from small granules. However, the increase in recovery by the second crop was less than the decrease in the first, and the total dry matter yield and nitrogen uptake were usually less than those from $NH_4H_2PO_4$. Different results would be expected under leaching conditions. Lunt, Kofranek, and Clark (*2*) also found slower release of nitrogen from surface-applied than from mixed application of magnesium ammonium phosphates. Granules larger than −6 +9 mesh might release nitrogen more slowly, but there is no evidence that such retardation would result in increased efficiency of utilization of the nitrogen. Granulation of a nitrification inhibitor (N-Serve) with $MgNH_4PO_4 \cdot H_2O$ significantly reduced the release of nitrogen. This indicates that N-Serve retarded dissolution of the granules, probably by retarding the rate of nitrification of the dissolving ammonium nitrogen.

The contrast between the magnesium phosphates and dicalcium phosphate as sources of phosphorus is of interest. After the harvest of the second crop, the residues of the −6 +9 mesh magnesium compounds were found petrographically to consist entirely of dimagnesium phosphate, $MgHPO_4 \cdot 3H_2O$.

As long as the granules contained $MgNH_4PO_4 \cdot 6H_2O$, they dissolved to give a solution $6.6 \times 10^{-3}M$ in phosphate. Moreno, Brown, and Osborn (*4*) showed that when dicalcium phosphate dissolves incongruently with precipitation of octacalcium phosphate, the solution is $2.2 \times 10^{-3}M$ in phosphate and has a pH of 6.4, which is close to that of the soil used in the phosphorus-source test. The smaller granule-size effect shown by the magnesium compounds in the first crop, when some of the original material remained in the granules, may reflect this difference in phosphate concentration.

The results of chemical and petrographic studies of the magnesium ammonium phosphates indicate that the granules would consist largely of $MgHPO_4 \cdot 3H_2O$ after the first crop. The pH of the solution within the granules would then fall to that of the surrounding soil, and the phosphate concentration in the solution released would be controlled by the solubility of the dimagnesium phosphate. At pH 6.3 and below, $Mg_3(PO_4)_2 \cdot 8H_2O$ would not persist. The uptake of phosphorus by the second crop from the magnesium and calcium compounds would therefore reflect the differences in the solubility of dicalcium and dimagnesium phosphates, the solubility products of which at 25° C. are 2.8×10^{-7} and 1.5×10^{-6}, respectively (*3*, *6*). Since the activity of magnesium in the soil solution is lower than that of calcium, the difference in phosphate ion concentration may favor dissolution of the magnesium compound even more than these values indicate.

The decrease from the first to the second crop of the granule-size effect shown by the magnesium compounds, in contrast to the behavior of dicalcium phosphate, probably reflects this change in phosphate solubility as ammonia was lost from the granules. A lower rate of hydrolysis of $MgNH_4PO_4 \cdot H_2O$ than that of the hexahydrate may also account for the greater granule-size effect of the monohydrate in the first crop. Little difference between the two hydrates was evident in the second crop.

The results provide a striking example of solublity and granule-size effects of phosphorus sources. With a soluble source, such as $NH_4H_2PO_4$, there is considerable movement of the phosphorus, and the amount of soil saturated with phosphorus does not vary greatly with different granule sizes of the source, the chemical character of the form in which the phosphorus is precipitated being the most important factor. With the less soluble materials, in which the phosphorus is virtually confined to the volume of the original granule, the phosphate concentration established within the granule becomes the dominant factor.

The changes in granule-size effects between the first and second crops may, however, be due only partly to changes in solubility with alterations within the granule. Translocation of phosphorus from the granules by the plant roots causes some redistribution of the phosphorus, and the second crop may recover some phosphorus from the decaying roots of the first. The amount of phosphorus taken up from decaying roots, however, probably is small in comparison with that taken up from the granule sites, where the concentration will be much higher than in the rest of the soil.

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PHOSPHORUS COMPONENTS

Crop Response to Water-Soluble and Water-Insoluble Phosphorus Components of Granular Fertilizers

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The water-insoluble phosphorus component makes up a considerable portion of the AOAC-available P_2O_5 content of many fertilizers, and it is important that its effectiveness for crop growth be determined, as well as that of the water-soluble fraction.

