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REACTION PRODUCTS OF POLYPHOSPHATES AND ORTHOPHOSPHATES WITH SOILS

by

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B. S., Andhra Pradesh Agricultural University, 1971

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973

Approved by

Major Professor

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ACKNOWLEDGEMENTS

I wish to express my deep felt gratitude to Dr. Roscoe Ellis, Jr., major professor, for the opportunity to work with him, for his invaluable advice during this study, and also for his guidance in preparing this manuscript. The advice of Dr. Larry S. Murphy and Dr. David A. Whitney was very helpful in conducting this research also.

I sincerely appreciate the assistance given by Dr. Page C. Twiss, professor and head of the Department of Geology, in the X-ray diffraction analysis; and Dr. Charles W. Pitts, Department of Entomology, in preparing the electron micrographs.

Finally, my special thanks to all those friends and relatives who made it possible for me to study at Kansas State University, Manhattan, Kansas.

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INTRODUCTION

Fixation of phosphorus by soil has been of great concern to agronomists as well as farmers since it is closely associated with the economics of phosphate usage. Sorption, hydrolysis, and potentials of added phosphates and their transformation in different soils are some of the many aspects investigated by soil chemists in their attempts to find methods of improving the efficiency of phosphatic fertilizers.

Phosphorus fixation in soils is a very complicated phenomenon, and the information obtained under one set of conditions may not hold good for other conditions.

Condensed phosphates (like ammonium polyphosphate) were introduced recently. Orthophosphates and polyphosphates behave differently in soils. Many investigations have been conducted on the transformation of applied orthophosphates under different soil conditions and in saturated fertilizer solution extracts of soil (2, 3, 9, 15, 20).

Studies have been made on the reactions of ammonium polyphosphates with suspensions of calcite, magnesite, gibbsite, goethite, kaolinite, montmorillonite and attapulgite (15, 18), but no attempt was made to identify the reaction products of these polyphosphates with soils.

The objectives of the present investigation were (I) to compare ammonium polyphosphate (APP) with ammonium orthophosphate (AOP) as a source of phosphorus in slightly acid and alkaline soils; (II) to identify the reaction products resulting from additions of APP and AOP to a slightly acid soil and an alkaline soil by using x-ray diffraction and electron microscopy.

REVIEW OF LITERATURE

Poly phosphoric acids having a general formula of $H_{n+2}P_nO_{3n+1}$ came into existence in the early 1950's (7). Ammonium polyphosphate was one of the first products to be introduced into the market on a commercial basis. In the last ten years many experiments have been conducted to evaluate the agronomic use of polyphosphate fertilizers.

According to Sutton, et al. (23), the value of pyrophosphate as a source of phosphorus for plants mainly depends on its rate of hydrolysis to orthophosphate.

In a study to determine the relative extractability and mobility of polyphosphates and orthophosphates in sod-podzolic soils, Prokosheva and Yanishevskii (19) reported that the soil receiving polyphosphates contained less mobile orthophosphate than that receiving $NH_4H_2PO_4$. However, the relative extractability of orthophosphate from polyphosphate was found to be higher than that from $NH_4H_2PO_4$. They concluded that $H_2PO_4^-$ from $NH_4H_2PO_4$ was fixed by the soil. Whereas that from polyphosphate was released by polyphosphate degradation.

Sutton and Larsen (22) reported that pyrophosphates were held less firmly than orthophosphates in clays. But Hashimoto, et al. (10) found that pyrophosphate was absorbed more strongly on clays and soils than was orthophosphate. Their results were contrary to the findings of Sutton and Larsen.

The work done by Hossner and Melton (11), showed that polyphosphates were hydrolyzed more rapidly in acid soils than in alkaline soils.

Several comparisons have been made with polyphosphates and orthophosphate as sources of phosphorus for crops. Sutton and Larsen (22)

noted that pyrophosphate was not as efficient a source of phosphorus for plants as was orthophosphate. Compared to orthophosphates P uptake from pyrophosphate was very low in acid soils, but the differences tended to be less in neutral soils.

Dobson, et al. (6) reported that APP and AOP were equally effective in supplying P for corn grown on acid soil.

Miner and Kamprath (16) studied the availability of polyphosphates and orthophosphates in two acid soils. They found no differences in their effectiveness as sources of phosphorus.

According to Blanchar and Hossner (4) the P uptake from soils treated with polyphosphate was the same as from soils treated with orthophosphate.

Ammonium polyphosphate was compared to AOP with barley as the first crop and tomatoes as the second crop on four calcareous soils in the greenhouse by Strochalein, et al. (21). They concluded that APP was a satisfactory P source and was superior to AOP for the second crop.

In a field experiment to test the ability of APP and MAP to provide P for corn and grain sorghum under both irrigated and dryland conditions, Webb (25) concluded that both sources are apparently equal.

Kundler, et al. (25) found no differences in the fertilizer effects of APP and DAP in a two year pot experiment with red clover.

Yanishevskii and Prokosheva (27) reported that APP both in solid and liquid form was better utilized than ammophos in pot experiments on sod-podzolic soils with oats, lupines, rye grass and corn as test crops.

Terman and Engelstad (24) stated that polyphosphate was equal to or slightly superior to orthophosphate especially on neutral soils.

Transformation of applied phosphates to crystalline phosphates of relatively lower solubility is said to be the prime reason for the low uptake of phosphorus.

Past research shows that the nature of phosphorus fixation in acid soils is quite different from that in alkaline soils. In acid soils it is due to formation of iron and aluminum compounds which have the general formula $M(H_2O)_3(OH)_2H_2PO_4$ where M is iron or aluminum. High pH coupled with high $CaCO_3$ content of the medium favors the formation of a series of basic calcium phosphates in alkaline soils.

The source of phosphorus used will influence the type of crystalline phosphates formed. The orthophosphates exist as $H_2PO_4^-$ in acid soils and as HPO_4^{--} in alkaline soils. Whereas the pyrophosphates exist largely as $H_2P_2O_7^{--}$ in slightly acid to neutral soils, as $HP_2O_7^{---}$ in slightly alkaline soils and as $P_2O_7^{----}$ in highly alkaline soils (22). Differences in the valences of the ions from these two sources at a given pH, leads to the formation of different reaction products.

Lindsay, et al. (15) identified $Ca_4H(PO_4)_3 \cdot 3H_2O$, $Ca_2(NH_4)_2(HPO_4)_3 \cdot 2H_2O$, $MgNH_4PO_4 \cdot 6H_2O$, $CaNH_4PO_4 \cdot H_2O$, $NH_4Al_2(PO_4)_2OH \cdot 8H_2O$, collophane (colloidal apatite) and finely divided $Ca_{10}(PO_4)_6(OH)_2$ in the precipitates of saturated DAP solution extracts of soil.

Soil extracts saturated with ammoniated super phosphoric acid (a condensed phosphate 11-33-0) solutions contained different kinds of crystalline phosphates such as $Ca(NH_4)_2P_2O_7 \cdot H_2O$, $Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ (A),

$Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ (B), $Ca_2P_2O_7 \cdot 4H_2O$, $Ca_2P_2O_7 \cdot 2H_2O$ (15).

According to Beaton, et al. (2) the major initial reaction product in saturated DAP extracts of a calcareous soil was hydroxy apatite.

Hashimi (9) reported that $CaHPO_4 \cdot 2H_2O$ was the main crystalline phosphate produced by the addition of DAP to dilute solutions that approximated ionic contents commonly found in soil solutions with a Ca:P ratio of 0.8 or less. With an initial Ca:P ratio of 0.9 or greater, $CaHPO_4 \cdot 2H_2O$ was unstable and transformed to $Ca_5H(PO_4)_3OH$ (hydroxy apatite). Some $CaHPO_4$ and possibly $Ca_4H(PO_4)_3 \cdot 2.5H_2O$ (OCP) were also identified when the initial Ca:P ratio was between 0.9 and 1.7.

Racz and Soper (20) found octa calcium phosphate, di magnesium phosphate trihydrate, and di calcium phosphate dihydrate in the saturated DAP extracts of soil.

Investigations have been carried out to identify the crystalline phosphates produced by the interaction of orthophosphates with soils. The formation of $MgHPO_4 \cdot 3H_2O$ by the addition of DAP to calcareous soils having a Ca:Mg ratio less than 1.5, was reported by Racz and Soper (20).

Bell and Black (3) reported the formation of $MgNH_4PO_4 \cdot 6H_2O$, $CaHPO_4 \cdot 2H_2O$, $Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$ (dimorph B) and $Ca_8(H_2PO_4)_6 \cdot 5H_2O$ from the addition of DAP to slightly acid to alkaline soils. The $MgNH_4PO_4 \cdot 6H_2O$ crystals dissolved with time, leaving a white powdery residue of $Mg_3(PO_4)_2 \cdot 22H_2O$.

