slurry-mix (and dry-mix) materials does not differ from the water-soluble fraction in availability to millet, and the relative availabilities approximate 100. This occurred on all three soils where the fertilizer was mixed with the soil. These materials thus behaved differently from the rock phosphate–dissolution materials.

The slurry-mix (and dry-mix) materials appear to be no different from the monoammonium phosphate, dicalcium phosphate, and ammonium nitrate constituents from which they were made. Petrographic analysis of these materials showed no evidence of solution erosion or chemical alteration.

Definition of rock phosphate–dissolution materials is more complex. As indicated before, the differences in response to these materials as compared to the dicalcium phosphates of the slurry-mix (and dry-mix) materials could be due to the relative unavailability of the citrate-soluble basic phosphates formed in the manufacturing process. This is also indicated by the high availability of the rock phosphate–dissolution materials in the very acid Miami soil where reaction with the soil should result in a greater similarity to the other materials.

The rock phosphate–dissolution materials were examined petrographically and the results are presented in Table IV. All samples contained a precipitated apatite with optical properties of cel'ophane as the major calcium phosphate constituent. Only the 74% sample contained appreciable quantities of dicalcium phosphate dihydrate.

In contrast to the results obtained with the rock phosphate–dissolution and

Table IV. Chemical Compounds in Rock Phosphate–Dissolution Materials as Indicated by Petrographic Analysis[a]

Water Solubility, %	Calcium Phosphate Compounds[b]
15	Ppt. apatite with optical properties of collophane
35	Same as 15%
42	Same as 15% with a small amount of $CaHPO_4 . 2H_2O$
59	Same as 15%
74	Same as 42% with a much greater content of $CaHPO_4 . 2H_2O$

[a] NH_4NO_3 and $NH_4H_2PO_4$ found in all five materials.
[b] Small amounts of unreacted phosphate rock were present in all five materials.

slurry-mix materials when they were mixed with the soil, band application did not differentiate very well between methods of preparation though there were indications that the rock phosphate–dissolution materials were not as effective at low water solubilities as the slurry-mix materials on the acid Miami soil (Figure 2). Water solubility in the band treatment appeared to be the most important fertilizer criteria. Webb (9) has recently shown that corn-yield response from starter fertilizers in Iowa is closely related to water solubility of the phosphorus. The influence of mixing the soil and fertilizer was greater on the slurry-mix materials; thus, there was a dissimilarity of the non-water-soluble fraction of the rock phosphate–dissolution and the slurry-mix materials, and

the effect was greater than could be attributed to the citrate-insoluble fraction alone. This again illustrates the inability to predict the agronomic value of a material from chemical measurements of citrate solubility and even water solubility.

Acknowledgment

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SURFACE AREA EFFECTS

Greenhouse Crop Response to Water-Insoluble Phosphates with Different Surface Areas

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Corn stover and alfalfa were grown in greenhouse cultures on slightly acid Chester soil to determine the effect of surface area of water-insoluble phosphorus in fertilizers upon yield and phosphorus uptake. Radioactive preparations of basic phosphate and of dicalcium phosphate with surface areas ranging from 0.7 to 22.8 square meters per gram were tested. Essentially the same yields of both corn and alfalfa were obtained with the dicalcium phosphates, although their surface areas differed by as much as 5 square meters per gram. Markedly lower yields resulted from using the basic phosphate despite the fact that its surface area was higher than that of any of the dicalcium phosphates. Thus, chemical composition appears to be more critical than surface area within the range studied.

THE REACTIVITY of a phosphate fertilizer, and perhaps its agronomic value also, is influenced by the extent of exposed surface, which in general depends on the fineness of the material as determined by appropriate methods. Particle size, though relatively unimportant in the case of very soluble fertilizers, is prominent among those factors that influence the nutritive value of water-insoluble phosphates. The fertilizer value of such materials is said to depend on particle size. Most of the water-insoluble phosphates present in mixed fertilizers possess finenesses that lie

near the bottom of the sieve range or below it. This finely divided material is a component of the fertilizer aggregate or granule. Differences in fineness must be inferred from surface-area measurements rather than from sieve analysis.

In the nutritive evaluation of the phosphorus in polynutrient fertilizers, special interest is attached to the quality of the water-insoluble phosphorus. The bulk of this insoluble phosphorus is usually carried in dicalcium phosphate and apatite-like basic phosphate. The specific surface of mixtures of these phosphates obtained as water-insoluble residues from commercial mixed fertilizers ranges up to 26 square meters per gram (1). The work reported herein was started with the intention of determining, in separate studies, the relationship between fineness and nutritive value for well-characterized preparations of dicalcium phosphate and of basic phosphate covering the range in specific surfaces observed for commercial materials. However, inability to prepare suitably characterizable test materials has so far prevented achievement of the goal. Thus, the dicalcium phosphate used in the vegetation experiment not only covers a narrower range in fineness, but also represents a range of alterations in composition.

