PHOSPHORUS AVAILABILITY

Crop Response to Phosphorus in Water-Insoluble Phosphates Varying in Citrate Solubility and Granule Size

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A series of water-insoluble phosphates varying in citrate solubility from 23 to 99% of the total phosphorus was prepared by leaching various fertilizers with water. Dicalcium phosphates and precipitated apatites were the principal phosphate compounds identified in these residues. The residues were granulated and mixed with Hartsells fine sandy loam. Corn was grown as the test crop. Effectiveness of the phosphorus in various sized granules of water-insoluble phosphates for two successive crops of corn averaged as follows: $-60 + 100 > 100 + 325 > -28 + 35 > -16 + 20$ mesh. Effectiveness of the $-16 + 20$- and $-28 + 35$-mesh sizes per unit of geometric surface area was rather closely related to citrate solubility of phosphorus in most of the phosphates. Dicalcium phosphate, however, was relatively more effective than the water-insoluble fractions of nitric phosphates and ammoniated superphosphate containing varying amounts of precipitated apatite. Effectiveness of the more finely divided phosphates increased in general with increase in citrate solubility, but the relationship was not specific. Plants undoubtedly obtained much of their phosphorus from the products of reaction of soil with the fine particles which had dissolved.

Phosphorus in commercial fertilizers sold in the United States is usually characterized chemically in terms of methods specified by the Association of Official Agricultural Chemists (A. O. A. C.). According to these methods, the phosphorus compounds in a fertilizer are classified into three categories: water-soluble; citrate-soluble—i.e., insoluble in water, but soluble in neutral normal ammonium citrate; and citrate-insoluble. The sum of the first two categories is usually expressed as the available content of phosphorus pentoxide, P_2O_5.

The utility of these separations depends on the relative contribution of each phosphorus fraction in a fertilizer to crop response. The correlation between plant response and water solubility of the phosphorus in various fertilizers is usually somewhat less than would be expected on the basis of experimental error, and response is not always directly proportional to water solubility. These facts indicate that plant response to phosphorus depends upon properties of the fertilizer in addition to water solubility—i.e., granule size, content of water-insoluble fractions, and composition of the water-soluble and water-insoluble fractions.

Black *et al.* (*2*) evaluated the relative contribution of water-soluble and water-insoluble phosphorus components of some superphosphate and nitric phosphate fertilizers hill-placed for corn. They found that the ratio of the availability coefficient of citrate-soluble phosphorus to that of water-soluble phosphorus decreased from 0.85 to 0.16 as the fraction of the fertilizer phosphorus in citrate-soluble form increased from 56 to 95%. This method of evaluating these two phosphorus fractions in fertilizers is based on the assumption that the effectiveness of the water-soluble fraction is independent of the fertilizer in which it occurs, while that of the citrate-soluble fraction may differ among fertilizers. As shown by Bouldin and Sample (*5*), this is not always a valid assumption, at least for certain soils and fertilizers. Later, Bouldin, DeMent, and Sample (*3*) found little measurable interaction in mixtures between water-soluble phosphorus present as monoammonium phosphate and water-insoluble phosphorus present as dicalcium phosphates. Crop response to water-soluble phosphorus (monoammonium phosphate) depended upon its content per granule, and response to water-insoluble phosphorus (dicalcium phosphate) depended upon the surface area of the granules. Finely divided dicalcium phosphates have been shown in several experiments (*6*) to be much more available to various crops than their water solubility would indicate.

Crop response to water-soluble *vs.* water-insoluble phosphorus in fertilizers is also influenced by the extent to which the phosphorus reacts with the soil (*6*). Concentrated placement and granulation of fertilizers tend to restrict the amount of soil contacted and thereby maximize differences among sources. Response to finely divided fertilizers well mixed with the soil may reflect the properties of the fertilizer-soil reaction products, rather than properties of the fertilizer initially applied; mixed placement of finely divided fertilizers thus minimizes the relative differences among sources.

The purpose of the experiments reported here was to study plant response to phosphorus in greenhouse cultures, as affected by water and citrate solubility, and granule size of the water-insoluble fractions of dicalcium phosphate and certain ammoniated superphosphate and nitric phosphate fertilizers.