The crystalline phosphates formed from reactions with DAP and APP are quite different. The pH of the medium and the amount and type of cations present are the main factors which determine the type of

crystalline phosphate produced.

A summary of the reaction products which have been identified with DAP and APP under different conditions are shown in Table 1.

Table 1. DAP and APP reaction products identified in soils and soil extracts, reacting with soil clay minerals and common soil constituents.

Crystalline phosphates identified in saturated fertilizer solution extracts of soil

P Source	Soil conditions	P Compound identified	Reference
$(NH_4)_2HPO_4$	Calcareous soils	Colloidal (Fe, Al) $PO_4 \cdot NH_2O$	15
		$MgNH_4PO_4 \cdot 6H_2O$	
		Mg-NH_4-P-No. 19 (unidentified)	
		Collophane (colloidal apatite)	
		$Ca_{10}(PO_4)_6(OH)_2$ Hydroxy apatite	
		$NH_4Al_2(PO_4)OH \cdot 8H_2O$	
		$Ca_2(NH_4)_2(HPO_4)_3 \cdot 2H_2O$	
		$CaNH_4PO_4 \cdot H_2O$	
	Calcareous soil	$Ca_{10}(PO_4)_6(OH)_2$ Hydroxy apatite	2
	Balmoral II with a pH of 7.85	$MgHPO_4 \cdot 3H_2O$ (DMPT)	20
		$CaHPO_4 \cdot 2H_2O$ (DCPD)	
		$Ca_4H(PO_4)_3 \cdot 3H_2O$) (OCP)	
	Balmoral I with a pH of 7.70	$Ca_4H(PO_4)_3 \cdot 3H_2O$ (OCP)	
	Soil solution with a Ca:P ratio less than 0.8	$CaHPO_4 \cdot 2H_2O$	
	Soil solution with a Ca:P ratio > 0.9	$Ca_5(PO_4)_3OH$	9
	Soil solution with a Ca:P ratio between 0.9 and 1.7	$CaHPO_4$	
		$Ca_4H(PO_4)_3 \cdot 2.5H_2O$	9

Ammoniated super phosphoric acid (11-33-0) liquid	Hartsells soil	None	15
	Webster soil	$Ca(NH_4)_2P_2O_7 \cdot H_2O$	

Table 1. continued
Crystalline phosphates identified by reacting with soil clay minerals and common soil constituents

P Source	Name of clay mineral or common soil constituent	P Compound identified	Reference
$(NH_4)_2HPO_4$	$CaCO_3$	$Ca_2(NH_4)_2(HPO_4)_3 \cdot 2H_2O$	15
		$Ca_4H(PO_4)_3 \cdot 3H_2O$	
		$CaNH_4PO_4 \cdot H_2O$	
		$Ca_4H(PO_4)_3 \cdot 3H_2O$	
		$Ca_{10}(PO_4)_6(OH)_2$	
	MgO	Mg-NH_4-P (No. 19)	
		$MgNH_4PO_4 \cdot 6H_2O$	
	$CaMg(CO_3)_2$	$Ca_2(NH_4)_2(HPO_4)_3 \cdot 2H_2O$	
		$MgNH_4PO_4 \cdot 6H_2O$	
	$Al(OH)_3$	$Al(OH)_3$ (added)	
	$Fe_2O_3 \cdot H_2O$	$Fe_2O_3 \cdot H_2O$ (added)	
	$CaSO_4 \cdot 2H_2O$	Collophane	
	CaF_2	CaF_2 (added)	
Ammonium poly phosphates			
$(NH_4)_2H_2P_2O_7$	Kaolinite	No reaction	18

$(NH_4)_3HP_2O_7$	Kaolinite	No reaction
$(NH_4)_2H_2P_2O_7$	Montmorillonite	$Mg(NH_4)_2H_4(P_2O_7)_2 \cdot 2H_2O$
		$Ca_3NH_4H_3(P_2O_7)_2 \cdot 3H_2O$
$(NH_4)_3HP_2O_7$	Montmorillonite	$Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ (A)
		$Ca_3(NH_4)_2(P_2O_7)_2 \cdot 6H_2O$
$(NH_4)_2H_2P_2O_7$	Attapulgite	$Mg(NH_4)_2H_4(P_2O_7)_2 \cdot 2H_2O$
$(NH_4)_3HP_2O_7$	Attapulgite	$Mg(NH_4)_2P_2O_7 \cdot 4H_2O$ (A)
$(NH_4)_2H_2P_2O_7$	Goethite	NH_4Fe Pyrophosphate
$(NH_4)_3HP_2O_7$	Goethite	NH_4Fe Pyrophosphate
$(NH_4)_2H_2P_2O_7$	Gibbsite	$Al(NH_4)_2P_2O_7OH \cdot 2H_2O$
$(NH_4)_3HP_2O_7$	Gibbsite	$Al(NH_4)_2P_2O_7OH \cdot 2H_2O$
$(NH_4)_3HP_2O_7$	Calcite	$Ca(NH_4)_3P_3O_{10} \cdot 2H_2O$
		$Ca(NH_4)_2P_2O_7 \cdot H_2O$
$(NH_4)_3HP_2O_7$	Magnesite	$MgNH_4$ tripoly phosphate
Ammoniated super phosphoric acid	$CaCO_3$	$Ca(NH_4)_2P_2O_7 \cdot H_2O$
		$Ca(NH_4)_2P_2O_7 \cdot H_2O$
	MgO	$Mg(NH_4)_2P_2O_7 \cdot 4H_2O$
	$CaMg(CO_3)_2$	$Ca(NH_4)_2P_2O_7 \cdot H_2O$
		$CaMg(CO_3)_2$ (added)
		$Mg(NH_4)_2P_2O_7 \cdot 4H_2O$
	$Fe_2O_3 \cdot H_2O$	None
	$Al(OH)_3$	None
	$CaSO_4 \cdot 2H_2O$	$Ca(NH_4)_2P_2O_7 \cdot H_2O$

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Table 1. continued
Crystalline phosphates identified in soils

P Source	Soil type	P Compound identified	Reference
$(NH_4)_2HPO_4$	Balmoral I pH 8.30	$MgHPO_4 \cdot 3H_2O$	20
	Balmoral II pH 8.15	$MgHPO_4 \cdot 3H_2O$	
	Norfolk loamy sand	$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$	3
		$CaHPO_4 \cdot 2H_2O$	
	Lloyd clay loam	$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$	
		$CaHPO_4 \cdot 2H_2O$	
	Webster silty clay loam	$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$	
		$CaHPO_4 \cdot 2H_2O$	
		$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	
	Harpster silty clay loam I	$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$	
		$CaHPO_4 \cdot 2H_2O$	
		$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	
	Harpster silty clay loam II	$Ca(NH_4)_2(HPO_4)_2 \cdot H_2O$	
		$CaHPO_4 \cdot 2H_2O$	
		$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	
	Darlings down clay	$MgNH_4PO_4 \cdot 6H_2O$	
		$Mg_3(PO_4)_2 \cdot 22H_2O$ (?)	
		$CaHPO_4 \cdot 2H_2O$	
		$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	

MATERIALS AND METHODS

Growth Chamber Experiment

A growth chamber experiment was carried out to compare ammonium polyphosphate (APP) with ammonium orthophosphate (AOP) as sources of P for corn. Two soils, an alkaline Ulysses silt loam soil levelled for irrigation, from Scott County, and a slightly acid alluvial soil (originally Eudora) levelled for irrigation, from Pottawatomie County, were used as growth media. Previous studies revealed that plants grown on the alkaline soil from Scott County showed a severe P deficiency. Chemical characteristics of the two soils are given in Table 3. APP and AOP were applied in dry forms at rates of 0, 20, 40, and 80 PPM of P. Different forms of phosphorus present in APP and DAP are given in Table 4. The complete treatment outline is presented in Table 2.

One kilogram of soil was placed in plastic pots. Hybrid corn (Dekalb XL 390), was used as the test crop. Seeds were planted in the pots on July 3, 1972. Treatments were replicated three times and placed in a completely random design in a growth chamber with a day time temperature of 30°C, a night time temperature of 20°C, and with a photoperiod of 14 hours light and 10 hours dark. Pots were watered to near field capacity. Plants were thinned to a uniform two plants per pot on July 11, 1972.