Materials and Methods

Test Fertilizers. The radioactive phosphate materials selected for this experiment were carefully prepared and characterized by laboratory measurements of certain physical and chemical properties which might seem to influence crop response. In order to evaluate surface area, apart from surface composition, radioactive preparations of basic phosphate and of dicalcium phosphate were tested against inactive triple superphosphate and commercial dicalcium phosphate.

The test sample R-150 of dicalcium phosphate was prepared by a procedure that previously had given high surface areas. A solution, approximately saturated, of diammonium phosphate was added dropwise to a hot agitated solution of calcium nitrate. The phosphate solution, as in each of the radioactive preparations, had previously been tagged with irradiated monopotassium phosphate, according to standard labeling procedures, to yield a finished product with a specific activity of 0.15 mc. per gram of phosphorus pentoxide. The temperature during this reaction was held at 95° to 100° C. The dicalcium phosphate was washed by decantation with water and with acetone, and was dried. The dried material was passed through a 100-mesh screen, as were all the radioactive preparations.

Lot R-151 was prepared by adding slowly 3.25 moles of solid calcium carbonate to 3.25 moles of phosphoric acid contained in a 5% solution. The mixture was kept at room temperature throughout the preparation. The product was washed as described above and dried. The omission of the heat treatment at 95° to 100° C. was expected to produce a partially hydrated product and, possibly, one with a different mole ratio of calcium oxide to phosphorus pentoxide.

Lot R-152, the basic phosphate, was prepared by adding dry calcium hydroxide to an approximately 5% phosphoric acid solution, with stirring at room temperature. The mole ratio of calcium oxide to phosphorus pentoxide was 3.2 to 1 instead of 2 to 1, as is used to prepare dicalcium phosphate. The precipitate was washed with water and with acetone, and was dried.

Lot R-155, pure dicalcium phosphate, was prepared by a method which has previously given low surface area. Stoichiometric amounts of calcium hydroxide and phosphoric acid were used. The calcium hydroxide was put into a slurry with four to six times its weight of water. The acid was added, dropwise as a 50% solution while the batch was held at room temperature, with stirring. The batch was then heated to 96° to 100° C. for 1 hour.

As shown in Table I, both surface and chemical composition varied in the test material.

The size of dicalcium phosphate particles normally falls in the subsieve range (2) and the corresponding surface areas exceed the geometric surface (0.05 square meter per gram) of 325-mesh crystals. The surface area was determined by means of the Brunauer-Emmett-Teller (BET) method with the use of nitrogen gas (4). Results by this method are to be regarded as representing the total surface of the sample. Experience with other insoluble phosphates (1, 3) indicates that the results are reproducible within 10% for surface areas of less than 5 square meters per gram and within 5% for surface areas of 5 square meters per gram or greater.

Soil. Chester silt loam, an acid soil of Eastern United States that has a low content of extractable phosphorus and a high-base exchange capacity, was used for this experiment in order to show more clearly small differences between materials. The lime requirement was determined in the laboratory in terms of calcium carbonate equivalent required per 2,000,000 pounds of soil to bring the soil to pH 6.5. Half of the requirement was supplied by calcium hydroxide and half by magnesium oxide, which is equivalent to 6500 pounds of calcium carbonate per acre.

Culture Preparation and Management. The soil was limed on May 14, 1955, brought to moisture equivalent, and permitted to equilibrate for 13 days. On May 27, 1955, the moist soil was sieved and fertilizers were added. Enamel-lined No. 10 tin cans were used as containers. Although the rates of phosphorus pentoxide varied from 50 to 200 pounds per acre under alfalfa and 100 to 400 pounds per acre under corn, the nitrogen and potassium oxide applied were constant for all cultures of any one crop. Ammonium sulfate and potassium chloride, equivalent to 400 pounds of nitrogen and 400 pounds of potassium oxide per acre under corn and 200 pounds of nitrogen and 400 pounds of potassium oxide under alfalfa, were added and mixed throughout the soil. The phosphate materials were applied in mixed placement under corn and in mixed and banded placement under alfalfa, in three replications.

