

Crop Response to Phosphorus in Nitric Phosphates

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Fertilizers produced on an experimental basis by the treatment of rock phosphate with nitric acid, either alone or mixed with sulfuric or phosphoric acid, have been evaluated under field and greenhouse conditions in more than 130 experiments in 11 states. The phosphate in most nitric phosphate fertilizers studied is as effective for cotton, small grains, and corn as phosphate in commercial-type fertilizer mixtures or in concentrated superphosphate. To be satisfactory for vegetable crops, nitric phosphate fertilizers should have a third or more of the phosphate present in a water-soluble form. Two nitric phosphates gave crop yield increases on both alkaline and acid soils similar to those given by concentrated superphosphate. The residual phosphorus from soil treatment with nitric phosphates was as effective in increasing crop yields as residual phosphorus from concentrated superphosphate treatments. Granulation of two nitric phosphate fertilizers had no significant effect on crop yields.

NITRIC PHOSPHATE is a term used by the Tennessee Valley Authority (TVA) to designate a group of fertilizers produced by the reaction of rock phosphate and nitric acid, either alone or in mixtures with sulfuric or phosphoric acid, followed by ammoniation and other process steps. Such materials are also designated as "nitrophosphates" and "nitraphosphates." Potash materials may be added during processing to give complete fertilizer products. Nitric phosphate materials are attractive for commercial production. They appear to have some cost advantage over the usual mixed fertilizers, and the nitric acid contributes to the final fertilizer grade.

Nitric acid has been used in Europe for the treatment of rock phosphate in fertilizer production for nearly 25 years. TVA has conducted laboratory and pilot plant investigations on various nitric acid-rock phosphate processes since 1948. The processes involved have been described by Hignett (2) and Walthall and Houston (5). Four general types of processes are employed:

Process I

Rock phosphate + phosphoric acid + nitric acid + ammonia (muriate of potash addition is optional)

Process II

Rock phosphate + sulfuric acid + nitric acid + ammonia (muriate of potash addition is optional)

Process III

Rock phosphate + nitric acid + ammonia + either potassium sulfate or ammonium sulfate

Process IV

Rock phosphate + nitric acid + ammonia + carbon dioxide (muriate of potash addition is optional)

The manufacturing processes must be such that deliquescent calcium nitrate is essentially eliminated from the final products. This requires a rather high degree of ammoniation and the presence of such ions as sulfate or carbonate to combine with the calcium released in the acidulation processes. The high degree of ammoniation converts much of the phosphate to the low water-soluble di-calcium form. The phosphate compounds produced by the various processes involving nitric acid may be present in different proportions than those occurring in superphosphates. Consequently, the effectiveness of the phosphate in nitric phosphates for crop production requires careful evaluation.

The nitrogen and potash in nitric phosphates are in compounds similar to those in commonly used fertilizer materials and are readily available to plants. Greenhouse and field tests have been primarily concerned, therefore, with the agronomic value of the phosphorus in nitric phosphate materials, and that is the primary concern of this paper.

Nitric phosphate fertilizers produced by TVA have been tested in greenhouse and field experiments conducted since 1948 by state agricultural experiment stations. Rogers (3) summarized the results of cooperative tests conducted during 1948 and 1949 with Process I and Process II materials. He concluded that corn, cotton, and small grains

responded as well to the phosphate in nitric phosphates on the soils of the Southeast as to phosphate in concentrated superphosphate (CSP) or commercial-type fertilizer mixtures. In most tests, crops were not increased in yield by raising the degree of water solubility of phosphorus above 10%. But in a few tests with corn on alkaline soils in Iowa and Nebraska, a higher degree of water solubility appeared to be important.

D'Leny (7) concluded that the phosphate in a nitric phosphate produced by a process similar to Process III (ammonium sulfate addition) in England was as effective in increasing crop yields as an equivalent amount of phosphate in the form of superphosphate.

Stewart (4) reported studies in England on the yields of grass, potatoes, and swedes treated with equivalent amounts of superphosphate and nitric phosphates (British, French, and Dutch). He concluded that, as a rule, the nitric phosphates were not so effective as superphosphate and did not behave consistently for the three crops. There were no statistically significant differences at odds of 19 to 1 in yields in his data, however, from treatments with the various materials.

Objectives of Present Report

Additional information concerning the nitric phosphates has accumulated since Rogers (3) summarized the then available data. As there is considerable interest in commercial production of some of these materials, the new information is summarized in this paper.