Plants were harvested after one month. Plant heights, fresh weights, and dry weights of the plant material were determined. Plant material was ground with a Wiley mill and was wet digested with a

Table 2. Treatment Outline for Growth Chamber Experiment with APP and AOP as P Sources

Treatment Number	Source of Phosphorus	Type of Soil	Rate of Application Parts Per Million
1	Control	Slightly acid soil	0
2	AOP	Slightly acid soil	20
3	AOP	Slightly acid soil	40
4	AOP	Slightly acid soil	80
5	APP	Slightly acid soil	20
6	APP	Slightly acid soil	40
7	APP	Slightly acid soil	80
8	Control	Alkaline soil	0
9	AOP	Alkaline soil	20
10	AOP	Alkaline soil	40
11	AOP	Alkaline soil	80
12	APP	Alkaline soil.	20
13	APP	Alkaline soil	40
14	APP	Alkaline soil	80

NOTES: 1 Slightly acid soil and alkaline soil were from Pottawatomie and Scott Counties respectively.

2 A uniform application of 100 PPM nitrogen in the form of ammonium nitrate, 5 PPM Zn in the form of $ZnSO_4$, 50 PPM sulfur in the form of $ZnSO_4$ and elemental sulfur was made in all the pots.

3 Solid (15-62-0) was used as source of APP and DAP (18-46-0) was used as source of AOP.

Table 3. Soil test data for soils used in growth chamber.

County	Soil description	pH	OM	Avail. P	Exchangeable K	Exchangeable Ca	Exchangeable Mg	DTPA extractable Fe	DTPA extractable Zn	DTPA extractable Mn	DTPA extractable Cu
			%	lbs/acre	lbs/acre	--meq/100 g--		----------PPM----------			
Pottawatomie	slightly acid alluvial sandy loam	6.8	1.4	20.0	233	4.5	0.65	11.94	0.42	6.8	0.39
Scott	calcareous silt loam	8.2	0.8	8.0	1,000	62.5*	5.50	1.89	0.29	5.3	0.69

*Value for exchangeable calcium in the alkaline soil is too high due to extraction of Ca from free $CaCO_3$.

Table 4. Composition of Phosphate Fertilizers*

Phosphate Species	Liquid APP 11-37-0	Solid APP 15-62-0	DAP 18-46-0
	Percent P_2O_5		
Ortho	20	41	100
Pyro	38	54	--
Tripoly	23	4	--
Tetrapoly & Higher	19	1	--

*Reference No. 7, page 30-36.

1:1:1 ternary digestion mixture of nitric acid, perchloric acid and deionized distilled water. The residue was dissolved in 0.1N HCL and was filtered into polyethylene bottles.

Solutions were analyzed for Zn, Cu, Fe, Mn, Ca, and Mg using the Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer. Potassium was determined by using a Perkin-Elmer Flame Photometer. Phosphorus was analyzed by the vanado molybdo phosphoric yellow color method in a nitric acid system, Jackson (13), designated by him as method $\underline{\underline{v}}$.

Soil Analyses

The pH values were measured in 0.01 M $CaCl_2$. Exchangeable cations were extracted with neutral 1N NH_4OAC (13). Available phosphorus was determined colorimetrically after extracting with 0.025N HCL + 0.03N NH_4 F (Bray's No. 1 solution). The microelements Zn, Mn, Cu, and Fe were extracted with DTPA, and analyzed by atomic absorption spectrophotometery. Calcium and magnesium potentials were determined essentially by the procedure developed by Aslyng as modified by Withee and Ellis (26). Fifteen grams of soil were shaken in 50 ml of 0.01 M $CaCl_2$ for 2 hours. After filtration Ca and Mg were determined with an atomic absorption spectrophotometer. Phosphorus could not be determined in the filtrate by the Troug and Meyer method described by Jackson (13), because of the low amount of phosphorus present.

Activities were calculated from concentrations and activity coefficients by using the second approximation of the Debye-Huckel equation to compute the activity coefficients. It was assumed that Cl^- was the only anion contributing to the ionic strength.

$$\text{Debye-Huckel equation} \quad -\log f_i = \frac{0.5\, z_i^2 \sqrt{u}}{1 + 1.5\sqrt{u}}$$

where f_i = activity coefficient

u = ionic strength = $\frac{1}{2} \sum c_i z_i^2$

c = concentration of ion in moles per liter

z = valence of ion

Soil Reactions with Fertilizer Saturated Solutions

A technique developed by Lindsay, et al. (15) was used to identify reaction products in the soil extracts. Saturated solutions of APP and DAP were made by shaking fertilizer grade salts in deionized distilled water for one day. One hundred fifty mls of these fertilizer solutions were shaken with 300 g. of soil for one hour. The suspensions were filtered and the filtrates were kept undisturbed to allow the crystalline phosphates to precipitate. The pH values of saturated fertilizer solutions and filtrates are given in Table 10. Samples of the crystalline precipitates were taken after 10 days and one month. X-ray diffraction patterns and electron micrographs were made for each sample.

Study of the Reaction Products in Soil

A method very similar to that of Bell and Black (3), where the soil and phosphorus fertilizers were allowed to react in plexiglass cylinders of 10 cms height and 3.8 cms internal diameter were used to study the reaction products in the soil. The top of the soil was covered with a glass fiber filter paper over which a thin layer of fertilizer grade phosphate was placed. The columns were inverted and placed in a saturated atmosphere in a desiccator to prevent water loss by evaporation. After 16 weeks, samples were taken with a spatula from the reaction surface for powder X-ray diffraction analysis.

X-ray diffraction patterns and electron micrographs were made for each soil sample. The X-ray diffraction patterns for the soils with added phosphate were compared with patterns from the same soils without added phosphate. The diffraction peaks which occurred in the phosphate treated soils and which were not found in untreated soils were considered to be those of the newly formed crystalline phosphates.

X-ray diffraction patterns were obtained by a Philips X-ray diffractometer with nickel-filtered copper Kα radiation with a pulse height analyzer.

RESULTS AND DISCUSSION

Growth Chamber Experiment

Ammonium polyphosphate (APP) was compared with ammonium orthophosphate (AOP) in an alkaline soil and a slightly acid soil as sources of P for corn. Data for plant heights, fresh weights, dry weights, and concentrations of P, Ca, Mg, K, Zn, Fe, Mn, and Cu are presented in Appendix Table I. Total uptakes of P, Ca. Mg, K, Zn, Fe, Mn, and Cu are presented in Appendix Table II. Soil samples were collected from each pot after the plants were grown and were analyzed for calcium and magnesium activities, exchangeable Ca and Mg, available phosphorus, and DTPA extractable Zn, Fe, Mn and Cu. Soil test data are presented in Appendix Table III.

In general, applications of P increased plant heights, fresh weights, and dry weights of the plant material when compared with control plants (Table 5). Additions of AOP increased dry weights of the plant material and also resulted in significantly more uptake of P, Mg, K, Fe, and Cu than applications of APP (Table 6). Dry weight and uptake of P, Mg, Ca, and Fe were greater in the slightly acid soil than in the alkaline soil (Table 7). The responses to P applications were higher in the slightly acid soil than in the alkaline soil (Table 8).

Previous studies (6, 24) indicated that APP was a better source of P when compared to AOP in slightly acid to neutral soils as measured by P uptake. In this study AOP was superior to APP in the slightly acid soil (Figure 1)

Table 5. Effect of 3 rates of AOP and APP on the dry weights and uptake of nutrients.

P_2O_5	Dry wt.	P	Mg	Ca	K	Mn	Fe	CU	Zn
PPM	gms	-------mgms/2 plants--------				-Micrograms/2 plants-			
0	0.8	1.16	8.13	10.07	47.63	161	76	11	86
20	1.4	2.17	12.39	14.36	71.20	285	117	17	127
40	2.0	3.00	15.06	15.44	87.68	328	134	20	134
80	2.6	5.33	16.97	16.01	110.22	374	142	25	138
LSD .05	0.14	0.40	1.24	1.58	8.93	34	11	2	13.6

Table 6. Effect of P sources on the dry weights and uptake of nutrients.

P Source	Dry Weight gms/ 2 plants	P	Mg	Ca	K	Mn	Fe	Cu	Zn
		-------mgms/2 plants--------				-Micrograms/2 plants-			
AOP	1.8	3.21	13.70	14.2	82.7	295	125	20	122
APP	1.7	2.61	12.57	13.7	75.7	279	110	17	121
LSD .05	0.10	0.29	0.88	NS	6.3	NS	7.8	1.5	NS

Table 7. Effect of soils on the dry weights and uptake of nutrients.