Methods and Materials

Analysis of Fertilizers. Methods used for analyses of the fertilizers were those of the A. O. A. C. (*7*). Water-soluble phosphorus was leached from large amounts of the fertilizers, using approximately the same time and fertilizer-water ratio as in the official method. Chemical analyses of the initial whole fertilizers and of the water-leached residues of these fertilizers are shown in Table I.

Ammoniation caused a marked reduction in water solubility of the P_2O_5 in the fertilizers. Citrate-insoluble P_2O_5 was rather high in the ammoniated ordinary superphosphates and was high to very high in the ammoniated superphosphate residues. As indicated in Table I, more than twice as much of the water-insoluble phosphorus fractions was citrate-insoluble in the water-leached residues than in the whole fertilizers. This apparently indicates a deficiency of the official methods when applied to samples containing varying amounts of water-insoluble phosphorus.

Greenhouse Procedure. Four greenhouse pot experiments were conducted: No. 1 at Ames, Iowa, during the winter of 1954-55, and Nos. 2, 3, and 4 at Muscle Shoals, Ala. No. 2 was conducted from March to November 1956; No. 3, from November 1957 to April 1958; and No. 4, from April to August 1959. No. 10 tin cans lined with polyethylene bags and containing 3 kg. of soil (dry weight basis) were used in the experiments. Nitrogen and potassium were equalized for all treatments at rates considered adequate for optimum growth. Such additions of nitrogen and potassium were repeated for successive crops, but phosphorus was added only for the first crop. Analyses of the soils used in the experiments are shown in Table II.

Experiment 1. Oats were grown to the early heading stage on acid Floyd silt loam (pH 5.4) and on calcareous Ida silt loam (pH 8.0), using equal parts of white sand and soil mixed together. Amounts of P_2O_5 used were 20 and 40 pounds per 2 million pounds of soil plus sand (40 and 80 p.p.2m. of soil) for all the fertilizers and also 60 pounds for concentrated superphosphate. All of the fertilizers were fine powders (−100 mesh).

Experiment 2. Oats were grown as the first crop, followed by sudangrass, millet, sudangrass, and ryegrass on Hartsells fine sandy loam (pH 4.8) limed at 2 rates, 1 ton (to pH 5.2) and 4 tons (to pH 7.0) of ground dolomite per 2 million pounds of soil. The −100 mesh phosphates were added to supply 40 and 80 pounds of P_2O_5 per 2 million pounds of soil (26.2 and 52.4 mg. of total phosphorus per pot); 120 pounds of P_2O_5 (78.6 mg. of total phosphorus per pot) was also applied as concentrated superphosphate.

Experiment 3. Wheat (Anderson variety) was grown as the first crop followed by oats (Columbia variety) on Hartsells fine sandy loam (pH 5.1) limed with 1 ton of ground dolomite 4

Table I. P_2O_5 Fractions of Fertilizers Used in Experiments

Fertilizer	TVA No.	Grade, Based on Avail. P_2O_5	Total P_2O_5, %	AOAC Fractions, % of Total P_2O_5			
				Water-soluble	Citrate-soluble	Available	Citrate-insoluble
Whole fertilizers[a]							
1. CSP	87	0–49–0	50.0	88	10	98	2
2. CSP + AN	251B	14–24–0	24.7	84	14	98	2
3. ACSP + AN	253B	14–28–0	30.0	52	43	95	5
4. OSP + AN	247B	7–16–0	17.2	67	29	96	4
5. AOSP + AN	248B	10–14–0	16.7	46	42	88	12
6. AOSP + AN	249B	9–14–0	17.9	24	55	79	21
7. AOSP + AN	250B	9–14–0	18.0	11	70	81	19
8. NP	151	12–33–0	36.5	40	52	92	8
9. NP	55	11–14–0	14.7	34	61	95	5
10. NP	76	17–22–0	23.2	14	83	97	3
11. DCP	193	0–48–0	48.4	1	98	99	1
12. DCP + AN	255B	14–23–0	22.9	3	97	100	0
13. ANP	128	15–15–15	15.9	28	71	99	1
14. ANP	131	11–14–16	15.2	5	93	98	2
Water-leached residues							
15. From ACSP	253L	0–25–0	34.8	2	70	72	28
16. From AOSP	248L	0–13–0	29.3	3	44	47	53
17. From AOSP	249L	0–13–0	34.1	2	37	39	61
18. From AOSP	250L	0–15–0	35.5	2	41	43	57
19. From NP	151L	0–35–0	42.1	2	83	85	15
20. From NP	76L	0–41–0	45.1	1	92	93	7
21. From DCP	255L	0–43–0	44.0	1	98	99	1
22. P-4	4L	0–22–0	42.4	<1	53	53	47
23. P-1	1L	0–21–0	43.0	<1	51	51	49
24. P-2	2L	0–12–0	40.1	<1	31	31	69
25. P-3	3L	0–8–0	38.4	<1	23	23	77

