Response of Corn to Phosphorus in Underacidulated Phosphate Rock and Rock-Superphosphate Fertilizers

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No measurable acidulation of fine phosphate rock was found in rock-superphosphate slurries in a laboratory study. Three pot experiments were also carried out to determine response of corn to P in Florida phosphate rock acidulated to varying degrees with H_3PO_4 or mixed with superphosphate. P-deficient Hartsells fine sandy loam limed to pH 6.2, Mountview silt loam limed to pH 6.5, and Davidson silty clay loam (pH 5.6) were the test soils. Effectiveness of P in the fertilizers was closely related to water-soluble P contents up to 50% or more of the total P, depending on the soil, granule size, and amount applied. Response to the $-6+9$ mesh fertilizers tended to be equal to or slightly greater than response to the same amounts of water-soluble P as concentrated superphosphate granulated with soil. Economies resulting from the use of underacidulated phosphate rock might thus be approximated by reducing the application rate of soluble phosphate fertilizers.

Acidulated phosphate rock as superphosphates, nitric phosphates, or ammonium phosphates has usually been a much more effective source of P for crop production than finely ground but chemically untreated phosphate rock. Since acidulation adds to the cost, reducing the amount of acids used for a given amount of product is economically attractive. Agronomic effectiveness of partially acidulated, as compared with completely acidulated, products per unit of applied P is, of course, an important consideration.

Dincu (*1*), McLean and Wheeler (*2*), McLean, Wheeler, and Watson (*3*), and others have concluded that partially and completely acidulated phosphate rocks may be equally effective for crop growth. Terman, Moreno, and Osborn (*4*) found that ordinary superphosphate mixed with phosphate rock to supply 25 to 50% of the total P and granulated to $-9+14$ mesh was 36 to 69% as effective for two successive crops of corn forage as 100% of the P from superphosphate. These mixtures were compared to simulate underacidulated rock.

This paper reports results from a laboratory study and from three pot experiments with corn fertilized with multiple rates of applied phosphate rock varying in degree of acidulation. These fertilizers were compared with equal amounts of water-soluble P supplied as concentrated superphosphate.

Materials and Methods

Laboratory Study. Five-gram samples of the PR-OSP and PR-CSP mixtures shown in Table I were placed in 25-ml. flasks, 2 ml. of water were added to each, and the flasks were stoppered and left to react for 2 weeks in the laboratory. The samples were then dried at 70° C., crushed, and P contents determined by AOAC methods.

Pot Experiments. Three greenhouse pot experiments were carried out with two successive crops of corn (Funk's G-76 hybrid, five plants per pot). The crops were grown in No. 10 cans lined with polyethylene bags and containing 3 kg. of soil. Phosphate from various sources at rates of 60, 120, and 240 mg. of P per pot (60 omitted for experiment 3) was applied for the first crop only. These amounts are equivalent to 40, 80, and 160 pounds of P per acre. Adequate, uniform amounts of N as NH_4NO_3 or as $Ca(NO_3)_2$ and $Mg(NO_3)_2$, K as K_2SO_4, and a micronutrient mix were applied for each crop. Phosphate treatments were replicated three times in each experiment. Yields of dry forage and uptake of P were determined for each replicate of each treatment for all crops. Growth periods were as follows:

Experiment	First Crop	Second Crop
1	Nov. 27–Jan. 22	Jan. 31–Mar. 28, 1963
2	April 30–June 25	June 30–Aug. 17, 1965
3	Nov. 3–Dec. 29	Jan. 4–March 1, 1966

For experiment 1 variation in degree of acidulation of Florida phosphate rock was simulated by dry mixing various proportions of finely ground rock (65% -200 mesh) and ordinary superphosphate (OSP) or concentrated superphosphate (CSP). These fertilizers (Table I) were pressure-granulated, crushed, and screened to $-6+9$ mesh granules, and placed in a circular band 4 cm. deep in the soil. Hartsells fine sandy loam limed to pH 6.2 with a 4 to 1 $CaCO_3$–$MgCO_3$ mixture was the test soil.