Soil	Dry weights	P	Mg	Ca	K	Mn	Fe	Cu	Zn
	gms/2 plants	mgms/2 plants				Micrograms/2 plants			
Slightly acid soil	2.2	4.29	19.7	17.1	35.1	245	146	18	116
Alkaline soil	1.2	1.53	6.6	10.8	123.3	328	88	19	126
LSD .05	0.10	0.29	0.88	1.12	6.3	24	7.8	1.5	9.6

Table 8. Effect of soil and P rate on P and Zn uptake.

Soil	P_2O_5 Rate	P	Zn
		mgms/2 plants	
Alkaline soil	0 PPM	649.0	77.7
Alkaline soil	20 PPM	1158.2	128.3
Alkaline soil	40 PPM	1745.5	140.7
Alkaline soil	80 PPM	2584.8	158.5
Slightly acid soil	0 PPM	1664.0	93.7
Slightly acid soil	20 PPM	3173.7	124.8
Slightly acid soil	40 PPM	4256.8	128.0
Slightly acid soil	80 PPM	8080.7	116.8
	LSD .05	571.5	19.2

Ammonium polyphosphate and AOP were similar in supplying P to the plants in the alkaline soil (Figure 2). Uptake of Zn decreased at the higher rates of P application in the slightly acid soil (Figure 3). Uptake of Zn increased with rate of application of P in the alkaline soil (Figure 4). The uptake of Zn by the plants in the alkaline soil was lower when APP was used as P source than AOP, but the difference was not significant at 0.05 test level. Similar kind of depressing effect of APP on the uptake of Zn was reported earlier (1,8,25).

Calcium activities were higher in the slightly acid soil than in the alkaline soil and so was the uptake of Ca by the plants (Table 9). Higher activities of magnesium in the alkaline soil did not result in higher uptake of Mg by the plants (Table 9). Luxury consumption of potassium (Table 7) by plants grown in the alkaline soil might have restricted uptake of magnesium.

Table 9. Ca and Mg activities in the soil and uptake by plants.

Soil	Ca activities	Ca uptake	Mg activities	Mg uptake
	moles/liter	mgms/2 plants	moles/liter	mgms/2 plants
Slightly acid soil	0.0114	17.1	0.0012	19.7
Alkaline soil	0.0085	10.8	0.0032	6.6
LSD .05	0.0003	1.1	0.0001	0.9

Soil test data for available P (Appendix Table III) showed no increase in available soil P from applications of APP in the alkaline soil. This was due to transformation of applied APP into calcium

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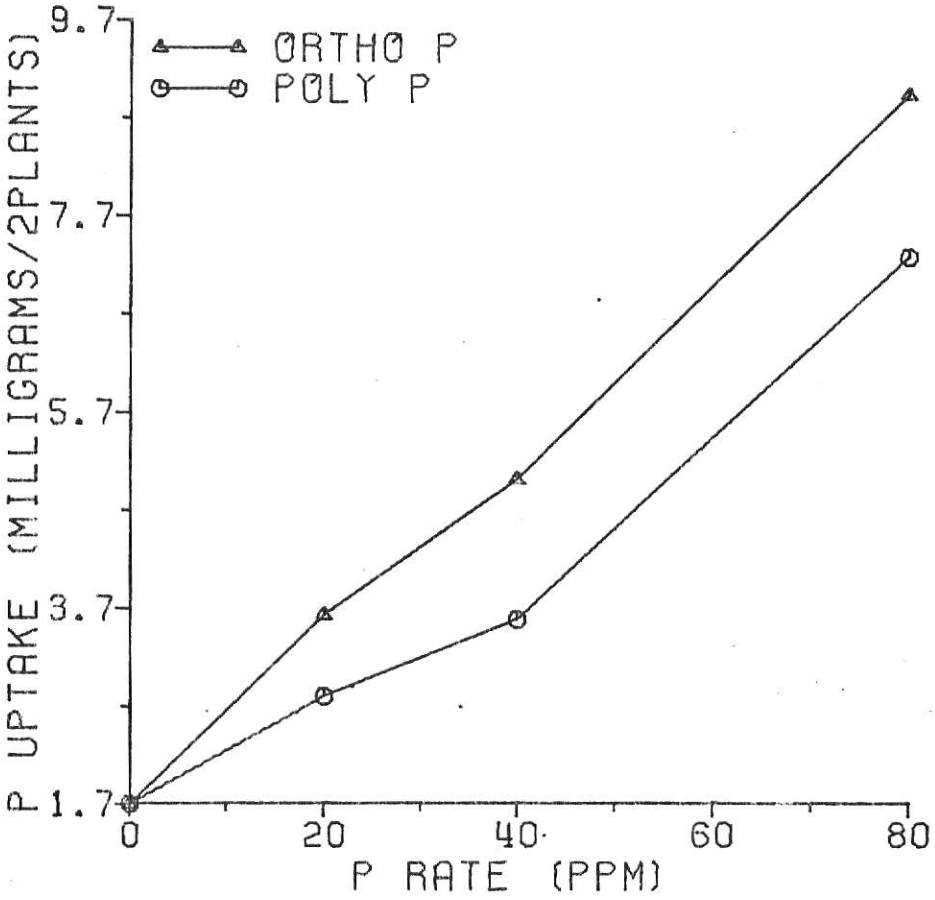

Fig. 1 EFFECT OF 3 RATES OF AOP AND APP ON P UPTAKE BY CORN PLANTS (SLIGHTLY ACID SOIL)

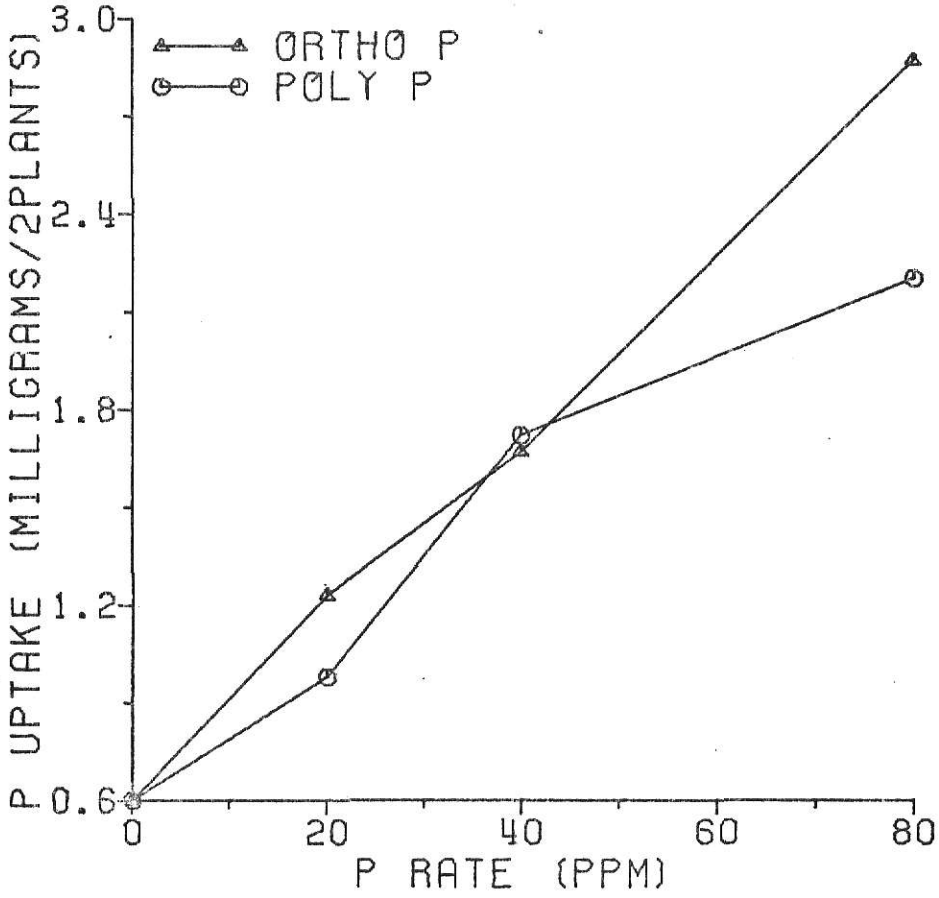

Fig. 2 EFFECT OF 3 RATES OF AOP AND APP ON P UPTAKE BY CORN PLANTS (ALKALINE SOIL)