[a] CSP, concentrated superphosphate; ACSP, ammoniated CSP; OSP, ordinary superphosphate; AOSP, ammoniated OSP; NP, nitric phosphate; DCP, anhydrous dicalcium phosphate; ANP, aluminum nitric phosphate; P-1 to P-4, heavily ammoniated nitric phosphate residues; and AN, ammonium nitrate granulated with the appropriate phosphate. Fertilizers 3, 5, 6, and 7 were ammoniated with approximately 3, 4, 6.5, and 8 pounds of free NH_3, respectively, per unit of available P_2O_5.

Major phosphate phases identified with a petrographic microscope in the water-leached residues were: DCP in all residues and precipitated apatite in all except 15 and 21.

Table II. Characteristics of Soils Used for Experiments

Soil Type and Source	pH	P Soluble in 0.5N $NaHCO_3$, P.P.M.	Exchangeable Cations, Meq./100 Grams	
			Ca	K
Floyd silt loam, Iowa	5.4	5.0	11.9	0.19
Ida silt loam, Iowa	8.0	1.0	28.4	0.41
Davidson clay loam, Virginia	5.8	6.6	5.3	0.16
Hartsells fine sandy loam, Alabama	5.1	2.1	1.6	0.24
Hartsells fine sandy loam, Tennessee	4.8	3.0	1.1	0.16

months prior to cropping (to pH 6.5) and on Davidson clay loam (pH 6.0). The phosphates were applied as fine powders (−100 mesh) in amounts to supply 60 mg. of total phosphorus, P, per pot (92 pounds of P_2O_5 per 2 million pounds of soil).

EXPERIMENT 4. Two successive crops of corn forage (5 singlecross hybrid plants per pot) were grown on Hartsells fine sandy loam (pH 5.2) and harvested when the largest plants were $2^1/_2$ to 3 feet tall. The phosphate powders were pressed into tablets with a Carver press, crushed, and sized into −16 + 20, −28 + 35, −60 + 100, and −100 + 325 (Tyler) mesh fractions (−16 + 20 mesh only for ammoniated concentrated superphosphate). All fractions were applied to supply 30 and 60 mg. of total phosphorus per pot. Additional amounts of 120 and 180 mg. of phosphorus were included for ammoniated concentrated superphosphate.

Analysis of Data. Except for Experiment 3, in which the phosphates were applied at only one rate, availability coefficient indexes (*4*) were calculated from yields of dry matter or of phosphorus obtained with the various rates of application by means of the Mitscherlich response function as follows:

$$\log (A - Y) = \log A - C(R + b)$$

where A is the limiting yield, Y is the yield at rate R of fertilizer addition, C is the availability coefficient index of the applied nutrient, and b is a constant. From this equation,

$$C = \frac{1}{R} \log \frac{A - Y_0}{A - Y}$$

where Y_0 is the yield with no applied phosphorus. Yields with unammoniated or ammoniated concentrated superphosphate were used to estimate the limiting yields.