Table I. Average Composition of Principal Fertilizers Used in Field Experiments

Nominal Grade	Type and Process ^a	Particle Size, U. S. Screen	Composition, %							Net Acidity, Lb. CaCO ₃ /Tcn
			N	Total	P ₂ O ₅		K ₂ O	Ca	S	
					Available	Water-soluble, % of available				
12-32-0	NP-I	-12 +50	12.4	36.5	32.7	43.7	...	12.5	0.2	-415
17-22-0	NP-I	-12 +50	16.9	23.2	22.4	14.3	...	13.1	...	-311
14-14-14	NP-I	-12 +50	14.8	14.5	14.1	9.2	15.0	8.6	0.2	-572
6-18-0	NP-II	-6	6.2	18.9	18.1	32.6	...	18.9	6.3	-200
11-14-0	NP-II	-12 +50	11.3	14.7	14.0	35.7	...	14.8	7.4	-396
11-11-11	NP-II	-12 +50	11.8	12.2	11.8	17.8	11.1	12.7	4.0	-217
11-11-11	NP-II	-40	11.4	12.5	12.0	10.0	11.3	13.6	4.3	-217
4-12-12	NP-II	-4	4.3	12.4	12.1	22.3	13.2	14.5	7.0	+141
12-12-12	NP-III	-12 +50	11.7	12.4	11.5	6.9	13.0	12.4	4.4	-6
14-11-11	NP-IV	-12 +50	14.7	11.4	11.1	1.0	11.1	12.0	0.5	-766
10-10-10 L	Com.	...	9.5	10.7	9.6	29.2	10.8	10.9	10.0	-598
10-10-10 H	Com.	...	9.9	10.4	9.9	57.6	9.7	10.0	11.2	-675
7-7-7 L	Com. ^b	...	7.3	8.7	7.6	9.2	8.1	13.0	7.0	...
7-7-7 H	Com. ^b	...	7.5	7.7	7.1	52.1	7.3	12.4	7.8	...
20-54-0	DAP	...	20.3	54.0	54.0	100.0
0-48-0	CSP	49.1	47.3	93.9

^a NP. Nitric phosphate.
 Com. Commercial-type fertilizer mixture.
 L. Low water-soluble phosphorus material.
 H. High water-soluble phosphorus material.
 DAP. Diammonium phosphate.
 CSP. Concentrated superphosphate.
^b Fertilizer rendered nonacid-forming by addition of dolomite.

This report covers a wider range of materials than was included in Rogers' paper. The new data also provide additional information about the agronomic significance of particle size, sulfur content, water solubility of phosphate, and relative response of crops to nitric phosphate on alkaline and acid soils.

Experimental Materials

The analyses of the principal nitric phosphates, superphosphates, and commercial-type mixtures used in the experiments reported are shown in Table I. The commercial mixtures were prepared by ammoniating normal superphosphate with an ammonia-ammonium nitrate solution and dry-mixing the ammoniated superphosphate with ammonium sulfate and potassium chloride. The different levels of water solubility of phosphorus were obtained by varying the degree of ammoniation.

Ammonium nitrate and potassium chloride were used as sources of nitrogen and potassium in the standard concentrated superphosphate treatment and also when supplemental applications of these nutrient elements were needed to balance soil treatments with different nitric phosphate and commercial fertilizer materials. The materials used represent a wide range of characteristics as to grade and water solubility of phosphorus. The materials produced by processes I and IV contain negligible amounts of sulfur.

Procedure

The data reported in this paper were obtained from field or greenhouse experi-

ments conducted in eleven cooperating states. The experiments were carried out on soils representing many of the major groups in the United States. Field experiments were usually of randomized block design. The treatments included no-phosphorus, concentrated superphosphate, various nitric phosphates, and comparable commercial-type materials. Field treatments were arranged so that in each experiment all plots, including the no-phosphorus plots, received the same quantities of nitrogen and potassium. The actual amounts used were determined to provide adequate quantities for crop needs and were varied with soil and crop situations. The tests were thus designed to study only crop responses to phosphate in the various materials included in the tests.

Treatment rates were based on equal weights of available phosphorus pentoxide furnished by each fertilizer tested. In most tests treatment rates were in the

range of 30 to 50 pounds of phosphorus pentoxide per acre. A few special investigations included treatment rates as low as 15 pounds, and a few others were as high as 300 pounds of phosphorus pentoxide per acre.

Most of the results were obtained from single-year experiments. There were, however, a few rotation experiments and one residual study of 5 years' duration.