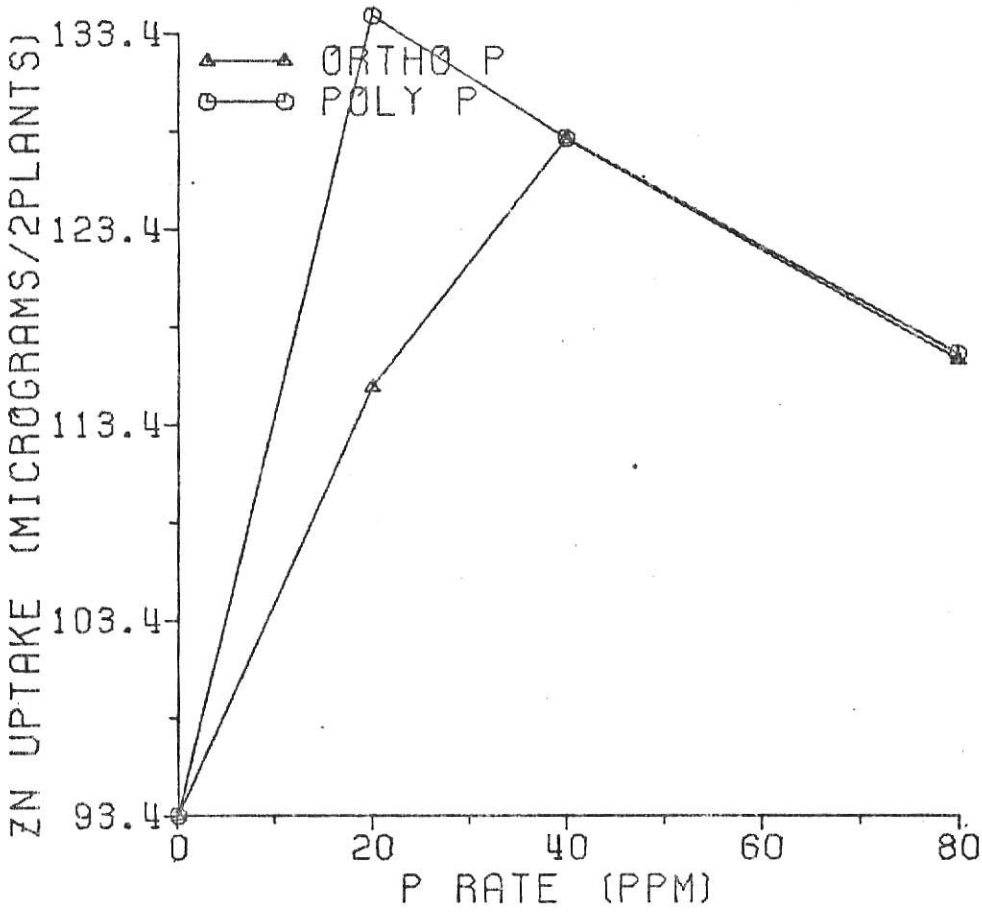

Fig. 3 EFFECT OF 3 RATES OF AOP AND APP ON ZN UPTAKE BY CORN PLANTS (SLIGHTLY ACID SOIL)

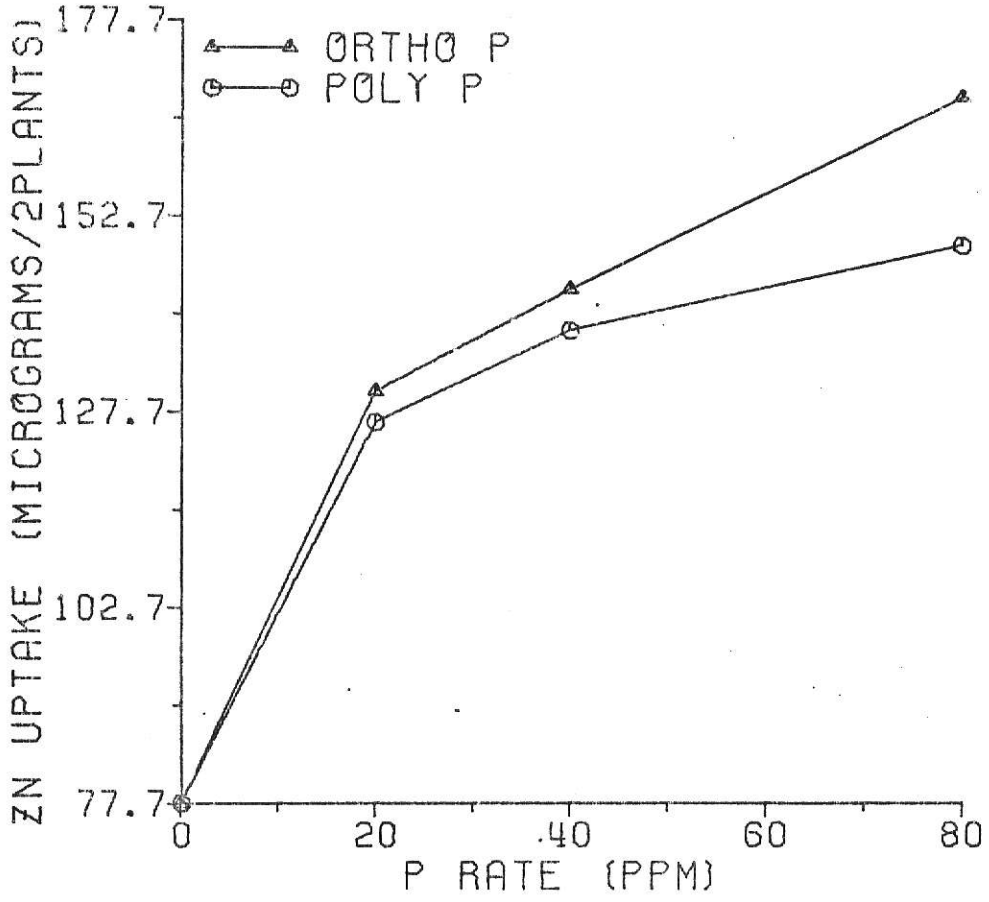

Fig. 4 EFFECT OF 3 RATES OF AOP AND APP ON ZN UPTAKE BY CORN PLANTS (ALKALINE SOIL)

phosphorus compounds of low solubility.

Crystalline Phosphates Formed in Saturated Fertilizer Solutions

The d" spacings from the X-ray diffraction patterns for the precipitates formed in the saturated APP solutions are given in Appendix Table IV.

Ammonium polyphosphate saturated filtrates from alkaline and slightly acid soils gave a copious precipitate identified as $Ca(NH_4)_2P_2O_7 \cdot H_2O$. In the extracts from the alkaline soil $(NH_4)_3HP_2O_7$ precipitated in the form of rod shaped crystals along with $Ca(NH_4)_2P_2O_7 \cdot H_2O$ (Figure 5a). In the slightly acid soil $Ca(NH_4)_2P_2O_7 \cdot H_2O$ precipitated directly (Figure 5b).

It took two days for the crystalline $Ca(NH_4)_2P_2O_7 \cdot H_2O$ to form in the alkaline soil extracts, and 20 days in the slightly acid soil extracts. Though the amount of exchangeable calcium present in the slightly acid soil was low, the formation of crystalline $Ca(NH_4)_2P_2O_7 \cdot H_2O$ in the extract might be due to the high activity of calcium present in solution in this soil.

No precipitates were found in the DAP saturated filtrates from either the alkaline or alightly acid soil.

Reaction of Soils with APP and DAP

The d" spacings from the X-ray diffraction patterns for the crystalline phosphates formed by the interaction of APP and AOP with the soils are presented in Appendix Table V.

The addition of ammonium polyphosphate to the alkaline soil

resulted in the formation of very minute blade like scales cemented together to form the rosette shaped crystals of $Ca(NH_4)_2P_2O_7 \cdot H_2O$ (Figure 5c, d, e). This $Ca(NH_4)_2P_2O_7 \cdot H_2O$ existed in the soil after 32 weeks. The amount of this crystalline phosphate formed increased with time. Addition of liquid ammonium polyphosphate (11-37-0) to this soil also resulted in the formation of $Ca(NH_4)_2P_2O_7 \cdot H_2O$, but the amount of this compound formed was very high when compared with solid APP.

Though the saturated APP extracts of both soils gave the precipitate $Ca(NH_4)_2P_2O_7 \cdot H_2O$, the added APP in the slightly acid soil did not transform into $Ca(NH_4)_2P_2O_7 \cdot H_2O$. In this soil APP hydrolyzed into $NH_4H_2PO_4$ and $(NH_4)_2H_2P_2O_7$ (monoclinic) (Figure 5 f, g). An extensive hydrolysis of the tripoly phosphates to pyrophosphates and then to orthophosphates when in contact with soil minerals has been reported by Philen and Lehr (18). The $NH_4H_2PO_4$ fraction slowly disappeared and transformed into $Ca_4H(PO_4)_3 \cdot 2.5H_2O$.