For experiments 2 and 3, the same Florida phosphate was acidulated to various degrees with H_3PO_4 (Table I). These were pressure granulated and $-6+9$ and -35 mesh granules screened out for use. In addition, CSP was granulated with the test soils in amounts to

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Table I. Phosphorus Content of the Experimental Phosphate Fertilizers by AOAC Methods

	Dry Mixtures of Products			After 2 Weeks' Moist Reaction	
		Total P, %		Total P, %	
P Source	Total P, %	Available	Water-soluble	Available	Water-soluble
		Experiment 1			
Phosphate rock (PR)[a]	13.8	12	<1	12	<1
75% PR; 25% OSP	12.6	33	22	32	15
50% PR; 50% OSP	11.5	56	43	53	34
25% PR; 75% OSP	10.5	77	65	79	54
Ordinary super (OSP)	9.7	97	82	98	77
75% PR; 25% CSP	15.6	38	28	35	15
50% PR; 50% CSP	17.6	61	52	56	29
25% PR; 75% CSP	19.4	79	71	79	52
Concentrated super (CSP)	22.2	99	92	99	91
		Experiments 2 and 3[b]			
0% (PR)	13.8	12	0	...	...
10% acidulation	15.8	37	22	...	...
25% acidulation	17.6	59	45	...	...
50% acidulation	20.2	83	71	...	...
75% acidulation	21.6	94	86	...	...
100% (CSP)	22.9	99	93	...	...

[a] Florida rock (65% −200 mesh) was used for acidulation and cropping studies.

[b] Fertilizers prepared by TVA Applied Research Branch, Division of Chemical Development. Water solubility of P indicates higher than estimated acidulation by H_3PO_4 for 10–75% levels.

supply the same amount of water-soluble P as was present in the variously acidulated phosphate rock fertilizers and equivalent numbers of granules per pot. The test soils were Mountview silt loam limed to pH 6.5 with a 2 to 1 $CaCO_3$-$MgCO_3$ mixture for experiment 2 and unlimed Davidson silty clay loam (pH 5.6 from Virginia) for experiment 3.

Results

Phosphate Rock Superphosphate Mixtures. LABORATORY STUDY. As shown in Table I, water-soluble P contents of the PR–OSP and PR–CSP mixtures were much lower after moist reaction for 2 weeks. This indicates that monocalcium phosphate in the superphosphates was hydrolyzed to dicalcium phosphate according to the following reaction:

$$Ca(H_2PO_4)_2 \cdot H_2O + H_2O \rightarrow CaHPO_4 \cdot 2H_2O + H_3PO_4 \tag{1}$$

Theoretically, the H_3PO_4 produced in this reaction should acidulate some PR in the mixtures. However, only in the 25% PR–75% OSP mixture was there any indication that such acidulation may have occurred. AOAC-available P (water-soluble plus citrate-soluble) in the the 75-25 and 50-50 PR-superphosphate mixtures actually decreased somewhat as a result of the moist reaction period. This indicates a net reversion of soluble P, rather than a solubilization of the rock.

The decrease in solubility may have occurred largely during the drying of the samples. However, somewhat similar conditions might prevail during granulation and drying of PR-superphosphate fertilizers in a commercial process.

POT EXPERIMENT 1. Total yields of dry matter and uptake of P by two successive crops of corn forage grown on the Hartsells soil are shown in Table II. Response by both crops increased markedly with increasing amount of P applied from all sources except PR alone. Response was similar to both granule sizes of all of the OSP fertilizers and of the 25% PR–75% CSP and 100% CSP fertilizers. Response was poorer to the −35 mesh than to the −6+9 mesh 75-25 or 50-50 PR–CSP fertilizers.