During the ammoniation of ordinary superphosphate, water solubility of the phosphorus decreases with increasing degree of ammoniation. At the same time, increasing amounts of apatite-type compounds of low solubility are being formed. Thus, the quality of the AOAC (Association of Official Agricultural Chemists) water-insoluble fraction of the phosphorus is changed along with the amount of the water-soluble fraction. Similar changes may occur during ammoniation of concentrated superphosphate and nitric phosphate. The

In a greenhouse pot test, variation in neutral citrate-soluble phosphorus content of five AOAC water-insoluble phosphates explained 93, 96, 80, and 3% of the variability in percentage recovery of applied phosphorus by corn from granular fertilizers formulated with 0, 25, 50, and 75% of the total phosphorus from a single water-soluble source. In other pot tests with corn, response to phosphorus was highest from an ammonium phosphate sulfate (91% of phosphorus water-soluble), less from two nitric phosphates (26 and 27% water-soluble, high alkaline citrate solubility), and least from an ammoniated ordinary superphosphate (28% of phosphorus water-soluble, low alkaline citrate solubility). AOAC-available phosphorus content was high in all four fertilizers. Similar results were obtained with wheat forage and corn grown in field tests in Mississippi.

extent of formation of water-insoluble compounds in nitric phosphate is controlled by the formulation. By use of a proper ammoniation technique, appreciable amounts of apatite can be prevented.

Bouldin, DeMent, and Sample (*1*) found in mixtures of monoammonium (water-soluble) and dicalcium (water-insoluble) phosphates that there was no apparent interaction between the two components as to their effect on response by oats. Effectiveness of water-soluble phosphorus depended upon amount per granule and effectiveness of water-insoluble phosphorus upon surface area of the granules. Terman, Bouldin, and Webb (*6*) found that effectiveness for corn of a series of −16+20 and −28+35 mesh water-insoluble phosphates (after leaching to remove the water-soluble phosphorus from the fertilizers, and granulation) per unit of surface area was closely related to citrate solubility. Finer granules tended to dissolve in the soil and their effectiveness for corn was poorly related to citrate solubility.

Attempts to evaluate simultaneously the water-soluble and water-insoluble phosphate components of granular fertilizers have been only partially successful. The purpose of the present experiments was to evaluate the effectiveness of water-soluble and water-insoluble phosphorus components of several fertilizers for crop growth.

Table I. Analyses of Fertilizers Compared in Pot Experiment 1

Fertilizer	Total N, %	Total P, %	Per Cent of Total P: Citrate-Soluble, Alkaline	Citrate-Soluble, Neutral	Water-soluble	AOAC-avail.	Surface Area of Granules, Cm./Sq. Gram P
WHOLE FERTILIZERS							
AOSP-302	6.0	6.1	31	34	60	94	...
AOSP-303	6.1	6.0	29	50	43	93	...
AOSP-199	7.0	6.0	23	69	27	96	...
AOSP-304	5.7	5.9	29	80	11	91	...
MAP		27.0	...	...	100	100	...
AOAC WATER-INSOLUBLE FRACTIONS							
DCP (reagent-grade)	...	22.7	...	96	<1	96	98
AOSP-302L	...	7.8	67	74	1	75	331
AOSP-303L	...	12.7	43	59	1	60	229
AOSP-304L	...	12.7	25	51	<1	52	234
AOSP-199L	...	14.1	20	43	1	43	233
NP-3	...	16.8	2	23	<1	23	158

AOSP—ammoniated ordinary superphosphates; MAP—monoammonium phosphate; DCP—anhydrous dicalcium phosphate; NP—nitric phosphate; L—water-leached fractions.

Experiments Conducted and Results

Greenhouse Pot Experiments. EXPERIMENT 1. This experiment was conducted to evaluate a series of AOAC water-insoluble phosphate fractions alone and granulated with increasing proportions of a single source of water-soluble phosphorus.

AOAC water-insoluble fractions of four ammoniated ordinary superphosphates (302, 303, 304, and 199, ammoniated to the extent of 2.0, 4.1, 6.5, and 7.2 pounds of NH_3 per unit of available P_2O_5) were obtained by leaching with 100 ml. of water per gram of fertilizer. These fractions, together with anhydrous dicalcium phosphate (DCP) and a nitric phosphate (NP-3), ammoniated so as to have a high content of apatite, were granulated with pressure into pellets, which were crushed and screened to obtain −9+14 mesh granules. Analyses of the fertilizers are shown in Table I. Methods for determining alkaline and neutral citrate solubilities were the same as those used by Hignett and Brabson (*2*), who found that low solubility in alkaline citrate is indicative of high apatite content. Geometric areas were calculated from the average diameter and number of granules of each phosphate. Water-soluble monoammonium phosphate (MAP) to supply 25, 50, and 75% of the total phosphorus was also granulated with the water-insoluble phosphates in −9+14 mesh granules. These fertilizers and MAP alone were mixed with the soil for crop 1 in amounts to supply 30, 60, and 120 mg. of phosphorus per pot (3 kg. of soil).

