000420 | 0 000001240 | 0 00000818 | 0 00000563 | 0 00000111 | 4 80000E-07 |
| 71 | 7 55 | 0 00310270 | 0 00001981 | 0 000007980 | 0 00005195 | 0 00004739 | 0 00000527 | 0 00000303 |
| 72 | 7.65 | 0 00309803 | 0 00000530 | 0 000001740 | 0 00001006 | 0 00000896 | 0 00000129 | 7 10000E-07 |

# APPENDIX B

## STATISTICAL ANALYSIS

## LSD TEST

Key:
Soil Type 1 = McLain sicl
Soil Type 2 = Quinlan cl

Note: All chemical species are in ionic forms.

```
                                                             LSD RUN ON ALL VARIABLES
                                                                   SOILTYPE=1

                                                          ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CA
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=6.0E-08
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=4.1E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING             MEAN      N  TRT

               A         0.0039620      3  APP_80
               A
       B       A         0.0037913      3  APP_60
       B       A
       B       A         0.0037640      3  APP_40
       B       A
       B       A         0.0037483      3  MAP_80
       B       A
       B       A         0.0036033      3  MCP_60
       B       A
       B       A         0.0035610      3  MAP_60
       B
       B                 0.0035083      3  MCP_40
       B
       B                 0.0034940      3  MCP_20
       B
       B                 0.0034893      3  MAP_20
       B
       B                 0.0034383      3  MCP_80
       B
       B                 0.0034223      3  MAP_40

               C         0.0027157      3  00
```

```
                                                   LSD RUN ON ALL VARIABLES
                                                          SOILTYPE=1

                                                 ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MG
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=5.0E-08
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.8E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T         GROUPING               MEAN      N  TRT

                A            0.0027210     3  MAP_60
                A
                A            0.0027050     3  MAP_80
                A
        B       A            0.0026053     3  MCP_80
        B       A
        B       A            0.0025247     3  APP_60
        B       A
        B       A            0.0025140     3  APP_80
        B       A
        B       A            0.0024757     3  MAP_20
        B       A
        B       A            0.0024743     3  APP_40
        B       A
        B       A            0.0024110     3  MAP_40
        B       A
        B       A            0.0023977     3  MCP_40
        B       A
        B       A            0.0023607     3  MCP_60
        B
        B       C            0.0022727     3  MCP_20
                C
                C            0.0019337     3  00
```

```
                                                        LSD RUN ON ALL VARIABLES
                                                               SOILTYPE=1

                                                      ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: NO3
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=7.0E-07
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=.0014178

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A           0.011893      3  APP_80
               A
       B       A           0.010907      3  APP_60
       B       A
       B       A           0.010904      3  MAP_80
       B       A
       B       A    C      0.010482      3  APP_40
       B            C
       B       D    C      0.010024      3  MAP_60
               D    C
       E       D    C      0.009358      3  MCP_80
       E       D
       E       D    F      0.008899      3  MAP_40
       E            F
       E            F      0.008373      3  MAP_20
       E            F
       E       G    F      0.008122      3  MCP_60
               G    F
               G    F      0.007850      3  MCP_40
               G    F
               G    F      0.007566      3  MCP_20
               G
               G           0.006880      3  00
```

```
                                                       LSD RUN ON ALL VARIABLES
                                                              SOILTYPE=1

                                                    ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: SO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=4.7E-09
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=1.2E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          0.0027240      3  MCP_80
               A
               A          0.0026517      3  APP_60
               A
       B       A          0.0026390      3  APP_80
       B       A
       B       A   C      0.0026263      3  MCP_60
       B           C
       B       D   C      0.0025237      3  MCP_40
               D   C
               D   C      0.0025187      3  APP_40
               D
               D          0.0024613      3  MAP_80
               D
               D          0.0024153      3  MCP_20
               D
               D          0.0024087      3  MAP_60

               E          0.0022813      3  MAP_40
               E
               E          0.0022727      3  00
               E
               E          0.0022510      3  MAP_20
```

```
                                                     LSD RUN ON ALL VARIABLES
                                                            SOILTYPE=1