Because uptake of P was essentially linear with amount of P applied from the OSP and CSP alone and in mixtures with PR, slopes were calculated by the least squares method and expressed as apparent percentage recoveries of applied P. These values plotted (Figure 1) against content of water-soluble P in the fertilizers show an approximately linear relationship for the −35 mesh fertilizers. The relationship is distinctly curvilinear for the granular fertilizers, however. This is particularly true for the CSP fertilizers, from which nearly as much P was recovered by corn from the 50-50 and 25-75 PR–CSP mixture as from 100% CSP.

In 1963 field experiments comparing OSP, 50% PR–50% OSP and PR for corn in Mississippi and for oats in Iowa, PR was 7 to 13% as effective and the 50-50 mixture 28 to 52% as effective for increasing yields as 100% OSP.

Partially Acidulated Phosphate Rock. POT EXPERIMENT 2. Total yields of dry matter by two successive crops of corn forage grown on the Mountview soil (Figure 2) showed marked increases in yield with increase in amount of P applied. Yields also increased markedly with increase in content of water-soluble P resulting from higher levels of acidulation of PR by H_3PO_4. Slightly higher yields resulted with −6+9 mesh than with −35 mesh fertilizers containing 45 to 93% water-soluble P. Yields were similar with the

Table II. Yield of Dry Matter and Uptake of P by Two Successive Crops of Corn Forage—Experiment 1

P Source	P Applied, Mg. per Pot	Yield of Dry Forage		Uptake of P		Recovery of Applied P, %[a]	
		−6+9 mesh, g./pot	−35 mesh, g./pot	−6+9 mesh, mg./pot	−35 mesh, mg./pot	−6+9 mesh	−35 mesh
PR	60	. . .	13.7	. . .	10.5	. . .	0.3
	120	. . .	15.1	. . .	11.4		
	240	. . .	14.6	. . .	11.0		
75% PR; 25% OSP	60	20.7	20.4	15.9	16.9	8.9	7.8
	120	30.3	26.2	23.1	20.0		
	240	42.3	39.9	31.4	29.6		
50% PR; 50% OSP	60	27.5	28.3	22.0	22.7	14.3	14.1
	120	40.8	40.9	31.0	31.5		
	240	57.8	56.3	45.1	44.8		
25% PR; 75% OSP	60	32.7	36.3	25.7	27.6	19.3	18.9
	120	49.2	47.9	38.0	36.0		
	240	68.6	68.0	57.4	57.2		
100% OSP	60	38.8	40.9	29.2	26.7	20.3	21.7
	120	55.6	56.7	42.4	45.0		
	240	70.8	72.6	60.2	62.4		
75% PR; 25% CSP	60	24.6	19.5	18.5	16.2	10.7	8.5
	120	30.7	28.2	24.0	21.7		
	240	47.0	40.3	36.1	30.6		
50% PR; 50% CSP	60	32.7	26.5	24.8	20.5	19.9	11.9
	120	49.5	36.4	37.1	27.8		
	240	68.5	52.3	58.4	39.3		
25% PR; 75% CSP	60	36.8	35.3	27.0	26.3	20.2	17.2
	120	53.1	52.6	40.0	38.4		
	240	66.5	67.1	59.5	52.6		
100% CSP	60	42.5	43.1	30.9	32.3	21.6	20.3
	120	56.5	61.0	40.7	45.8		
	240	72.4	75.4	64.1	60.8		
No P	0	12.9		10.1			

[a] Slopes calculated by the least squares method, relating uptake of P to amount applied.