Two successive crops of a commercial double-cross hybrid corn were grown from October 10 to December 6, 1960, and from December 12 to February 15, 1961, on unlimed Hartsells fine sandy loam (pH 5.2) and on this soil limed to pH 7.5 with a 4 to 1 mixture of $CaCO_3$ and $MgCO_3$. A third crop was grown on the limed soil from March 7 to April 24. To prevent nutrients other than phosphorus from limiting yields, a total of 400, 400, and 500 mg. of nitrogen per pot was supplied as NH_4NO_3, $Ca(NO_3)_2$, or $Mg(NO_3)_2$ to crops 1, 2, and 3, respectively. K_2SO_4 was added for each crop to supply 200 mg. of potassium per pot. Yields of dry matter and contents of phosphorus were determined.

Table II. Yields of Dry Corn Forage Obtained for the Various Cropping Situations (Experiment 1)

Soil	Crop	P Applied, Mg./Pot: 0	30	60	120
		Yield, Grams/Pot			
Unlimed	1	3.7	10.0	16.1	23.7
	2	3.6	5.8	10.2	15.6
Limed	1	3.9	13.2	19.8	26.4
	2	5.6	12.0	23.1	30.3
	3	3.9	6.7	8.6	20.0

Marked response to applied phosphorus was obtained, as evidenced by the yields for the various cropping situations shown in Table II.

Plots (not shown) of yield of dry matter against yield of phosphorus indicated essentially the same efficiency of phosphorus per unit of dry matter for all crops and sources. Thus, availability coefficient indexes based on yields of dry

Table III. Percentage Recovery[a] of Applied Phosphorus from −9+14 Mesh Fertilizers Varying in Citrate and Water Solubility (Experiment 1)

P Source	AOAC-Avail. P, % of Total	Water-Soluble P in Granules, % of Total	Soil at pH 5.2, Crop 1, %	Soil at pH 7.5	
				Crop 1, %	Total, 3 crops, %
DCP	96	0	1.9	2.6	17.5
		25	3.9	7.6	21.8
		50	7.8	10.2	31.1
		75	12.7	13.5	37.3
AOSP-302L	74	0	1.9	3.6	19.1
		25	5.0	9.2	25.0
		50	8.6	13.0	33.8
		75	10.4	14.0	39.4
AOSP-303L	59	0	1.9	4.8	13.7
		25	5.1	8.1	22.6
		50	8.6	10.6	29.2
		75	12.0	13.6	37.9
AOSP-304L	51	0	1.4	2.3	7.2
		25	4.9	7.1	18.8
		50	8.0	11.5	29.2
		75	10.1	14.1	39.7
AOSP-199L	43	0	0.9	2.5	5.3
		25	4.8	7.8	16.8
		50	8.4	11.8	30.0
		75	11.4	14.8	39.8
NP-3	23	0	0.1	1.0	1.2
		25	3.5	7.8	13.6
		50	8.0	11.6	26.0
		75	10.1	15.0	38.4
MAP	100	100	14.1	16.0	45.0

[a] Slopes of linear regressions of yield of P on amount applied ×100.

matter or phosphorus would result in essentially the same conclusions.

Yields of phosphorus were essentially linear for 0, 30, and 60 mg. of applied phosphorus per pot, but usually became slightly curvilinear at the 120-mg. rate for fertilizers containing a large proportion of water-soluble phosphorus, especially for the first crop. Linear regressions of uptake on amount of applied phosphorus were considered to be the best estimate of relative availabilities of the various phosphates.

Percentage recoveries of applied phosphorus (Table III) were linearly related to content of water-soluble phosphorus in all the fertilizers for all cropping situations. Decrease in recoveries with decreasing content of AOAC-available phosphorus was marked with the granular water-insoluble fractions alone, but was somewhat less with 25% of the phosphorus in water-soluble form. Recoveries from fertilizers containing 50 and 75% water-soluble phosphorus, however, were not appreciably different among the water-insoluble phosphate fractions.