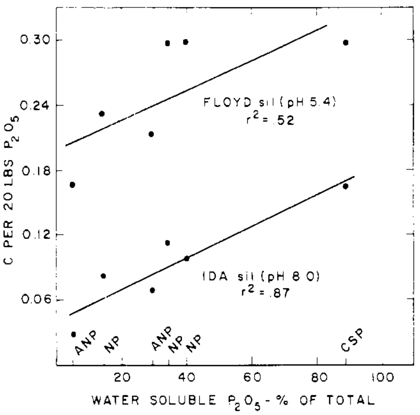

Figure 1. Regressions of availability coefficient indexes, C, per unit of P_2O_5 on water-soluble P_2O_5 content of fertilizers applied for oats grown on two Iowa soils

Table III. Availability Coefficient Indexes per 20 Pounds of Total P_2O_5 Supplied in Whole Fertilizers and in Their Water-Insoluble Fractions (Experiment 1)

Phosphorus Source[b]	AOAC Fractions in Whole Fertilizers, % of Total P_2O_5: Water-soluble	Citrate-soluble	C per 20 Lb. of P_2O_5[a]: Floyd silt: Whole fertilizer	Leached residue	Ida silt: Whole fertilizer	Leached residue
1	88	10	0.295	0.173	0.164	0.092
8	40	52	0.298	0.184	0.102	0.127
9	34	61	0.294	0.226	0.110	0.116
10	14	83	0.231	0.217	0.081	0.125
13	28	71	0.214	0.177	0.070	0.093
14	5	93	0.167	0.229	0.029	0.100

[a] Based on yields of oats (dry matter) as follows: 7.4 grams per pot with no P and limiting yield of 18.2 grams on Floyd sil, and 3.9 grams with no P and limiting yield of 26.5 grams on Ida sil.

[b] Numbers refer to Table I.

Table IV. Availability Coefficients Indexes per 40 Pounds of Total P_2O_5 Applied as −100 Mesh CSP and Water-Insoluble Phosphates (Experiment 2)

Phosphorus Source[b]	Avail. P_2O_5, % of Total	C per 50 Lb. of P_2O_5[a]: Crop 1	Crops 1-3	Crops 1-5
Soil limed to pH 5.2				
11	99	0.327	0.324	0.255
1	98	0.188	0.204	0.181
22	53	0.059	0.103	0.092
23	51	0.071	0.150	0.134
24	31	0.044	0.121	0.101
25	23	0.007	0.060	0.058
Soil limed to pH 7.0				
11	99	0.219	0.233	0.190
1	98	0.172	0.159	0.119
22	53	0.071	0.067	0.061
23	51	0.046	0.056	0.053
24	31	0.026	0.029	0.026
25	23	0.010	0.002	0.008

[a] Based on cumulative yields of dry matter by oats followed by sudangrass, millet sudangrass. and millet.

[b] Numbers refer to Table I.

Table V. Availability Coefficient Indexes per 30 Mg. of Total P Supplied as ACSP and Six Water-Insoluble Phosphate Residues Varying in Granule Size (Experiment 4)

Phosphorus Source[b]	Avail. P_2O_5, % of Total	C per 30 Mg. of P[a]: −16 + 20 mesh: First crop	Both crops	−28 + 35-mesh: First crop	Both crops	−60 + 100 mesh: First crop	Both crops	−100 + 325 mesh: First crop	Both crops
25	23	0.025	0.035	0.048	0.063	0.107	0.109	0.084	0.078
24	31	0.034	0.039	0.060	0.070	0.108	0.112	0.111	0.103
17	39	0.043	0.061	0.079	0.099	0.143	0.136	0.146	0.140
22	53	0.073	0.071	0.106	0.100	0.143	0.127	0.105	0.106
20	93	0.074	0.094	0.140	0.149	0.218	0.175	0.129	0.123
21	99	0.103	0.139	0.211	0.201	0.287	0.224	0.256	0.208
3	95	0.181	0.175	...	...	...	...	...	...

[a] Based on yields of dry matter by first crop and two successive crops of corn.

[b] Numbers refer to Table I.