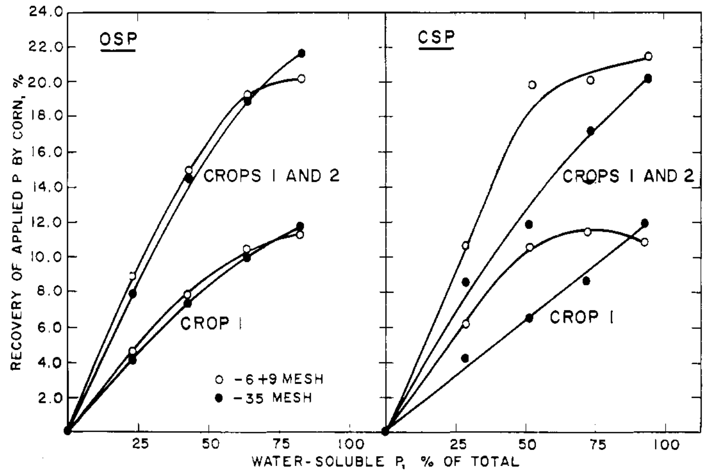

Figure 1. Recovery of added P (total P basis) by corn plotted against percentage of water-soluble P in granulated mixtures of phosphate rock and ordinary (OSP) and concentrated (CSP) superphosphate (experiment 1)

−6+9 mesh phosphates varying in degree of acidulation and with corresponding amounts of water-soluble P granulated into −6+9 mesh granules with Mountview soil. This indicates that this early growth response by corn was due largely to the water-soluble P in the fertilizers.

Uptake of P from phosphates having 0 to 45% water-soluble P was linear with the 60-, 120-, and 240-mg. rates of applied P, while uptake from fertilizers having 71 to 93% water-soluble P became curvilinear at the highest rate. Consequently, slopes relating uptake and the 0-, 60-, and 120-mg. rates were calcu-

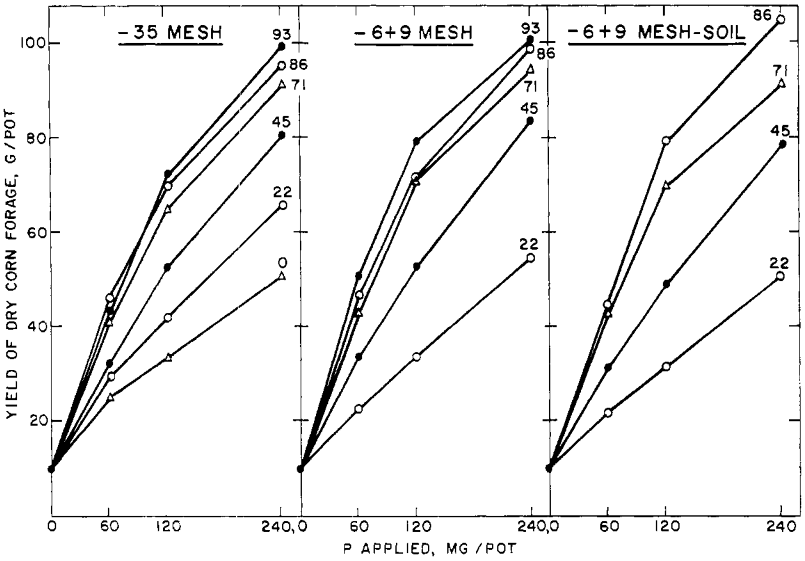

Figure 2. Total forage yields by two successive corn crops, as affected by rate of application of phosphates varying in content of water-soluble P resulting from degree of acidulation of phosphate rock by H_3PO_4 (experiment 2)

lated and expressed as apparent percentage recovery of applied P. These recoveries for crop 1 and both crops are plotted in Figure 3 against percentage of water-soluble P in the fertilizers. These plots show poorer recovery from granular than from fine fertilizers low in water-soluble P, but similar recoveries from the −35 and −6+9 mesh fertilizers and −6+9 mesh CSP-soil granules high in water-soluble P.

As in experiment 1, recovery of applied P by corn from the −35 mesh fertilizers increased linearly with increase in content of water-soluble P. Recovery from the −6+9 mesh fertilizers, however, again became curvilinear at the higher water-soluble P contents. Because of this, the recovery from the 71% water-soluble P level by crop 1 was nearly as high as from the 86 and 93% levels. With continued cropping, however, total recovery of P by both crops at these two highest levels was appreciably higher than at 71% water-soluble P.