Percentage recoveries of applied phosphorus (Table III) increased linearly with increase in water-soluble phosphorus content with all of the six water-insoluble phosphate fractions in all cropping situations. Correlations of the average recoveries from the six phosphates with amount of water-soluble phosphorus present in the granules indicated that the latter explained 99, 96, and 99%, respectively, of the variation in phosphorus recovery by crop 1 at pH 5.2, crop 1 at pH 7.5, and the total of three crops at pH 7.5. This indicates the dominance of water-soluble phosphorus on response by corn in early growth response studies on phosphorus-deficient soils.

There was also a pronounced increase in recovery of phosphorus with increase in AOAC-available phosphorus content of the fractions granulated with none or low amounts of the water-soluble source. The same was also true with increase in alkaline citrate-soluble P, since the correlation between AOAC and alkaline citrate-soluble phosphorus was very high (r = 0.98). The effect of increasing contents of water-soluble phosphorus on masking differences in crop recovery of phosphorus in the water-insoluble fractions by the three successive crops of corn is shown clearly by the fitted regressions in Figure 1. Because of the increasing effects of water solubility on crop uptake of phosphorus, an interaction between the effects of water-soluble and citrate-soluble fractions of phosphate fertilizers is indicated for the early growth response experiments as conducted. This is not in complete agreement with the lack of interaction found by Bouldin, DeMent, and Sample (*1*) between the effects of MAP and DCP granulated together in several sizes of granules.

In the present experiment, however, phosphate fractions varying in citrate solubility were compared, and amount of water-soluble phosphorus was the more important property. Variation in neutral citrate-soluble phosphorus content of the five AOSP and NP phosphates (Figure 1) explained 93, 96, 80, and 3% of the variability in percentage recovery of applied phosphorus from the fertilizers with 0, 25, 50, and 75% of the total phosphorus in water-soluble form.

On the basis of amount of phosphorus applied, DCP fertilizer (96% of phosphorus citrate-soluble, no apatite) supplied about 15 times as much phosphorus to the three successive crops of corn as fertilizer NP-3 (23% of the phosphorus citrate-soluble, largely apatite). As indicated in Table I, the external surface area of the DCP granules was much less than that of the other fertilizers. If recovery of applied phosphorus is expressed on the basis of surface area per unit of applied phosphorus, the estimated effectiveness of DCP is much higher. On this basis, 23 times as much phosphorus was used from DCP as from the NP-3 fertilizer. Percentage recovery from the other water-insoluble phosphates was also calculated on the basis of surface area per unit of applied phosphorus. On this basis, variation in citrate solubility of the AOSP and NP fertilizers explained 86% of the difference in recoveries, which was no improvement over the calculations based just on amount applied.

Effects of differences in surface areas of the fertilizers containing water-soluble phosphorus were not evaluated, since it is well established that water-soluble phosphorus diffuses into a volume of soil around each granule, the size of which is dependent in a given soil on the amount of water-soluble phosphorus per fertilizer granule (*3, 4*).

Experiments 2 and 3. The purpose of these experiments and of the field experiments was to evaluate four NPK

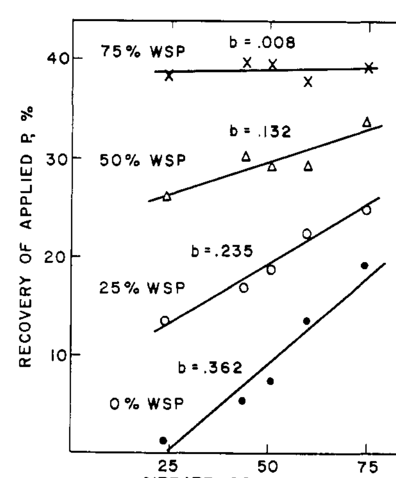

Figure 1. Total recovery of applied phosphorus by three corn crops from granular fertilizers, as affected by level of added water-soluble phosphorus and neutral citrate solubility of water-insoluble phosphate fractions

fertilizers (approximately 1:1:1 N–P_2O_5–K_2O ratio), particularly the AOAC water-insoluble fractions, as sources of phosphorus for crop growth.