                                                  ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CASO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=9.5E-09
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=1.6E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          0.0018452      3  APP_80
               A
       B       A          0.0017744      3  APP_40
       B       A
       B       A   C      0.0016803      3  APP_60
       B           C
       B           C      0.0016405      3  MCP_60
       B           C
       B       D   C      0.0016190      3  MAP_80
               D   C
               D   C      0.0015795      3  MCP_20
               D   C
               D   C      0.0015685      3  MCP_80
               D   C
       E       D   C      0.0015208      3  MCP_40
       E       D
       E       D          0.0014567      3  MAP_60
       E
       E       F          0.0013857      3  MAP_40
               F
       G       F          0.0012441      3  MAP_20
       G
       G                  0.0011179      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=1

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MGSO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=5.8E-09
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=1.3E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          0.0009511      3  MCP_80
               A
       B       A         .000931457      3  MAP_80
       B       A
       B       A         .000924993      3  APP_80
       B       A
       B       A         0.00091824      3  APP_40
       B       A
       B       A   C     0.00088992      3  APP_60
       B       A   C
       B       A   C     0.00088845      3  MAP_60
       B       A   C
       B       A   C     .000854757      3  MCP_60
       B       A   C
       B   D   A   C     .000824683      3  MCP_40
       B   D       C
       B   D       C     0.00082138      3  MCP_20
           D       C
           D       C     .000768743      3  MAP_40
           D
           D   E         0.00069923      3  MAP_20
               E
               E         0.00063269      3  00
```

```
                                                          LSD RUN ON ALL VARIABLES
                                                                SOILTYPE=1

                                                        ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: PH
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=.0037384
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=0.103533

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

              A               7.7000     3  00
              A
              A               7.6667     3  MCP_80
              A
              A               7.6333     3  MCP_40
              A
              A               7.6333     3  MCP_20
              A
       B      A               7.6167     3  MCP_60
       B      A
       B      A    C          7.6000     3  APP_40
       B           C
       B      D    C          7.5233     3  APP_60
              D    C
       E      D    C          7.5000     3  MAP_20
       E      D
       E      D    F          7.4500     3  APP_80
       E      D    F
       E      D    F          7.4333     3  MAP_40
       E           F
       E           F          7.4000     3  MAP_60
                   F
                   F          7.3500     3  MAP_80
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=1

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: HCO3
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=6.1E-08
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=4.2E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          0.0041368      3  00

               B          0.0033345      3  MAP_20
               B
       C       B          0.0031614      3  MCP_60
       C       B
       C       B          0.0031290      3  APP_60
       C       B
       C       B          0.0031113      3  MCP_20
       C       B
       C       B          0.0030996      3  APP_40
       C       B
       C       B   D      0.0030316      3  MAP_40
       C       B   D
       C       B   D      0.0030027      3  MCP_40
       C       B   D
       C       B   D      0.0029894      3  MCP_80
       C           D
       C           D      0.0027784      3  MAP_60
                   D
                   D      0.0026606      3  MAP_80
                   D
                   D      0.0026255      3  APP_80
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=1

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: HPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=3.5E-12
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.2E-06

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         .000021177      3  MAP_80
               A
       B       A         0.00002084      3  MCP_80
       B       A
       B       A         .000020727      3  APP_80
       B       A
       B       A   C     .000018663      3  APP_60
       B           C
       B           C     .000017977      3  MCP_60
                   C
               D   C     .000017247      3  MAP_60
               D   C
       E       D   C     0.00001587      3  APP_40
       E       D
       E       D   F     .000014683      3  MCP_40
       E       D   F
       E       D   F     .000014463      3  MAP_40
       E           F
       E       G   F     0.00001292      3  MCP_20
               G   F
               G   F     .000012133      3  MAP_20
               G
               G         .000010477      3  00
```

```
                                                    LSD RUN ON ALL VARIABLES