Experimental Results

Crop Response to Finely Divided Phosphates. Results with concentrated superphosphate and five nitric phosphate fertilizers for oats on two Iowa soils (Experiment 1) are presented in Table III and Figure 1. Linear correlations between availability coefficient index, C, and water-soluble phosphorus in the fertilizer (Figure 1) would explain fair proportions of the differences in plant response to the several sources of phosphorus. However, extrapolations to zero water-soluble phosphorus would indicate considerable response to water-insoluble fractions, particularly on the acid Floyd soil. Also, deviations of several of the points are greater than would be expected on the basis of experimental error alone. Thus, only a portion of the variation in plant response can be explained by water-soluble phosphorus content of the fertilizers.

Results with the water-insoluble residues (Table III) indicate considerable differences in plant response to these residues, which are greater in some cases than the corresponding responses to the whole fertilizers. These results again suggest that response to the whole, or unleached fertilizers depends on both the water-soluble and water-insoluble fractions.

Assuming that the presence of the water-soluble fraction does not appreciably influence plant response to the water-insoluble fraction and that response to the water-soluble fraction is proportional to the content of water-soluble phosphorus in the fertilizers,

$$Y = KF + Z(1 - F),$$

where Y is the availability coefficient index of the whole fertilizer, F is the fraction of the total phosphorus which is water-soluble, K is a constant, and Z is the availability coefficient index of the water-insoluble fraction.

Values of $Y - Z(1 - F)$ were calculated and correlated with F. The resulting correlations indicated that 84 and 98% of the variation in the availability coefficient indexes of the water-soluble fractions is explained by variation in water-soluble phosphorus content of the fertilizers on the Floyd and Ida soils, respectively. These values represent an improvement over the 52 and 87% of the variation in availability coefficient indexes for the whole fertilizers (Figure 1) in these soils explained by variation in content of water-soluble phosphorus.

Results with anhydrous dicalcium phosphate, concentrated superphosphate, and four nitric phosphate residues applied as powders (Experiment 2) are shown in Table IV. Effectiveness of the water-insoluble residues was much less than for superphosphate or for dicalcium phosphate. Availability coefficient indexes for the residues tended to increase with repeated cropping of the soil at pH 5.2, but remained about the same in the soil at pH 7.0. Those for superphosphate and dicalcium phosphate tended to decrease with repeated cropping, especially following the third crop. Dicalcium phosphate was more effective than superphosphate for the first two crops and much more effective than the residues for all five crops.

As shown in Figure 2, the total uptake of applied phosphorus by wheat and oats increased with increase in content of available P_2O_5 in a series of leached phosphate residues applied on Hartsells fine sandy loam and on Davidson clay loam (Experiment 3). Uptake of phosphorus was least with pure, crystalline hydroxyapatite (HAp, 5% of its P_2O_5 estimated to be available) and highest from pure, crystalline dicalcium phosphate dihydrate (DCPD). Pure, crystalline anhydrous dicalcium phosphate (DCPA) was poorer than the leached residue of a commercial dicalcium phosphate (DCP) on the Davidson soil, but the two were equally effective on the Hartsells soil. The scattering of points about the lines probably reflects solubility differences in both the applied phosphates and in their reaction products with the soils.

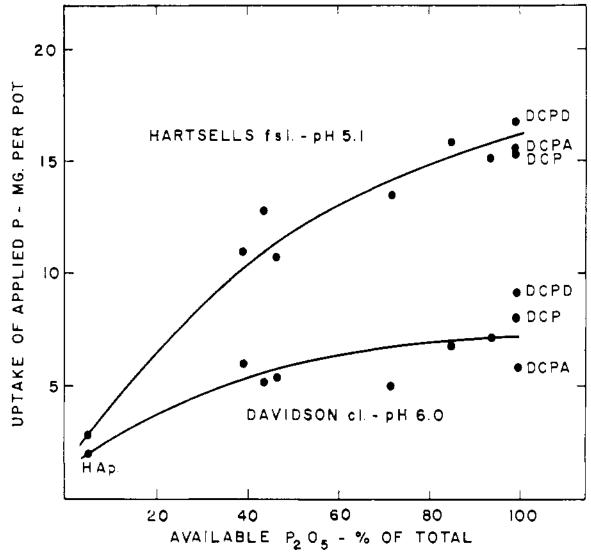

Figure 2. Total uptake of applied phosphorus by wheat and oats grown on two Virginia soils, as affected by available P_2O_5 content of −100-mesh water-insoluble phosphates