Analyses of the −6+14 mesh fertilizers prepared by the TVA Division of Chemical Development are shown in Table IV. Analyses of water-leached fractions of 415, 416, and 417, prepared by leaching 1 gram of fertilizer on a filter paper with 100 ml. of water, are also shown, as well as of concentrated superphosphate (CSP) and anhydrous dicalcium phosphate (DCP). All of the original fertilizers are high in available phosphorus, as shown by solubility in neutral ammonium citrate (AOAC method). The ammoniated ordinary superphosphate (415) is lower in availability as determined by the Netherlands alkaline citrate method (*2*). This indicates a higher content of hydroxyapatite (about 50% of the water-insoluble phosphorus).

Hartsells fine sandy loam from Alabama, limed to pH 6.2 with a 4 to 1 mixture of $CaCO_3$ and $MgCO_3$, was used for both experiments. Yields of dry matter and contents of phosphorus in all crops were determined.

In experiment 2, the −6+14 mesh NPK fertilizers were mixed with the soil for crop 1 to supply 26, 52, and 104 mg. of total phosphorus and CSP to supply 60 and 120 mg. of phosphorus per pot (3 kg. of soil). Two successive crops of hybrid corn were grown from May 15 to July 6 and from July 20 to September 10, 1962. For crop 1, NH_4NO_3 was added at planting to equalize total nitrogen to 240 mg. per pot, and 600 mg. of nitrogen was added later in 200-mg. increments. For crop 2, a total of 500 mg. of nitrogen was added. K_2SO_4 was also added to supply 300 mg. of potassium for crop 1 and 200 mg. for crop 2.

Yields of dry matter and of phosphorus from each source shown in Table V were essentially linear with the 26-, 52-, and 104-mg. amounts of phosphorus applied as fertilizers 414 through 417 and the 60- and 120-mg. amounts of phosphorus applied as CSP. Regression coefficients relating uptake and amounts of applied phosphorus were calculated by the least-squares method in terms of percentage recovery. Results for crop 1 and both crops are shown in Table V.

The order of recoveries of phosphorus by the crops from the granular fertilizers were as follows:

Crop 1—APS > CSP > AOSP-415 > NP-416 = NP-417

Both crops—APS > CSP > NP-416 > NP-417 > AOSP-415.

In experiment 3, the water-insoluble fractions of the AOSP and NP fertilizers (Table IV) were included as −6+14 mesh granules mixed with the soil in amounts to supply 60 and 120 mg. of total phosphorus per pot (3 kg. of soil). Hybrid corn was grown from January 10 to March 8, followed by inoculated Korean lespedeza from March 12 to May 1, and a second crop of corn from May 9 to June 27, 1963. To prevent lack of nutrients other than phosphorus from limiting growth, nitrogen was added to a total of 500 mg. per pot for crop 1, 100 mg. for crop 2, and 400 mg. for crop 3. K_2SO_4 to supply 200 mg. of potassium per pot was added for each crop.

Yields of dry matter and uptake of phosphorus by crop 1 (corn) and the totals for the three crops are shown in Table VI. The first corn crop grew satisfactorily, but phosphorus deficiency of crop 3 was apparent throughout, especially with the water-insoluble phosphorous fractions. Yields of lespedeza were poor.

Since yields were approximately linear with the 60- and 120-mg. amounts of phosphorus, slopes, or linear regression coefficients, in terms of percentage recovery of applied phosphorus, were determined. These results are also shown in Table VI.

Yields by the first corn crop were highest for APS and CSP (highly water-soluble), intermediate for AOSP and NP (26 to 28% water-soluble), and lowest for the water-insoluble DCP and water-leached residues. Yields of the second corn crop (including lespedeza), as compared with the first-crop yields, were much lower for APS, CSP, and AOSP; about the same for the NP fertilizers; and much higher for the sources containing little or no water-soluble phosphorus. Of this last group, leached AOSP produced the lowest yield and 416-L the highest. The higher yield for this latter water-leached fraction than for DCP probably resulted from a higher surface area of the granules of 416-L per unit of applied phosphorus. The order of total response by the three crops to AOSP-415, NP-416, and NP-417 was the same as for the respective water-leached fractions.