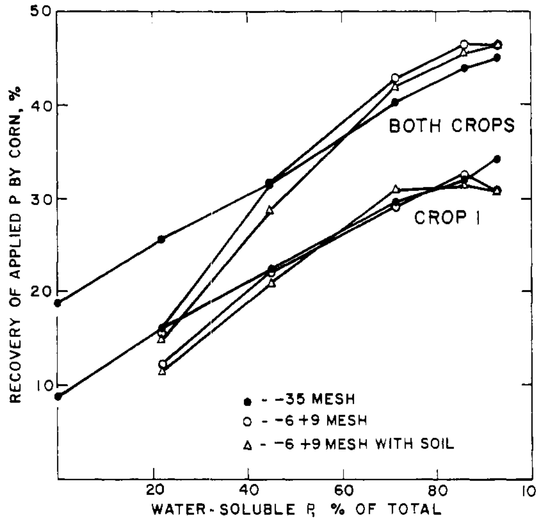

Figure 3. Recovery of applied P (by difference at 120 mg. of applied P) from granular and fine phosphates, as related to content of water-soluble P (experiment 2)

Pot Experiment 3. Total yields of dry matter by two successive crops of corn forage grown on the Davidson soil are shown in Figure 4. As in previous experiments, yields increased markedly with amount of P applied and content of water-soluble P. However, there was little increase in response to the −6+9 mesh fertilizers above 71% water-soluble P. Yields of crop 1 were markedly higher with the −6+9 mesh than with the −35 mesh fertilizers, while the reverse was true of crop 2. This latter result, as yet unexplained, has been noted in a number of previous experiments. The effects of −6+9 mesh fertilizers tended to be greater than the same amounts of water-soluble P granulated with soil.

Since uptake of P by corn was not linear with the 0-, 120-, and 240-mg. rates of P from fertilizers high in water solubility, apparent recovery of applied P was calculated by difference at the 120-mg. P level. These recoveries (Table III) increased with increase in content of water-soluble P, but did not level off, as in the previous experiments.

Discussion

All three pot experiments were conducted on P-deficient soils and showed marked response by corn to multiple rates of applied P. This allowed comparisons among sources of P on the steeply ascending portion of the response curve, an important consideration in meaningful comparisons among different sources of a given nutrient.

Under these conditions of response by early growth of corn forage, recovery of the applied P by all crops from the nongranular (−35 mesh) fertilizers increased linearly with increase in content of water-soluble P, which increased with higher acidulation levels. The same was true from granular (−6+9 mesh) by corn grown on Davidson silty clay loam (experiment 3), a soil having a rather high P-fixing capacity. Recovery of P from the granular fertilizers by corn grown on Hartsells fine sandy loam (experiment 1, and on Mountview silt loam, however, leveled off at water-soluble P contents of about 50 to 70%. These latter soils have

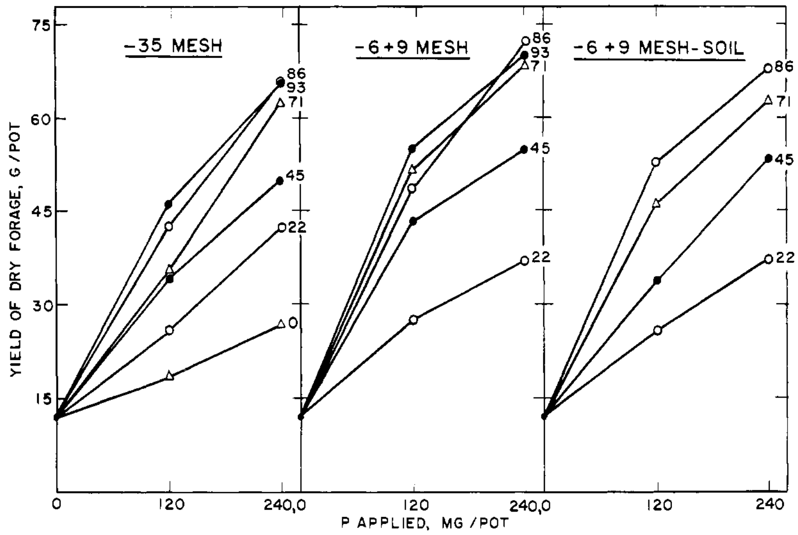

Figure 4. Total forage yields by two successive corn crops, as affected by rate of application of phosphates varying in water solubility (experiment 3)