Banded placement was not used with corn because the bands would have been destroyed in preparing the soil for the seeding of the second crop. In all cases of band placement, the fertilizer was applied in two parallel bands 3.5 inches apart, center to center, and equidistant from the center of the can. These bands were 0.5 inch wide, 0.75 inch below the surface of the soil, and extended to the periphery of the can. The thickness of the bands varied with the amount of fertilizer applied. In the mixed placement, the fertilizer was mixed throughout the soil. A no-phosphorous treatment was also included for each crop of mixed-placement cultures.

Corn and alfalfa were planted in two parallel rows 2.5 inches apart on the same day that the cultures were fertilized.

Table I. Composition of Test Fertilizers

Materials	Type of Material	Sample No.	Surface Area, Sq. M²/G.ᵃ	P₂O₅, %			P:Ca Mole Ratio
				Total	Avail.	W. S.	
Triple superphosphate	Commercial	3032	(−28 mesh)	50.0	48.8	44.0	...
Dicalcium phosphate	Commercialᵇ	2961a	1.5	51.4	50.8	0.6	1.002
Dicalcium phosphate	Radioactive	R-150	0.7	51.9	51.6	0.5	0.946
Dicalcium phosphate	Radioactive	R-155	1.5	51.3	49.1	0.3	0.964
Dicalcium phosphate	Radioactive	R-151	5.5	49.8	49.4	0.6	0.908
Basic phosphate	Radioactive	R-152	22.8	40.5	20.9	0.4	0.626

ᵃ BET with N gas (4).
ᵇ Food grade.

Table II. Response of Alfalfa to Basic and Dicalcium Phosphates in Banded and Mixed Placement on Chester Silt Loam

Treatment[a] Fertilizer	P₂O₅ applied, lb./acre	Yield, Grams per Culture				P₂O₅ Uptake, Mg. per Culture				% Plant P from Fertilizer			
		1st crop	2nd crop	Sum	Mean	1st crop	2nd crop	Sum	Mean	1st crop	Mean	2nd crop	Mean
BAND PLACEMENT													
Triple superphosphate, −28 mesh	50	2.93	4.79	7.72		14.4	21.7	36.1					
	100	3.31	5.79	9.10		18.7	28.9	47.6					
	200	3.51	5.80	9.31	8.71	18.4	27.4	45.8	43.2				
Dicalcium phosphate, 1.5 sq. m./g.	50	2.35	4.53	6.88		13.1	22.3	35.4					
	100	2.54	5.02	7.56		15.4	24.7	40.1					
	200	2.69	5.28	7.97	7.47	15.3	29.7	45.0	40.2				
Dicalcium phosphate, 0.7 sq. m./g.	50	2.02	4.41	6.43		12.1	20.2	32.3		43.6		52.6	
	100	2.66	4.81	7.47		15.6	21.3	36.9		54.7		57.8	
	200	3.18	5.57	8.75	7.55	18.2	29.2	47.4	38.9	70.8	56.4	65.6	58.7
Dicalcium phosphate, 1.5 sq. m./g.	50	2.25	4.41	6.66		12.9	20.9	33.8		58.7		43.0	
	100	2.57	5.04	7.61		15.6	23.1	38.7		61.9		54.2	
	200	2.64	5.24	7.88	7.38	18.3	23.4	41.7	38.1	66.1	62.3	60.7	52.6
Dicalcium phosphate, 5.5 sq. m./g.	50	2.16	4.62	6.78		12.6	20.9	33.5		48.8		64.7	
	100	2.60	4.92	7.52		14.3	25.2	39.5		56.3		74.9	
	200	2.68	5.07	7.75	7.35	16.3	25.5	41.8	38.3	62.5	55.9	79.5	73.0
Basic phosphate, 22.8 sq. m./g.	50	2.03	4.34	6.37		12.1	19.9	32.0		28.8		45.4	
	100	2.27	4.52	6.79		13.0	20.2	33.2		37.5		49.4	
	200	2.50	4.98	7.48	6.88	14.1	30.3	44.4	36.5	48.0	38.1	57.6	50.8
MIXED PLACEMENT													
Triple superphosphate, −28 mesh	50	2.49	4.33	6.82		12.5	16.2	28.7					
	100	2.70	4.63	7.33		12.1	18.2	30.3					
	200	3.41	5.37	8.78	7.64	16.5	26.7	43.2	34.1				
Dicalcium phosphate, 1.5 sq. m./g.	50	2.22	3.94	6.16		9.6	16.3	25.9					
	100	2.74	4.38	7.12		13.1	20.2	33.3					
	200	3.20	5.15	8.35	7.21	17.4	25.2	42.6	33.6				
Dicalcium phosphate, 0.7 sq. m./g.	50	2.70	4.57	7.27		12.8	14.0	26.8		39.3		29.4	
	100	3.12	4.60	7.72		16.6	17.9	34.5		56.6		44.3	
	200	3.46	5.27	8.73	7.91	18.9	26.2	45.1	35.5	67.8	54.6	57.3	43.7
Dicalcium phosphate, 1.5 sq. m./g.	50	2.48	4.03	6.51		11.6	20.8	32.4		49.8		25.2	
	100	2.95	5.01	7.96		15.5	22.0	37.5		62.0		46.5	
	200	3.28	5.20	8.48	7.65	19.3	23.7	43.0	37.6	70.3	60.7	54.9	42.2
Dicalcium phosphate, 5.5 sq. m./g.	50	2.19	4.22	6.41		11.2	16.8	28.0		37.5		32.4	
	100	2.92	4.73	7.65		15.1	20.1	35.2		52.0		44.0	
	200	3.36	5.48	8.84	7.63	16.3	22.4	38.7	34.0	68.2	52.6	62.1	46.2
Basic phosphate 22.8 sq. m./g.	50	2.07	3.45	5.52		9.3	12.8	22.1		16.8		14.2	
	100	2.32	3.85	6.17		10.3	14.3	24.6		27.0		27.5	
	200	2.93	4.62	7.55	6.38	14.1	17.9	32.0	26.3	43.6	29.1	48.0	29.9
No phosphorus	…	1.82	3.53	5.35	5.35	8.1	13.0	21.1	21.1				
Least significant difference: 1% level		0.74	1.31	1.77	1.03	4.2	6.7	8.9	5.2	17.2	10.0	10.4	6.0
5% level		0.56	0.99	1.33	0.77	3.2	5.1	6.7	3.9	12.9	7.5	7.8	4.5
Levels of significance[b]													
Materials		1	1	1		1	1	1		1		1	
Rates		1	1	1		1	1	1		1		1	
Placement		1	1	NS		1	1	1		5		1	
Materials × rates		NS	NS	NS		NS	NS	NS		NS		NS	
Materials × placement		1	NS	NS		5	5	1		NS		1	
Rates × placement		NS	NS	NS		5	NS	NS		NS		1	
Materials × rates × placement		NS	NS	NS		NS	NS	NS		NS		NS	