                                                           SOILTYPE=1

                                                  ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: H2PO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=1.8E-12
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=2.3E-06

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T         GROUPING               MEAN       N  TRT

                A          .000014037       3  MAP_80

                B          .000010677       3  APP_80
                B
        C       B          .000010187       3  MAP_60
        C
        C       D          0.00000821       3  APP_60
                D
        E       D           7.867E-06       3  MAP_40
        E       D
        E       D   F       6.577E-06       3  MCP_80
        E       D   F
        E       D   F       6.403E-06       3  MCP_60
        E           F
        E       G   F      0.00000591       3  MAP_20
        E       G   F
        E       G   F       5.617E-06       3  APP_40
                G   F
                G   F       5.063E-06       3  MCP_40
                G   F
                G   F       4.443E-06       3  MCP_20
                G
                G           3.827E-06       3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=1

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CAHPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=1.3E-11
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=6.1E-06

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         0.00005072      3  APP_80
               A
       B       A         .000049447      3  MAP_80
       B       A
       B       A   C     .000045933      3  MCP_80
       B           C
       B           C     .000044167      3  APP_60
                   C
               D   C     .000041573      3  MCP_60
               D
       E       D         0.00003769      3  MAP_60
       E       D
       E       D         0.00003683      3  APP_40
       E
       E       F         .000032493      3  MAP_40
       E       F
       E       F         0.00003174      3  MCP_40
               F
               F         .000028577      3  MCP_20
               F
               F         .000028243      3  MAP_20

               G          0.0000221      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=1

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MGHPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=2.0E-11
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=7.6E-06

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         .000056507      3  MAP_80
               A
       B       A         .000054953      3  MCP_80
       B       A
       B       A   C     .000051327      3  APP_80
       B           C
       B       D   C     .000048393      3  MAP_60
               D   C
       E       D   C     0.00004629      3  APP_60
       E       D
       E       D   F     0.00004359      3  MCP_60
       E           F
       E       G   F     0.00003891      3  APP_40
               G   F
       H       G   F     .000036513      3  MAP_40
       H       G
       H       G         .000034167      3  MCP_40
       H
       H       I         0.00003132      3  MAP_20
       H       I
       H       I         .000029713      3  MCP_20
               I
               I         .000024987      3  00
```

```
                                                     LSD RUN ON ALL VARIABLES
                                                            SOILTYPE=1

                                                  ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CAPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=2.5E-13
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=8.4E-07

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          5.763E-06      3  MCP_80

               B          4.617E-06      3  MCP_60
               B
       C       B         0.00000412      3  APP_80
       C       B
       C       B          4.043E-06      3  APP_60
       C       B
       C       B   D      3.927E-06      3  APP_40
       C           D
       C       E   D      3.713E-06      3  MCP_40
       C       E   D
       C   F   E   D      3.327E-06      3  MCP_20
           F   E   D
       G   F   E   D     0.00000312      3  MAP_80
       G   F   E
       G   F   E           0.000003      3  00
       G   F
       G   F             0.00000273      3  MAP_60
       G
       G                  2.403E-06      3  MAP_40
       G
       G                  2.343E-06      3  MAP_20
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=1

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MGP04
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=2.2E-13
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=8.0E-07

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN     N  TRT

               A          4.373E-06     3  MCP_80

               B          3.047E-06     3  MCP_60
               B
       C       B          2.673E-06     3  APP_60
       C       B
       C       B          2.623E-06     3  APP_40
       C       B
       C       B          2.617E-06     3  APP_80
       C       B
       C       B          2.547E-06     3  MCP_40
       C
       C       D          2.247E-06     3  MAP_80
       C       D
       C       D          2.187E-06     3  MCP_20
       C       D
       C       D         0.00000212     3  00
       C       D
       C       D         0.00000211     3  MAP_60
               D
               D         0.00000169     3  MAP_40
               D
               D          1.643E-06     3  MAP_20