rather low P-fixing capacities, and presumably a sufficiently high concentration of water-soluble P for good growth was maintained at these granule sites. Similar results were obtained with granular fertilizers at a given level of water solubility provided either by the degree of acidulation or by granulating the same amount of water-soluble P as CSP with soil. This result definitely indicates that content of water-soluble P in the granules is the important consideration in early growth of corn. Costs would then determine the most economical P source from which to supply the desired level of water solubility. Because of the higher analyses of CSP and ammonium phosphate fertilizers, probably this water-soluble P can be supplied more economically from these fertilizers than from partially acidulated PR.

Another important point for consideration is that farmers increasingly demand that solid fertilizers be well granulated. Previously, Terman, Moreno, and Osborn (*4*) showed that granulating finely ground PR markedly reduced its effectiveness for crop growth. Thus the unreacted rock in partially acidulated, granular products tends to be low in effectiveness.

The conclusions from this study are in considerable contrast to those of McLean and Wheeler (*2*) and of McLean, Wheeler, and Watson (*3*). A possible reason is that their conclusions in the first paper were based largely on nongranular fertilizers applied at a single rate (90 pounds of P per acre). Although there was a marked response to applied P, this rate may have supplied adequate P from a rather wide range of acidulation levels of PR with H_3PO_4. Also, all of the fine fertilizers may have reacted more completely with the more acidic, higher P-fixing soils used in their experiments.

The same limitations apply to results reported in the second paper. The application rate of variously acidulated PR fertilizers was 66 pounds of P per acre. Multiple rate application of a 20% acidulated fertilizer showed that yields and P uptake leveled off at the 66-pound rate on soils showing only a moderate response to applied P. On these soils, the 10 and 100% acidulation levels produced similar yields. On a second group of soils more responsive to P, however, yields increased to the highest rate of applied P (132 pounds per acre). On these soils, a 50% acidulation level of PR was necessary to produce the highest yield. This is rather strong evidence that under conditions of greater response to applied P, yields tend to increase with acidulation level or content of water-soluble P, as was discovered in the present study.

Table III. Apparent Recovery of Applied Phosphorus by Two Successive Crops of Corn Forage—Experiment 3

Degree of Acidulation and WSP, % of Total	Recovery of Applied P, %[a]					
	−35 Mesh		−6+9 Mesh		−6+9 Mesh-Soil[b]	
	Crop 1	Both crops	Crop 1	Both crops	Crop 1	Both crops
100% (CSP-93)	18	35	24	36	...	...
75% (86)	17	30	22	31	22	34
50% (71)	12	25	22	31	22	31
25% (45)	10	27	18	29	13	18
10% (22)	8	17	9	15	8	12
0% (PR)	3	8	...	...	...	...

[a] Calculated from difference between uptake at 120 mg. and no applied P.

[b] Equivalent amount of WSP (water-soluble P) from CSP granulated with soil.

Literature Cited

(1) Dincu, I., *Analele Inst. Cercetari Agron. Acad. Rep. Populare Romine, Ser. A.* **27**, 65 (1959).
(2) McLean, E. O., Wheeler, R. W., *Soil Sci. Soc. Am. Proc.* **28**, 545 (1964).
(3) McLean, E. O., Wheeler, R. W., Watson, J. D., *Ibid.*, **29**, 625 (1965).
(4) Terman, G. L., Moreno, E. C., Osborn, G., *Ibid.*, **28**, 104 (1964).

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