Table VI. Correlations (r^2 in Per Cent) of Contents of Available P_2O_5 and Availability Coefficient Indexes for Six Water-Leached Residues per Unit of P and per Unit of Surface Area (Experiment 4)

	r^2 for C/30 Mg. of P		r^2 for C/Cm.	
Mesh Size	First crop	Both crops	First crop	Both crops
−16 + 20	85	89	92	95
−28 + 35	90	92	93	95
−60 + 100	81	77	..	..
−100 + 325	52	55	..	..

Table VII. Availability Coefficient Indexes per Unit Surface Area of −16 + 20- and −28 + 35-Mesh Phosphates (Experiment 4)

				C/Sq. Cm.					
		Surface Area, Sq. Cm./30 Mg. P		First crop			Both Crops		
Phosphorus Source[a]	Avail. P_2O_5, % of Total	−16 + 20 mesh[b]	−28 + 35 mesh[c]	−16 + 20 mesh	−28 + 35 mesh	Av.	−16 + 20 mesh	−28 + 35 mesh	Av.
25	23	1.39	2.53	0.019	0.019	0.019	0.025	0.025	0.025
24	31	1.29	2.35	0.026	0.026	0.030	0.030	2.030	0.030
17	39	1.76	3.20	0.024	0.025	0.025	0.035	0.031	0.033
22	53	1.48	2.69	0.049	0.039	0.044	0.048	0.037	0.043
20	93	1.25	2.28	0.059	0.061	0.060	0.075	0.065	0.070
21	99	1.36	2.48	0.076	0.085	0.081	0.102	0.081	0.092

[a] Numbers refer to Table I.
[b] Based on counted numbers of particles.
[c] Calculated from −16 + 20 mesh particles, using ratio of mean radii of 1.82.

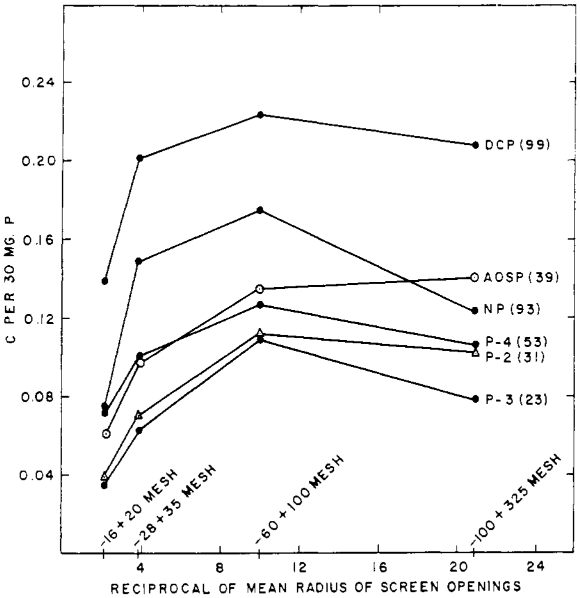

Figure 3. Availability coefficient indexes, C, for two crops of corn, as affected by granule size and content of available P_2O_5 (in parentheses) of various water-insoluble phosphates