Reaction of Soils with AOP

High amounts of exchangeable potassium and magnesium contained in the alkaline soil lead to the formation of $Mg_2KH(PO_4)_2 \cdot 15H_2O$ when reacted with AOP. After 28 weeks there was formation of $Ca_4H(PO_4)_3 \cdot 2.5H_2O$. In a similar type of study (3), $CaHPO_4 \cdot 2H_2O$ has been reported as the major reaction product formed in soils. The formation of $CaHPO_4 \cdot 2H_2O$ was not found in this study. The possibility remains that $CaHPO_4 \cdot 2H_2O$ might have formed in this soil before 16 weeks, when the first sampling was done, and was then later converted to $Ca_4H(PO_4)_3 \cdot 2.5H_2O$.

$MgHPO_4 \cdot 3H_2O$ was identified as the reaction product formed

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Figure 5. Scanning electron micrographs of the crystalline phosphate compounds identified.

a. Rod shaped crystals of added long chain polyphosphate precipitated along with $Ca(NH_4)_2P_2O_7 \cdot H_2O$ in the APP saturated solution extracts of alkaline soil.

b. Crystals of $Ca(NH_4)_2P_2O_7 \cdot H_2O$ formed in the APP saturated solution extracts of the slightly acid soil.

c, d, e. The formation of $Ca(NH_4)_2P_2O_7 \cdot H_2O$ by the addition of APP to the alkaline soil. Flower shaped crystals (transitory stage) transformed into blade like scales (d) which cemented together to form the rosette shaped structures (e) of $Ca(NH_4)_2P_2O_7 \cdot H_2O$.

f. The tetragonal rods of $NH_4H_2PO_4$ formed on the soil surface by the addition of APP to the slightly acid soil.

g. Stacked together are the crystals (monoclinic) of $(NH_4)_2H_2P_2O_7$ resulted from the addition of APP to the slightly acid soil.

h. Monobasic ammonium phosphate transformed over time into $Ca_4H(PO_4)_3 \cdot 2.5H_2O$ in the slightly acid soil.

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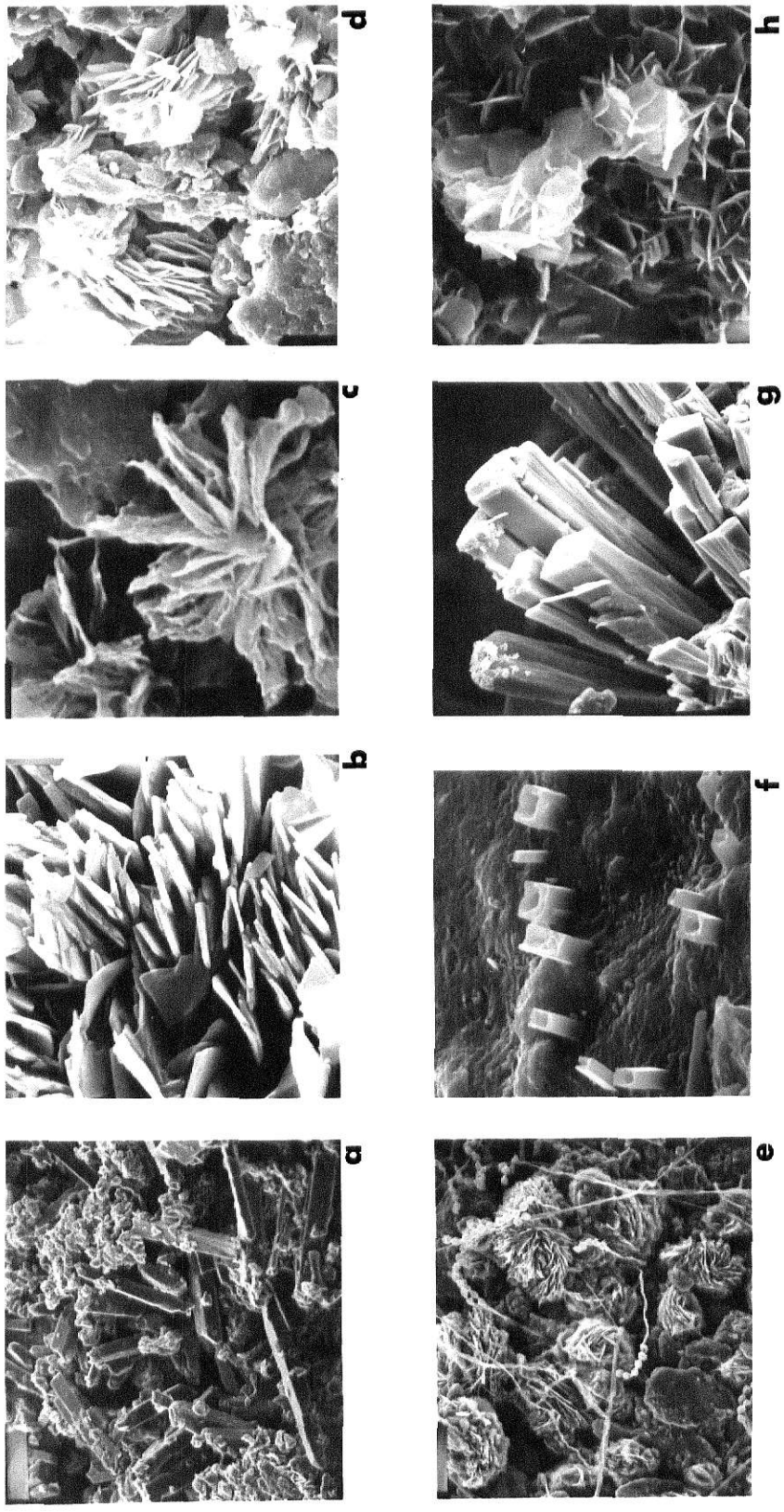
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after 16 weeks by the addition of AOP to the slightly acid soil. This transformed into $MgHPO_4 \cdot 7H_2O$ after 28 weeks. Though the exchangeable magnesium content was very low, the activities of magnesium were high enough to favor the formation of magnesium compounds. Several crystalline phosphates existed in minute amounts in the slightly acid soil when AOP was added which could not be detected by x-ray diffraction analysis. The reaction products identified by the addition of APP and AOP to two different kinds of soils are summarized in Table 10.

Table 10. Summary of the Crystalline Phosphates Formed in Soil Extracts and Soils

Reaction Products Formed in Soil Extracts

Fertilizer solution	pH of the fertilizer solution	pH of the filtrate	Solids precipitated in filtrates
	Alkaline soil		
APP	5.3	5.55	long chain poly phosphate (added) and $Ca(NH_4)_2P_2O_7 \cdot H_2O$
DAP	7.4	7.10	No precipitate
	Slightly acid soil		
APP	5.3	5.15	$Ca(NH_4)_2P_2O_7 \cdot H_2O$
DAP	7.4	7.10	No precipitate

Reaction Products Formed in Soils

Fertilizer	Crystalline phosphates identified after indicated time of incubation 16 weeks	28 weeks
	Alkaline soil pH 8.2	
APP Solid (15-62-0)	$Ca(NH_4)_2P_2O_7 \cdot H_2O$	$Ca(NH_4)_2P_2O_7 \cdot H_2O$
DAP (18-26-0)	$Mg_2KH(PO_4)_2 \cdot 15H_2O$	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$
	Slightly acid soil	
APP Solid (15-62-0)	$NH_4H_2PO_4$ $(NH_4)_2H_2P_2O_7$	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$
DAP (18-46-0)	$MgHPO_4 \cdot 3H_2O$	$MgHPO_4 \cdot 7H_2O$

CONCLUSIONS

Ammonium polyphosphate and AOP were evaluated as sources of P for plants and their reaction products were identified in soils. Ammonium polyphosphate was equal to AOP in supplying P to the plants in the alkaline soil, but was inferior to AOP in the slightly acid soil. Though the alkaline soils had higher magnesium activities the uptake of Mg was more in the slightly acid soil due perhaps to the higher uptake of K in the alkaline soil. The available soil phosphorus did not increase in the alkaline soil with applications of ammonium polyphosphate.

Reaction Products Identified

Saturated APP solution extracts of the slightly acid soil and the alkaline soil gave a precipitate $Ca(NH_4)_2P_2O_7 \cdot H_2O$. The time and the way of formation of $Ca(NH_4)_2P_2O_7 \cdot H_2O$ were quite different in these soil extracts. In the alkaline soil extract $(NH_4)_3HP_2O_7$ from the added APP precipitated as rod shaped crystals almost immediately along which the formation of $Ca(NH_4)_2P_2O_7 \cdot H_2O$ occurred. In the slightly acid soil extract $Ca(NH_4)_2P_2O_7 \cdot H_2O$ directly precipitated after 20 days.