[a] All cultures were limed to pH 6.5 and treated with 200 pounds of nitrogen and 400 pounds of potassium oxide per acre prior to planting.
[b] NS, 1, and 5 indicate no significance, significance at 1% level, and significance at 5% level, respectively.

Thus, with banded placement, the seed was approximately 0.5 inch from the band. Minor elements in solution were added on the same day. All cultures were then brought to moisture equivalent, and, in order to maintain the moisture near this level, the cultures were weighed about twice a week throughout the growing season.

The first cutting of corn was made on July 22, 1955, 56 days after planting.

The second crop of corn was seeded on July 26, 1955, after the soil was sieved and an additional 400 pounds of nitrogen and 200 pounds of potassium oxide per acre were added. The second crop of corn was harvested on September 13, 1955, 109 days after fertilization.

The first and second cuttings of alfalfa were made after 82 and 125 days, respectively.

The dry-weight yield was determined by drying the cuttings in a forced-draft oven at 65° C. The plant material was then ground, ashed, and analyzed for total phosphorus and phosphorus-32.

Statistical analyses of the yield, phosphorus uptake, and percentage of plant phosphorus from the fertilizer were performed for each cutting as well as for the sum of the two cuttings (Tables II and III).

Table III. Response of Corn (Stover) to Basic and Dicalcium Phosphates in Mixed Placement on Chester Silt Loam