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CA
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=9.8E-08
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=5.3E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT

T        GROUPING              MEAN      N  TRT

               A          0.0031673      3  APP_80
               A
       B       A          0.0030540      3  APP_60
       B       A
       B       A   C      0.0028810      3  MAP_80
       B       A   C
       B       A   C      0.0028660      3  APP_40
       B       A   C
       B       A   C      0.0026500      3  MCP_20
       B       A   C
       B       A   C      0.0026440      3  MCP_40
       B           C
       B           C      0.0026297      3  MCP_60
       B           C
       B           C      0.0025777      3  MAP_60
       B           C
       B           C      0.0025603      3  MAP_40
                   C
                   C      0.0025237      3  MCP_80
                   C
                   C      0.0023860      3  MAP_20

               D          0.0016953      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MG
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=3.8E-08
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.3E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          0.0015640      3  APP_80
               A
       B       A          0.0015310      3  MAP_80
       B       A
       B       A   C      0.0014147      3  MAP_60
       B       A   C
       B   D   A   C      0.0014113      3  APP_60
       B   D   A   C
   E   B   D   A   C      0.0013130      3  APP_40
   E   B   D       C
   E   B   D       C      0.0012063      3  MAP_40
   E       D       C
   E       D       C      0.0011990      3  MAP_20
   E       D       C
   E       D   F   C      0.0011093      3  MCP_80
   E       D   F
   E       D   F          0.0010827      3  MCP_60
   E           F
   E           F          0.0010623      3  MCP_20
   E           F
   E           F          0.0010213      3  MCP_40
               F
               F          0.0008490      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: NO3
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=5.1E-07
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=.0012104

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          0.0080390      3  APP_80
               A
       B       A          0.0075223      3  MAP_80
       B       A
       B       A   C      0.0072133      3  APP_60
       B           C
       B       D   C      0.0067557      3  MAP_60
               D   C
       E       D   C      0.0062987      3  APP_40
       E       D
       E       D          0.0059930      3  MAP_40
       E       D
       E       D          0.0059630      3  MCP_60
       E       D
       E       D   F      0.0057900      3  MCP_80
       E       D   F
       E       D   F      0.0056390      3  MCP_20
       E           F
       E           F      0.0053247      3  MCP_40
       E           F
       E           F      0.0052643      3  MAP_20
                   F
                   F      0.0047333      3  00
```

```
                                                   LSD RUN ON ALL VARIABLES
                                                          SOILTYPE=2

                                                ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: SO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=4.0E-10
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.4E-05

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A           0.000445      3  00

               B         .000403667      3  MAP_40
               B
       C       B         .000397333      3  MAP_20
       C       B
       C       B         .000395667      3  MCP_60
       C       B
       C       B   D       0.000384      3  MCP_80
       C       B   D
       C       B   D       0.000382      3  APP_80
       C       B   D
       C       B   D     .000380333      3  MCP_40
       C       B   D
       C       B   D     .000377667      3  APP_40
       C       B   D
       C       B   D     .000375333      3  APP_60
       C           D
       C           D     .000369333      3  MCP_20
       C           D
       C           D     .000366667      3  MAP_60
                   D
                   D       0.000355      3  MAP_80
```

```
                                                       LSD RUN ON ALL VARIABLES
                                                              SOILTYPE=2

                                                    ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CASO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=5.4E-10
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.9E-05

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         .000205563      3  APP_80
               A
       B       A         .000204073      3  APP_60
       B       A
       B       A         .000195033      3  APP_40
       B       A
       B       A    C    0.00017874      3  MCP_20
       B       A    C
       B       A    C    .000178283      3  MCP_40
       B       A    C
       B       A    C    0.00017825      3  MCP_80
       B       A    C
       B       A    C    0.00017726      3  MAP_40
       B       A    C
       B       A    C    .000175257      3  MAP_60
       B       A    C
       B       A    C    .000173637      3  MCP_60
       B            C
       B       D    C    .000165837      3  MAP_20
               D    C
               D    C    0.00014701      3  MAP_80
               D