The addition of APP to the alkaline soil resulted in the formation of $Ca(NH_4)_2P_2O_7 \cdot H_2O$ which existed in the soil for 32 weeks. The amount of this compound formed was more with liquid APP and increased with time. In the slightly acid soil APP hydrolyzed into $NH_4H_2PO_4$ and $(NH_4)_2H_2P_2O_7$ (monoclinic). Monobasic ammonium phosphate transformed into $Ca_4H(PO_4)_3 \cdot 2.5H_2O$ after 28 weeks. High amounts of exchangeable potassium and magnesium contained in the alkaline soil lead to the

formation of $Mg_2KH(PO_4)_2 \cdot 15H_2O$ and $Ca_4H(PO_4)_3 \cdot 2.5H_2O$.

Dimagnesium phosphate trihydrate ($MgHPO_4 \cdot 3H_2O$) formed after 16 weeks in the slightly acid soil from the addition of AOP and transformed into $MgHPO_4 \cdot 7H_2O$ at 28 weeks.

The low available soil P test in the alkaline soil was due to the transformation of APP to the less soluble $Ca(NH_4)_2P_2O_7 \cdot H_2O$. The transformation of APP and AOP into the less soluble crystalline phosphates $Ca(NH_4)_2P_2O_7 \cdot H_2O$, $Mg_2KH(PO_4)_2 \cdot 15H_2O$, and $Ca_4H(PO_4)_3 \cdot 2.5H_2O$, explains the low uptake of phosphorus from the alkaline soil.

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Table I. Effects of Soil, Source, and Rate of Application of P on Concentration of Elements in Plant Material

Treatment P_2O_5	P Source	Plant Height	Fresh Weight	Dry Weights	P	Mg	Ca	K	Mn	Fe	Cu	Zn
PPM												
Slightly acid soil		cms	--gms/2 Plants--		PPM							
0	---	78.4	9.1	2.02	840.0	6033.0	6533.0	20333.0	77.2	51.8	6.00	46.0
20	AOP	88.8	14.3	3.88	929.0	5067.0	4600.0	9667.0	64.6	43.8	5.10	29.8
40	AOP	91.2	18.3	5.46	918.0	4500.0	3633.0	5667.0	54.3	33.6	3.80	23.5
80	AOP	93.5	20.8	6.36	1415.0	4067.0	2800.0	5167.0	49.5	26.5	3.60	18.5
20	APP	90.3	14.5	3.60	774.0	4900.0	5267.0	10000.0	64.4	38.9	3.60	37.3
40	APP	91.7	17.7	5.04	707.0	4100.0	3600.0	6000.0	53.1	30.0	3.70	25.6
80	APP	94.7	20.2	6.44	1238.0	4333.0	3167.0	5667.0	50.8	26.1	3.40	19.9
Alkaline soil												
0	---	59.5	4.6	1.06	608.0	3900.0	6600.0	51333.0	157.9	44.9	9.80	73.0
20	AOP	70.8	8.5	1.96	652.0	3267.0	5467.0	56667.0	171.2	40.5	8.90	66.3
40	AOP	82.8	12.1	2.70	641.0	2900.0	4500.0	55333.0	141.3	38.9	7.60	53.0
80	AOP	87.5	17.8	4.70	619.0	1967.0	3267.0	44000.0	97.2	30.0	7.40	35.8
20	APP	76.7	9.1	2.04	508.0	2967.0	4967.0	49333.0	157.0	29.6	8.50	62.1
40	APP	80.5	12.2	2.66	674.0	2767.0	4467.0	52667.0	131.8	36.5	7.50	52.4
80	APP	85.0	14.2	3.54	652.0	2200.0	3567.0	48667.0	118.4	29.3	6.20	42.8
LSD .05												
Soil		1.98	0.58	0.10	77.6	194.0	260.0	1653.0	6.10	NS	0.14	3.21
Source		NS	NS	0.10	77.6	NS	NS	NS	NS	1.50	0.14	NS
Rate		2.8	0.82	0.14	109.7	275.0	368.0	2338.0	8.6	2.13	0.20	4.5
Soil x Source		NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
Soil x Rate		3.96	NS	0.20	155.1	NS	NS	3306.0	12.2	3.01	0.28	NS
Source x Rate		NS	1.16	NS	NS	NS	NS	NS	NS	NS	0.28	NS
Soil x Source x Rate		NS	NS	0.29	NS	NS	NS	NS	NS	NS	0.40	NS

Table II. Effects of Soil, Source, and Rate of Application of P on Total Uptake of Elements in Plant Material

Treatment P_2O_5	P Source	P	Mg	Ca	K	Mn	Fe	Cu	Zn
PPM		----------Mgms/2 Plants----------				------Micrograms/2 Plants------			
Slightly acid soil									
0	---	1.66	12.11	13.12	40.38	154	104	12	94
20	AOP	3.59	19.60	17.79	37.38	250	169	20	115
40	AOP	4.97	24.61	19.85	30.93	297	183	21	128
80	AOP	8.91	25.69	17.71	32.52	314	168	23	117
20	APP	2.76	17.53	18.89	35.70	232	139	13	134
40	APP	3.54	20.45	18.00	30.00	265	150	19	128
80	APP	7.25	25.32	18.51	33.23	297	153	20	117
Alkaline soil									
0	---	0.65	4.15	7.03	54.87	168	48	10	78
20	AOP	1.28	6.41	10.64	111.43	337	80	17	130
40	AOP	1.72	7.83	12.21	149.33	382	104	21	143
80	AOP	2.92	9.20	15.35	204.77	458	143	35	168
20	APP	1.03	6.03	10.10	100.30	320	81	17	126
40	APP	1.77	7.33	11.71	140.47	367	97	20	138
80	APP	2.25	7.68	12.47	170.37	425	103	22	149
LSD .05									
Soil		.285	.879	1.117	6.313	24.3	7.8	1.50	9.61
Source		.285	.879	NS	6.313	NS	7.8	1.50	NS
Rate		.404	1.244	1.579	8.929	34.4	11.0	2.12	13.6
Soil x Source		.404	NS	NS	8.929	NS	NS	NS	NS
Soil x Rate		.571	1.759	NS	12.628	48.6	15.6	3.00	19.2
Source x Rate		.571	NS	NS	NS	NS	NS	3.00	NS
Soil x Source x Rate		NS	NS	NS	NS	NS	22.0	4.24	NS

Table III. Chemical Analysis Data for Soils from Pots Used in Growth Chamber Experiment

Treatment P_2O_5	P Source	Available P	DTPA Extractable Zn	Mn	Cu	Fe	Exchangeable Ca	Mg	Activities Ca	Mg
PPM		lbs/acre	----------PPM----------				-meq/100 grams-		---Moles/Liter---	
Slightly acid soil										
0	---	26.7	2.26	13.3	0.56	15.9	5.2	0.77	0.0113	0.0012
20	AOP	39.8	2.25	15.6	0.61	16.4	4.8	0.70	0.0111	0.0012
40	AOP	43.2	2.26	15.5	0.59	16.3	4.7	0.68	0.0113	0.0012
80	AOP	60.0	2.21	16.6	0.54	17.4	5.0	0.69	0.0111	0.0012
20	APP	36.5	2.14	15.4	0.55	16.9	4.8	0.69	0.0118	0.0012
40	APP	45.0	2.12	16.0	0.57	16.5	4.8	0.69	0.0119	0.0012
80	APP	65.9	2.34	16.2	0.60	17.0	4.8	0.67	0.0111	0.0010
Alkaline soil										
0	---	5.5	1.80	7.3	0.66	4.2	75.3*	5.73	0.0086	0.0032
20	AOP	7.7	1.65	8.6	0.70	4.1	63.9*	5.58	0.0086	0.0032
40	AOP	21.2	1.72	7.8	0.66	4.0	64.3*	5.58	0.0086	0.0032
80	AOP	19.2	1.73	8.9	0.71	4.4	61.9*	5.59	0.0086	0.0030
20	APP	9.7	1.62	8.1	0.68	4.5	71.4*	5.59	0.0086	0.0032
40	APP	9.2	1.82	8.2	0.70	4.3	62.4*	5.50	0.0081	0.0031
80	APP	9.0	1.74	8.0	0.67	4.1	65.5*	5.84	0.0081	0.0031
LSD .05										
Soil		8.5	0.08	0.66	0.03	0.40	4.0	0.08	0.0003	0.0001
Source		NS	NS	NS	NS	NS	NS	NS	NS	NS
Rate		12.0	NS	0.93	NS	NS	NS	NS	NS	0.0001
Soil x Source		NS	NS	NS	NS	NS	NS	NS	0.0004	NS

*Values recorded for exchangeable calcium in the alkaline soil are too high due to extraction of Ca from the free $CaCO_3$.