Treatment[a] Fertilizer	P₂O₅ applied, lb./acre	Yield, Grams per Culture 1st crop	2nd crop	Sum	Mean	P₂O₅ Uptake, Mg. per Culture 1st crop	2nd crop	Sum	Mean	% Plant P from Fertilizer 1st crop	Mean	2nd crop	Mean
Triple superphosphate, −28 mesh	100	18.9	12.5	31.4		45.4	32.2	77.6					
	200	23.5	20.6	44.1		61.4	55.9	117.3					
	400	29.2	26.0	55.2	43.6	65.3	106.6	171.9	122.3				
Dicalcium phosphate, 1.5 sq. m./g.	100	18.9	15.1	34.0		42.4	40.6	83.0					
	200	21.9	21.7	43.6		56.6	64.5	121.1					
	400	25.8	28.4	54.2	43.9	63.8	113.5	177.3	127.1				
Dicalcium phosphate, 0.7 sq. m./g.	100	19.2	15.1	34.3		52.5	38.4	90.9		45.6		31.8	
	200	23.4	20.2	43.6		57.7	60.6	118.3		57.2		45.8	
	400	27.5	26.1	53.6	43.8	65.1	90.7	155.8	121.7	73.6	58.8	55.4	44.3
Dicalcium phosphate, 1.5 sq. m./g.	100	18.3	12.7	31.0		52.2	31.5	83.7		47.0		27.5	
	200	21.9	22.2	44.1		61.0	74.3	135.3		54.8		44.3	
	400	27.6	28.2	55.8	43.6	74.1	112.5	186.6	135.2	69.3	57.0	52.4	41.4
Dicalcium phosphate, 5.5 sq. m./g.	100	19.7	12.5	32.2		61.3	27.0	88.3		47.3		30.9	
	200	22.1	19.8	41.9		62.8	60.2	123.0		61.3		46.8	
	400	27.8	24.2	52.0	42.0	75.9	92.8	168.7	126.7	66.3	58.3	62.3	46.7
Basic phosphate, 22.8 sq. m./g.	100	13.1	10.0	23.1		36.2	30.7	66.9		26.8		23.6	
	200	14.8	13.4	28.2		36.3	41.2	77.5		35.1		40.2	
	400	19.2	22.1	41.3	30.9	46.8	62.3	109.1	84.5	48.2	36.7	45.9	36.6
No phosphorus	...	5.8	4.6	10.4	10.4	11.7	11.5	23.2	23.2				
Least significant difference: 1% level		2.8	4.1	4.8	2.8	16.0	15.5	21.5	12.5	8.8	5.1	11.3	6.6
5% level		2.1	3.0	3.6	2.1	11.9	11.5	16.0	9.3	6.5	3.8	8.3	4.8
Levels of significance[b] Rates		1	1	1		1	1	1		1		1	
Materials		1	1	1		1	1	1		1		1	
Rates × materials		NS	NS	NS		NS	1	1		NS		NS	

[a] All cultures were limed to pH 6.5 and treated with 400 pounds per acre each of nitrogen and potassium oxide prior to planting.
[b] NS, 1, and 5 indicate no significance, significance at 1% level, and significance at 5% level, respectively.

Influence of Surface Area on Corn and Alfalfa Responses

The arrangement of data in the tables permits comparisons between materials and rates by placement. Least significant differences, requisite for valid comparisons and levels of significance between sources of variation, are given at the bottom of the tables. Differences due to materials, rates of application, and placement were highly significant for the experiment as a whole.

Yield. Essentially the same yields of both corn and alfalfa were obtained with the four dicalcium phosphates, although their surface areas differed by as much as 5 square meters per gram. On the other hand, markedly lower yields resulted from using the basic phosphate despite the fact that its surface area was higher than that of any of the dicalcium phosphates. The dicalcium phosphates were about as effective as triple superphosphate except in band placement under alfalfa. Especially poor growth was obtained with the basic phosphate in a mixed placement. Mixed placement under alfalfa resulted in higher dry matter yield from the first crop than band placement, whereas crop response was greater with the banded treatment in the second crop. These effects balance each other in the sum of the two crops, so that significant differences in yield by placement were not obtained. Increased

rates of application of all phosphate materials resulted in increased yields of both crops.

Uptake. The salient comparisons again are that markedly higher phosphorus uptakes were found when the dicalcium phosphates were applied in mixed placement under corn and alfalfa than when the basic phosphate was similarly applied. This trend closely follows the pattern indicated by the yield data. There was no significant difference between the dicalcium and basic phosphates, however, in band placement under alfalfa.

Similarly, the principal difference in percentage of plant phosphorus derived from the fertilizers exists between the dicalcium and basic phosphates. As indicated in Tables II and III, the percentage of plant phosphorus from the basic phosphate in mixed placement is approximately the same in both crops, whereas, in band placement, it is considerably higher in the second crop. The percentage of plant phosphorus from dicalcium phosphate was higher in the first crop except in band placement, where the highest surface area in the second crop gave a significantly higher percentage of plant phosphorus in the plant than all other dicalcium phosphates.

However, as properties other than surface area changed from material to material, a true relationship, if one exists, might be masked by conflicting

factors. Comparison of the observed yields, total phosphorus uptake, and percentage of the plant phosphorus derived from fertilizer indicates that chemical composition was more critical than surface area within the range here studied. The sparse significant differences between the dicalcium phosphates are probably attributable to differences in surface area. Total surface area, therefore, was not a particularly good indicator of nutrient value of the phosphate because it was readily overshadowed by other factors that were subject to wide variation in fertilizers, especially in mixtures.

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