               D         .000127667      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MGSO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=1.1E-10
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=1.8E-05

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         .000081427      3  APP_80
               A
       B       A         .000075813      3  MAP_60
       B       A
       B       A   C     .000074803      3  APP_60
       B       A   C
       B   D   A   C     .000073003      3  MAP_80
       B   D   A   C
       B   D   A   C     0.00007153      3  APP_40
       B   D   A   C
   E   B   D   A   C     .000066053      3  MAP_20
   E   B   D   A   C
   E   B   D   A   C     .000066003      3  MAP_40
   E   B   D       C
   E   B   D       C     0.00006281      3  MCP_80
   E       D       C
   E       D       C     .000056773      3  MCP_20
   E       D
   E       D             .000056553      3  MCP_60
   E       D
   E       D             .000054977      3  MCP_40
   E
   E                     .000050973      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: PH
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=.0019886
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=.0755117

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING                MEAN       N  TRT

               A               7.9333       3  00
               A
       B       A               7.8667       3  MCP_20
       B       A
       B       A               7.8667       3  MCP_40
       B
       B                       7.8500       3  MAP_20
       B
       B                       7.8333       3  MCP_60
       B
       B                       7.8333       3  MCP_80

               C               7.7500       3  MAP_40
               C
               C               7.7333       3  APP_40
               C
               C               7.7000       3  APP_60
               C
       D       C               7.6833       3  MAP_60
       D
       D       E               7.6167       3  APP_80
               E
               E               7.5833       3  MAP_80
```

```
                                               LSD RUN ON ALL VARIABLES
                                                      SOILTYPE=2

                                             ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: HCO3
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=4.8E-08
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.7E-04

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T         GROUPING              MEAN      N  TRT

                A          0.0037676      3  00

                B          0.0033805      3  MCP_40
                B
       C        B          0.0032901      3  MCP_60
       C        B
       C        B          0.0032728      3  MCP_80
       C        B
       C        B    D     0.0031961      3  APP_40
       C        B    D
       C        B    D     0.0031625      3  APP_60
       C        B    D
       C        B    D     0.0030835      3  MCP_20
       C        B    D
       C        B    D     0.0030197      3  APP_80
       C             D
       C             D     0.0029820      3  MAP_40
                     D
                     D     0.0028855      3  MAP_80
                     D
                     D     0.0028718      3  MAP_60
                     D
                     D     0.0028278      3  MAP_20
```

```
                                                       LSD RUN ON ALL VARIABLES
                                                              SOILTYPE=2

                                                     ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: HPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=3.4E-13
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=9.8E-07

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN       N  TRT

                 A          6.147E-06     3  APP_80
                 A
         B       A          5.727E-06     3  MCP_80
         B       A
         B       A          5.637E-06     3  MAP_80
         B
         B       C         0.00000484     3  APP_60
                 C
         D       C         0.00000413     3  MAP_60
         D       C
         D       C          3.977E-06     3  MCP_60
         D
         D       E          3.207E-06     3  APP_40
                 E
                 E         0.00000241     3  MAP_40
                 E
                 E          2.337E-06     3  MCP_40

                 F          8.800E-07     3  MAP_20
                 F
                 F          8.500E-07     3  MCP_20
                 F
                 F          4.867E-07     3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: H2PO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=6.1E-14
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=4.2E-07

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          2.263E-06      3  MAP_80
               A
               A          2.203E-06      3  APP_80

               B          1.437E-06      3  APP_60
               B
               B          1.293E-06      3  MAP_60
               B
       C       B          1.234E-06      3  MCP_80
       C
       C       D          8.700E-07      3  APP_40
       C       D
       C       D          8.600E-07      3  MCP_60
               D
               D          6.500E-07      3  MAP_40
               D
       E       D          4.700E-07      3  MCP_40
       E
       E                  1.900E-07      3  MAP_20
       E
       E                  1.700E-07      3  MCP_20
       E