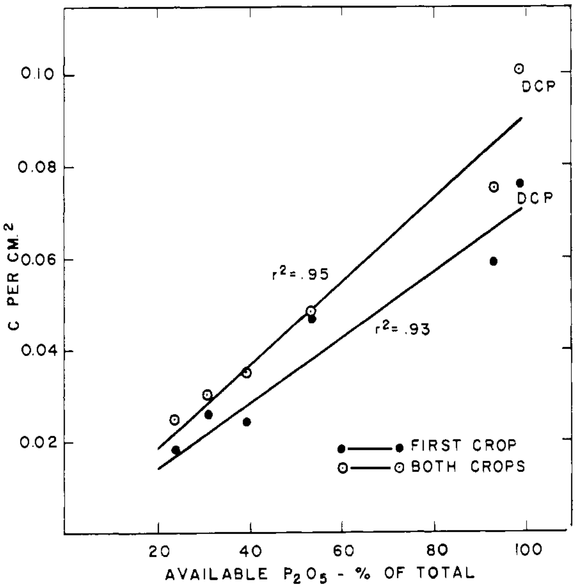

Figure 4. Regressions of availability coefficient indexes per unit of surface area (C per sq. cm.) for first crop and two crops of corn on available P_2O_5 content of $-16 + 20$-mesh water-insoluble phosphates

Crop Response to Phosphates Varying in Granule Size. Availability coefficient indexes for the first crop and the total of two crops of corn fertilized with ammoniated concentrated superphosphate and six water-insoluble phosphates varying in granule size (Experiment 4) are shown in Table V. Effectiveness of the $-16 + 20$- and $-28 + 35$-mesh sizes was rather closely related to the citrate-soluble P_2O_5 content of the phosphates, as shown by the correlation coefficients in Table VI.

The relationship between effective of the $-60 + 100$- and $-100 + 325$-mesh granules and citrate solubility was poorer. This probably reflects greater dissolution and reaction with soil of the phosphorus from the fine than from the coarse granules. Thus, with fine granules, the fertilizer-soil reaction products largely determined the solubility of the fertilizer phosphorus and its availability to plants. Response to a fine material is also affected by its tendency to remain aggregated, even after mixing with the soil. However, the $-100 + 325$-mesh dicalcium phosphate (99% available P_2O_5) was much more effective for corn than the same size of nitric phosphate (also largely dicalcium phosphate, with 97% available P_2O_5). Differences in granule size due to aggregation of the fine particles may also have caused differences in effectiveness for corn.

As shown in Figure 3, effectiveness of all of the phosphates increased with decrease in granule size from $-16 + 20$ to $-60 + 100$ mesh. Effectiveness then decreased for $-100 + 325$-mesh granules of all of the phosphates except ammoniated ordinary superphosphate. Despite certain inconsistencies, especially with the $-100 + 325$-mesh nitric phosphate residue, Figure 3 also shows a general increase in effectiveness with increase in citrate solubility.

Estimates of geometric surface area for the $-16 + 20$-mesh granules of each phosphate were based on counts of the number of granules per unit weight of material. Using the calculated surface areas and the average availability coefficient indexes per 30 mg. of phosphorus (Table V) C per sq. cm for the phosphates were calculated and are shown in Table VII. Relative effectiveness per unit of surface area was not changed greatly from effectiveness based on unit weight of applied phosphorus.

Using the ratio of 1.82 between the radii of the $-16 + 20$- and the $-28 + 35$-mesh size openings, corresponding values were also estimated for the $-28 + 35$-mesh granules (Table VII). There was good agreement in C per sq. cm. between the $-16 + 20$- and $-28 + 35$-mesh sizes for the three phosphates having the lowest citrate solubilities (21, 33, and 39%). The $-28 + 35$-mesh granules of the phosphates having the higher citrate solubilities (53, 93, and 99%), however, were relatively less effective for both crops per unit of surface area than the $-16 + 20$-mesh granules. This indicates that the latter group had undergone considerable dissolution, so that effectiveness for corn was no longer as dependent on the surface area. As shown in Table VI, 92 to 95% of the differences in effectiveness per unit of surface area for the various phosphates were explained by variation in citrate-soluble P_2O_5. This is somewhat higher than the corresponding values based on effectiveness per unit of applied phosphorus.

In Figure 4 the availability coefficient indexes per unit of surface area of the $-16 + 20$-mesh granules are plotted against available P_2O_5 content. Effectiveness for the first crop, and especially for the second crop, increased with increase in citrate solubility. Effectiveness for the dicalcium phosphate residue was considerably greater than would be predicted by the trend for the other phosphates containing varying amounts of precipitated apatite.

Acknowledgment

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