Table IV. Analyses of the −6+14 Mesh Fertilizers Compared as Sources of Phosphorus in Additional Experiments

Fertilizer	Total N, %	Total P, %	Avail. P, % of Total: Alkaline citrate	Avail. P, % of Total: AOAC	Water-Sol. P, % of Total	Total K, %	Expt. in Which Compared
APS-414	12.8	5.6	99	99	91	12.6	2, 3, Iowa, Miss.
AOSP-415	10.5	5.0	64	96	28	8.9	2, 3, Iowa, Miss.
NP-416	9.6	5.3	94	97	27	7.2	2, 3, Iowa, Miss.
NP-417	11.9	5.6	95	98	26	8.8	2, 3, Iowa, Miss.
415L	...	14.4	24	48	2	...	3
416L	...	9.2	87	98	3	...	3
417L	...	13.6	86	93	2	...	3
DCP	...	22.7	...	96	2	...	3
CSP	...	21.7	...	93	88	...	2, 3, Iowa

APS—ammonium phosphate sulfate, commercial 13–13–13 product; AOSP—ammoniated ordinary superphosphate; NP—nitric phosphate; DCP—dicalcium phosphate; CSP—concentrated superphosphate; L—water-leached fractions.

Table V. Yield of Dry Matter, Yield of Phosphorus, and Percentage Recovery of Applied Phosphorus by Two Successive Corn Crops (Experiment 2)

P Source	P Applied for Crop 1, Mg./Pot	Yield of Dry Matter, Grams/Pot: Crop 1	Yield of Dry Matter, Grams/Pot: Total, 2 crops	Yield of P, Mg./Pot: Crop 1	Yield of P, Mg./Pot: Total 2 crops	Recovery of Applied P,[a] %: Crop 1	Recovery of Applied P,[a] %: Total 2 crops
APS-414	26	14.4	24.1	13.8	26.3		
	52	22.3	38.9	20.8	40.6	31.4	59.0
	104	36.7	62.5	37.4	71.3		
AOSP-415	26	10.0	20.1	10.7	24.2		
	52	14.4	27.0	13.3	31.9	20.8	43.0
	104	21.9	46.8	21.7	50.6		
NP-416	26	10.7	21.6	10.2	24.4		
	52	15.8	31.8	14.3	36.4	19.8	48.0
	104	28.0	54.4	25.2	60.0		
NP-417	26	9.1	19.7	9.7	24.0		
	52	13.9	30.1	16.8	39.0	19.0	44.1
	104	21.2	47.0	23.9	55.6		
CSP	60	28.5	49.8	25.2	51.0	27.4	56.7
	120	42.8	71.7	37.1	77.4		
No P	0	4.3	8.7	4.3	9.5	...	...

[a] Slopes of linear regressions of yield of phosphorus on amount applied.

Table VI. Yields of Dry Matter and Phosphorus and Percentage Recovery of Applied Phosphorus by Corn-Lespedeza-Corn Crops (Experiment 3)

P Source	P Applied for Crop 1, Mg./Pot	Yield of Dry Matter, Grams/Pot: Crop 1	Yield of Dry Matter, Grams/Pot: Total, 3 crops	Yield of P, Mg./Pot: Crop 1	Yield of P, Mg./Pot: Total, 3 crops	Recovery of Applied P,[a] %: Crop 1	Recovery of Applied P,[a] %: Total, 3 crops
ASP-414	60	26.9	44.4	15.0	37.4	15.0	34.4
	120	37.5	64.0	22.3	57.1		
AOSP-415	60	17.0	33.1	10.9	31.5	11.6	23.7
	120	23.0	42.2	18.2	44.2		
NP-416	60	15.8	35.5	11.4	37.8	9.7	34.6
	120	26.4	56.7	16.0	57.3		
NP-417	60	14.1	36.2	11.0	39.8	7.7	30.2
	120	22.7	51.4	13.5	52.1		
415 L	60	8.0	22.1	5.9	21.2	1.8	8.0
	120	9.4	26.2	6.5	25.4		
416 L	60	11.2	33.6	8.2	36.5	7.4	27.0
	120	15.7	41.8	13.2	48.2		
417 L	60	9.0	27.2	7.7	30.4	2.5	21.1
	120	11.4	37.6	7.3	41.1		
DCP	60	8.9	28.0	6.0	29.4	3.7	21.0
	120	11.3	34.9	8.7	41.0		
CSP	60	25.8	45.8	15.4	42.7	17.4	38.7
	120	37.4	64.2	25.2	62.2		
No P	0	6.8	17.5	4.3	15.8	...	...

[a] Slopes of linear regressions of yield of P on amount applied.