       E                  9.000E-08      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CAHPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=1.5E-12
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=2.1E-06

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         .000011737      3  APP_80
               A
       B       A         .000010183      3  MAP_80
       B
       B                  9.153E-06      3  APP_60
       B
       B                 0.00000904      3  MCP_80

               C          6.653E-06      3  MAP_60
               C
               C         0.00000662      3  MCP_60
               C
       D       C          5.837E-06      3  APP_40
       D
       D                  3.953E-06      3  MAP_40
       D
       D                  3.813E-06      3  MCP_40

               E          1.403E-06      3  MCP_20
               E
               E          1.377E-06      3  MAP_20
               E
               E          5.233E-07      3  00
```

```
                                                        LSD RUN ON ALL VARIABLES
                                                              SOILTYPE=2

                                                     ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MGHPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=8.5E-13
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=1.6E-06

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T         GROUPING               MEAN      N  TRT

                A          9.087E-06       3  APP_80
                A
                A          8.607E-06       3  MAP_80

                B          6.663E-06       3  APP_60
                B
                B          6.363E-06       3  MCP_80
                B
        C       B          5.817E-06       3  MAP_60
        C
        C       D         0.00000428       3  MCP_60
                D
                D          4.173E-06       3  APP_40
                D
        E       D         0.00000296       3  MAP_40
        E
        E       F         0.00000234       3  MCP_40
                F
        G       F          1.073E-06       3  MAP_20
        G       F
        G       F          9.033E-07       3  MCP_20
        G
        G                  4.100E-07       3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: CAPO4
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=4.1E-14
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=3.4E-07

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A         0.00000163      3  MCP_80
               A
       B       A          1.373E-06      3  APP_80
       B
       B                 0.00000126      3  APP_60
       B
       B       C          1.193E-06      3  MCP_60
       B       C
       B       C   D      1.053E-06      3  MAP_80
               C   D
       E       C   D      8.833E-07      3  MAP_60
       E           D
       E           D      8.233E-07      3  APP_40
       E           D
       E           D      7.467E-07      3  MCP_40
       E
       E       F          5.933E-07      3  MAP_40
               F
       G       F          2.700E-07      3  MCP_20
       G       F
       G       F          2.567E-07      3  MAP_20
       G
       G                  1.133E-07      3  00
```

```
                                                      LSD RUN ON ALL VARIABLES
                                                             SOILTYPE=2

                                                   ANALYSIS OF VARIANCE PROCEDURE

T TESTS (LSD) FOR VARIABLE: MGP04
NOTE: THIS TEST CONTROLS THE TYPE I COMPARISONWISE ERROR RATE,
      NOT THE EXPERIMENTWISE ERROR RATE.

ALPHA=0.05  DF=22  MSE=6.1E-15
CRITICAL VALUE OF T=2.07387
LEAST SIGNIFICANT DIFFERENCE=1.3E-07

MEANS WITH THE SAME LETTER ARE NOT SIGNIFICANTLY DIFFERENT.

T        GROUPING              MEAN      N  TRT

               A          7.033E-07      3  MCP_80
               A
       B       A          6.733E-07      3  APP_80
       B       A
       B       A   C      5.767E-07      3  APP_60
       B           C
       B           C      5.667E-07      3  MAP_80
                   C
               D   C      4.867E-07      3  MCP_60
               D   C
               D   C      4.833E-07      3  MAP_60
               D
       E       D          3.667E-07      3  APP_40
       E
       E                  2.900E-07      3  MCP_40
       E
       E                  2.767E-07      3  MAP_40

               F          1.267E-07      3  MAP_20
               F
               F          1.100E-07      3  MCP_20
               F
               F          5.333E-08      3  00
```

# VITA

Arkan Mahmoud Al-Showk

Candidate for the degree of

Doctor of Philosophy

Thesis: IRON CHLOROSIS IN SOYBEANS AND PHOSPHORUS INFLUENCE ON DTPA EXTRACTABLE MICRONUTRIENTS AND SOIL SOLUTION CHEMISTRY

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Personal Data: Born in Baghdad, Iraq, June 22, 1947, the son of Mahmoud and Makeia Al-Showk. Married to Suhair J. Al-Jieb on July 28, 1974.

Education: Graduated from Al-mahmodia High School, Mahmodia, Baghdad, in 1965; received the Bachelor of Science in Agriculture from the University of Baghdad, Baghdad, Iraq in May 1969; received a Master of Science from the University of Nebraska, Lincoln, Nebraska in May 1977; and completed requirement for Doctor of Philosophy in Soil Science at Oklahoma State University in December 1985.

Professional Experience: Governmental employee, State Organization of Soils and Land Reclamation, Baghdad, Iraq , working on field and laboratory projects, 1971-1975, 1977-1982; Graduate Assistant, Oklahoma State University, 1982-1985.