Table IV. X-ray diffraction patterns of crystalline phosphates formed in saturated APP solutions.

Crystalline phosphates in alkaline soil extract

D Spacings Å	Relative intensities*	Compound(s) identified
7.248	VS	
5.330	S	
4.870	M	
3.750	VS	long chain polyphosphate (added) and $Ca(NH_4)_2P_2O_7 \cdot H_2O$
3.400	M	
3.076	S	
2.990	M	
2.919	W	
2.890	M	
2.710	M	
2.372	W	
2.010	W	

Table IV. continued
Crystalline phosphates in slightly acid soil extracts

D Spacings Å	Relative intensities*	Compounds(s) identified
7.190	VS	
5.480	M	
5.300	M	
4.990	M	$Ca(NH_4)_2P_2O_7 \cdot H_2O$
4.830	S	
4.187	W	
3.840	M	
3.740	M	
3.490	M	
3.200	M	
3.070	W	
2.990	M	
2.904	M	
2.53	M	

* VS--very strong
S--strong
M--medium
W--weak
VW--very weak

Table V. X-ray diffraction data of crystalline phosphates formed by adding APP and AOP in soils.

Ammonium polyphosphate added to the alkaline soil

After 16 weeks			After 28 weeks		
D Spacings	Relative intensities*	Compound(s) identified	D Spacings	Relative intensities*	Compound(s) identified
O A			O A		
7.19	VS		7.20	VS	
4.88	VS	$Ca(NH_4)_2P_2O_7 \cdot H_2O$			
4.25	S		4.89	S	
3.85	M		3.85	M	$Ca(NH_4)_2P_2O_7 \cdot H_2)$
3.41	M		3.39	M	
3.19	M		2.99	M	
2.99	S		2.92	M	
2.90	M		2.85	M	
			2.52	M	
			2.45	M	
			2.130	M	
			1.980	M	

Table V. continued
Ammonium polyphosphate added to the slightly acid soil

D Spacings	After 16 weeks Relative intensities*	Compound(s) identified	D Spacings	After 28 weeks Relative intensities*	Compound(s) identified
Å		$NH_4H_2PO_4$ and $(NH_4)_2H_2P_2O_7$	Å		
5.82	M		9.84	VW	
5.31	S		6.34	VW	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$
4.03	M		6.30	VW	
3.84	W		4.03	W	
3.745	S		3.75	S	
3.66	S		3.648	S	
3.23	M		3.601	S	
3.184	M		3.517	M	
3.140	S		3.469	M	
3.070	M		3.288	M	
3.017	M		3.241	M	
2.923	S		3.186	S	
2.65	W		3.14	VW	
2.278	S		2.85	W	
2.154	W		2.751	S	
2.004	W		2.35	S	
1.923	W		2.28	S	
1.796	W		2.236	S	
1.772	W		2.125	S	
1.748	W		1.872	M	

Table V. continued
Reaction of soils with diammonium phosphate
Alkaline soil

After 16 weeks			After 28 weeks		
D Spacings	Relative intensities*	Compound(s) identified	D Spacings	Relative intensities*	Compound(s) identified
Å			Å		
4.50	M		4.47	S	
4.467	M		4.037	S	
4.145	M		3.76	S	
4.060	M		3.67	S	
4.050	S	$Mg_2KH(PO_4)_2 \cdot 15H_2O$	3.477	S	$Ca_4H(PO_4)_3 \cdot 2.5H_2O$
3.297	W		3.437	S	
3.259	M		3.287	S	
3.200	S		3.210	S	
3.04	W		3.04	S	
2.96	W		2.955	S	
2.89	W		2.88	S	
2.58	W		2.84	S	
2.458	M		2.822	S	
2.238	M		2.45	S	
1.832	W		2.24	S	
1.826	W		2.13	S	
1.816	W		2.09	S	
1.800	W		2.08	S	
			1.83	S	

Table V. continued
Diammonium phosphate with slightly acid soil

After 16 weeks			After 28 weeks		
D Spacings	Relative intensities*	Compound(s) identified	D Spacings	Relative intensities*	Compound(s) identified
Å			Å		
5.90	W	$MgHPO_4 \cdot 3H_2O$	6.34	M	
5.31	S		4.48	M	
4.68	W		4.22	S	
4.30	M		4.037	M	$MgHPO_4 \cdot 7H_2O$
4.13	W		3.96	W	
4.05	S		3.87	W	
3.779	S		3.60	S	
3.757	M		3.47	W	
3.675	W		3.30	M	
3.620	W		3.186	S	
3.559	W		2.62	W	
3.195	M		2.59	M	
3.129	M		2.53	M	
3.074	M		2.51	S	
3.03	W		2.09	W	
2.986	M		2.03	W	
2.90	M		1.569	W	
2.41	M				
2.405	M				
2.24	M				
2.16	W				

* YS--very strong
S--strong
M--medium
W--weak
VW--very weak

REACTION PRODUCTS OF POLYPHOSPHATES AND ORTHOPHOSPHATES WITH SOILS

by

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Agronomy

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1973

A growth chamber experiment was conducted to compare ammonium polyphosphate and ammonium orthophosphate as P sources for hybrid corn (Dekalb XL 390) in an alkaline soil and a slightly acid soil.

Ammonium orthophosphate was a superior source of P when compared with ammonium polyphosphate in the slightly acid soil. The two sources of phosphorus gave similar results in the alkaline soil. Responses to phosphorus as measured by concentration in the plant material, and total uptake of P were higher in the slightly acid soil than in the alkaline soil.

Calcium activities were higher in the alkaline soil and so was the uptake of calcium. The activities of magnesium were higher in the alkaline soil, but the uptake of magnesium was higher in the slightly acid soil. Luxury consumption of potassium by the plants grown in the alkaline soil may have restricted the uptake of magnesium.

Applications of APP in the alkaline soil failed to increase the available soil phosphorus.

In an attempt to explain the poor responses to P applications in the alkaline soil, and also the lower soil P test, an experiment was designed wherein x-ray diffraction and electron microscopy techniques were used to identify the reaction products of APP and AOP in saturated fertilizer soil extracts and soils.

Although the same crystalline compound $Ca(NH_4)_2P_2O_7 \cdot H_2O$ was formed in the alkaline and slightly acid soil extracts, the mechanism of formation was quite different. In the alkaline soil extract added long chain polyphosphate precipitated immediately in the form of rod shaped crystals along with $Ca(NH_4)_2P_2O_7 \cdot H_2O$. In the slightly acid

soil extract $Ca(NH_4)_2P_2O_7 \cdot H_2O$ precipitated directly after 20 days.

Ammonium polyphosphate transformed into a less soluble crystalline compound ($Ca(NH_4)_2P_2O_7 \cdot H_2O$) in the alkaline soil which existed for eight months. In the slightly acid soil ammonium polyphosphate hydrolyzed into $NH_4H_2PO_4$ and $(NH_4)_2H_2P_2O_7$ (monoclinic). After 28 weeks $NH_4H_2PO_4$ transformed into $Ca_4H(PO_4)_3 \cdot 2.5H_2O$.

The compound ($Mg_2KH(PO_4)_2 \cdot 15H_2O$) was identified at 16 weeks and the compound ($Ca_4H(PO_4)_3 \cdot 2.5H_2O$) was identified at 28 weeks when AOP was added to the alkaline soil. Ammonium orthophosphate transformed into $MgHPO_4 \cdot 3H_2O$ and later to $MgHPO_4 \cdot 7H_2O$ when added to the slightly acid soil. The exchangeable magnesium content was very low in this soil, but the formation of magnesium compounds could have been due to the high activities of magnesium in solution. Minute amounts of several crystalline phosphates were seen in the electron micrographs which could not be detected by x-ray diffraction analysis.

The transformation of APP and AOP into the less soluble crystalline phosphates $Ca(NH_4)_2P_2O_7 \cdot H_2O$, $Mg_2KH(PO_4)_2 \cdot 15H_2O$, and $Ca_4H(PO_4)_3 \cdot 2.5H_2O$, explain the low uptake of phosphorus by corn plants in the growth chamber experiment in the alkaline soil. The transformation of APP into less soluble $Ca(NH_4)_2P_2O_7 \cdot H_2O$ in the alkaline soil explains the low available soil phosphorus.