Table VII. Yields of Corn Grain and Wheat Forage in Field Experiments

P Source	P_2O_5 Applied, Pounds per Acre	Yield of Corn, Bu./Acre: Iowa 1962	Yield of Corn, Bu./Acre: Mississippi 1962	Yield of Corn, Bu./Acre: Mississippi 1963	Yield of Wheat Forage in Miss., Lb./Acre: Brooksville 1963	Yield of Wheat Forage in Miss., Lb./Acre: Holly Springs 1963
APS-414	15	73	46	61	1280	2360
	30	75	51	71	2190	3560
	45	75	55	80	2530	4450
	60	...	60	88	2680	4710
AOSP-415	15	70	40	52	1100	1750
	30	71	46	65	1500	2300
	45	72	52	71	1980	2900
	60	...	50	84	2340	3560
NP-416	15	71	40	58	1200	2090
	30	71	46	68	1600	3500
	45	72	52	84	2710	4140
	60	...	57	91	3090	4300
NP-417	15	72	45	58	1180	1760
	30	73	46	72	1750	3230
	45	72	52	84	2500	3590
	60	...	56	91	3180	4250
No P	0	67	35	34	560	620
L.S.D., 5% level		3	8	8	310	330

Table VIII. Relative Average Yield Increases over No Applied Phosphorus in Mississippi Field Tests

P Source	Water-Sol. P, % of Total	Corn—Brooksville: 1962	Corn—Brooksville: 1963	Corn—Brooksville: Av.	Wheat—1964: Brooksville	Wheat—1964: Holly Springs	Wheat—1964: Av.
APS-414	91	100	100	100	100	100	100
AOSP-415	28	67	83	75	67	60	64
NP-416	27	78	100	89	89	92	91
NP-417	26	83	102	93	87	79	83

Field Experiments. These experiments were conducted to evaluate under field conditions the four NPK fertilizers compared in pot experiments 2 and 3. Analyses of the fertilizers are given in Table IV. All were applied as −6+14 mesh granules. Randomized block designs were used in all experiments.

IOWA. Corn was grown in 1962 on Cresco slit loam (pH 6.0) in northeastern Iowa. Each fertilizer was applied at planting in a band 2 inches to the side and 2 inches below the seed level at rates of 15, 30, and 45 pounds of AOAC-available P_2O_5 (6.6, 13.1, and 19.7 pounds of phosphorus) per acre, together with NH_4NO_3 and KCl to supply a total of 45 pounds of nitrogen and 45 of potassium per acre. Additional N was sidedressed prior to the second cultivation. Each treatment was replicated 8 times.

Response of corn in Iowa in 1962 to applied phosphorus (Table VII) averaged only 5 bushels per acre, and there was little response to rates higher than 15 pounds of P_2O_5 per acre. Slightly higher yields resulted with APS than with the other fertilizers.

MISSISSIPPI. Corn was grown in 1962 on Brooksville clay (pH 6.2) at Brooksville. Each fertilizer was applied in row-side bands at rates of 15, 30, 45, and 60 pounds of AOAC-available P_2O_5 (6.6, 13.1, 19.7, and 26.2 pounds of phosphorus) per acre, together with NH_4NO_3 and KCl to supply a total of 120 pounds of nitrogen and 50 of potassium per acre. Micronutrients were also supplied. These treatments were applied to the same plots for corn in 1963. Each treatment was replicated four times.

The same treatments were applied in the drill row for wheat forage in fall, 1962, on the Brooksville clay and on Grenada silt loam (pH 6.2) at Holly Springs, Miss. In these experiments NH_4NO_3 and KCl were applied to give total acre applications of 60 pounds of nitrogen and 60 of potassium. An additional 60 pounds of nitrogen was topdressed in early spring. No yields were obtained in spring, 1963, because of winter killing. Consequently, the treatments were applied on the same plots in fall, 1963, and yields of wheat forage were obtained in spring, 1964. Each treatment was replicated five times.

Since yields of corn in Mississippi in both 1962 and 1963 (Table VII) were largely linear with amount of phosphorus applied, average relative yield increases over no applied phosphorus were used to evaluate the fertilizers. These values are shown in Table VIII. In both years, relative yield increases were in the order: APS-414 > NP-416 = NP-147 ≥ AOSP-415.

Yields of wheat forage were also essentially linear with 15, 30, and 45 pounds of applied P_2O_5, but became distinctly curvilinear with 60 pounds, especially from APS. Consequently, yield increases over no applied phosphorus were calculated from the lower three rates only.

Average relative response of wheat forage to the fertilizers in the two tests (Table VIII) decreased as follows: APS > NP-416 > NP-417 > AOSP-415. This is the same order of effectiveness as found by multiple cropping by corn in both greenhouse pot experiments.

Discussion

Results from pot experiment 1 showed conclusively that water solubility of granular phosphate fertilizers is the dominant factor in early growth response by corn. Thus, there is little possibility of measuring differences in crop response to citrate-soluble components of large granules in similar experiments, if the content of water-soluble phosphorus is high. Since relative crop response to water-soluble, and water-insoluble phosphorus components depends upon granule size, different results would be expected with fine granular or nongranular fertilizers, as found by Bouldin, DeMent, and Sample (*1*).

Results from pot experiments 2 and 3 also showed greater response to the granular, highly water-soluble ammonium phosphate sulfate fertilizer. However, with the three fertilizers containing 26 to 28% of their phosphorus in water-soluble forms, crop response to water-insoluble phosphorus in two nitric phosphates (low apatite content) was higher than that in an ammoniated ordinary superphosphate (high apatite content). Response to these four phosphates was closely related to contents of water-soluble plus alkaline citrate phosphorus, but not to water-soluble plus neutral citrate phosphorus (AOAC-available phosphorus). Similar results were found with wheat forage and corn in field experiments.

In contrast, a high correlation was found between available phosphorus in water-insoluble phosphates used in experiment 1, as determined by the neutral and alkaline citrate methods. The high availability of the NPK fertilizers used in experiments 2 and 3 by the neutral citrate method and the poor correlation for available phosphorus by the two methods result largely from the small amount of water-insoluble phosphorus in the gram samples analyzed. The amount of water-insoluble phosphorus per sample varied from about 75 to 225 mg. for the water-insoluble phosphate fractions (Table I), but only from 5 to 41 mg. in the NPK fertilizer samples (Table IV). Terman, Hoffman, and Wright (*7*) have discussed more fully the effect of fertilizer sample size on the available phosphorus content.

Results from this study emphasize the rather close agreement between response to phosphate fertilizers previously found in greenhouse pot experiments and early growth response under field conditions (*5*). Water solubility of the phosphorus is very important under both situations. Results from both field and greenhouse tests also show that content of water-soluble plus alkaline citrate-soluble phosphorus in NPK fertilizers is more closely related to crop response than is water-soluble plus neutral (AOAC) citrate-soluble phosphorus. This agrees with the results obtained by Wright, Lancaster, and Anthony (*8*).

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DEFOLIANT RESIDUES

The Microcoulometric Determination of *S,S,S*-Tributyl Phosphorotrithioate in Cottonseed

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In the mechanical harvesting of cotton, it is general practice to apply desiccants or defoliants about 10 days prior to harvest to facilitate harvesting and to reduce the quantity of cotton trash which would otherwise be mixed with the cotton. Two such products which are widely used are DEF (Chemagro Corp.) and Folex, (Virginia Carolina Chemical Corp.).

The active pesticide chemical ingredient in DEF is *S,S,S*-tributyl phosphorotrithioate and in the Folex (Merphos) is *S,S,S*-tributyl phosphorotrithioite.

These products are applied at the rate of 1.5 to 2.0 pounds of active ingredient per acre in the form of a dust or emulsifiable concentrate diluted with water. Detailed directions for use are on the container labels.

Loeffler and MacDougall (*3*) developed a photofluorometric method for the determination of residues of *S,S,S*-tributyl phosphorotrithioate in cottonseed. This method involves hydrolysis to form butyl mercaptan and distillation of the butyl mercaptan into a solution of palladium chelate of 8 - hydroxy - 5 - quinolinesulfonic acid. The mercaptan combines with a portion of the palladium, liberating an equivalent amount of the complexing agent. Addition of magnesium chloride results in the formation of highly fluorescent magnesium chelate whereas the palladium chelate is not fluorescent.

Boyd and Barber (*1*) described a method for the determination of residues of *S,S,S*-tributyl phosphorotrithioite in cottonseed which is based upon hydrolysis and colorimetric determination of the butyl mercaptan.

The purpose of the present investigation was to develop a gas chromato-