Methods of Compiling Data

Data used in this paper have been restricted to those obtained in experiments in which there was a statistically significant (19 to 1 odds) response to phosphorus. Usually the data have been combined for individual or closely related crops. In such cases averages are reported for actual yields. In some instances yield data for a number of dissimilar crops have been combined, by computing a relative yield index

Table II. Yields and Relative Yield Increases of Corn (Grain) in Relation to Soil Treatments with Phosphate Fertilizers

(Data from Alabama, Georgia, Kentucky, Virginia, Tennessee, Iowa, and New York)

Fertilizer	No. of Expts.	Av. Yield Exptl. Fertilizer, Bu./A.	Rel. Yield Increase, % CSP	Rel. Yield, % CSP
12-32-0 NP-I	28	63.6	92	99
17-22-0 NP-I	29	61.2	78	95
14-14-14 NP-I	19	46.2	94	98
11-11-11 NP-II	16	49.3	84	94
4-12-12 NP-II	2	38.4	95	94
12-12-12 NP-III	2	43.0	63	81
14-11-11 NP-IV	2	24.3	74	88
10-10-10 L-Com.	12	52.0	78	92
10-10-10 H-Com.	11	53.6	84	95
21-53-0 DAP	8	59.6	88	96

Table III. Yields and Relative Yield Increases of Seed Cotton in Relation to Soil Treatments with Fertilizers

(Data from Alabama, Mississippi, and Tennessee)

Fertilizer	No. of Expts.	Av. Yield Exptl. Fertilizer, Lb./A.	Rel. Yield Increase, % CSP	Rel. Yield, % CSP
12-32-0 NP-I	8	965	106	103
17-22-0 NP-I	8	950	115	108
14-14-14 NP-I	19	1,034	82	94
11-11-11 NP-II	19	1,114	104	101
10-10-10 L-Com.	11	1,102	101	100

expressed as a percentage of the yield obtained with concentrated superphosphate. In such cases concentrated superphosphate-treated plots have a relative yield of 100.

In comparing fertilizers, the increase in yield from different fertilizers is often of greater interest than the actual yields obtained. In nearly all tables presented, the relative yield increase is reported. This value was calculated as follows:

$$\text{Relative yield increase} = \frac{\text{yield of experimental fertilizer} - \text{yield of no P}}{\text{yield of CSP} - \text{yield of no P}} \times 100$$

In such cases the yield increase from concentrated superphosphate is 100, and other materials might have greater or lower values. Where actual yield responses are small, slight differences between actual yields from concentrated superphosphate and experimental fertilizer plots may be reflected in greatly different relative yield increase figures. This tendency for wide fluctuations in relative yield increase values must be recognized in comparing results on this basis.

Experimental Results

Response Data for Crops The average yields, relative yields, and relative yield increase data for the various crops are recorded in Tables II to V.

The average yield, relative yield, and relative yield increase data for corn are shown in Table II. In these tests two nitric phosphates, 12-12-12 and 14-11-11, produced by Processes III and IV, appear to be distinctly inferior to the other materials. However, these materials were used in only two of the experiments. Consequently, comparisons must be made with considerable caution. Except for 12-12-12 and 14-11-11, the nitric phosphates increased corn yields as much as did the commercial-type fertilizer mixtures, but the increases were less than for concentrated superphosphate.

The yields for cotton in relation to various fertilizer treatments are shown in Table III. All of the materials except 14-14-14 gave yield increases equal to or greater than concentrated

superphosphate. This material was particularly poor in the tests in Alabama. If only experiments in Mississippi and Tennessee are considered, the relative yield with 14-14-14 was 104.

Definite sulfur deficiencies were encountered in 10 experiments (not summarized here) in the Coastal Plains area of Alabama. In these tests 14-14-14, which contains no appreciable amount of sulfur, gave yield increases only one half

as great as did the sulfur-containing 11-11-11. Yield increases from concentrated superphosphate in these tests were intermediate between those from 14-14-14 and 11-11-11. As nitric phosphate fertilizers prepared by either

Process I or Process IV are low in sulfur, these materials should be used in sulfur-deficient areas only when supplemented with sulfur-containing materials.

Yield data for fertilizer treatments on various vegetable crops in western Washington are shown in Table IV. In these tests, 12-32-0 gave yield increases for all of the crops greater than those produced by the other nitric phosphate materials, except 6-18-0 on corn. Also, 6-18-0 gave generally better average yield increases than 14-14-14 for all crops except potatoes. The nitric phosphates were as effective as the two 10-10-10 commercial-type mixtures for the fertilization of vegetable crop soils under these conditions. The yield increases for the various fertilizer materials used in these tests were in approximately the same relative order as the

Table IV. Yields and Relative Yield Increases of Vegetable Crops in Western Washington as Related to Soil Treatment with Phosphate Fertilizers

Crop and Fertilizer	No. of Expts.	Av. Yield Exptl. Fertilizer, Tons/A.	Rel. Yield Increase, % CSP	Rel. Yield, % CSP
Pole beans				
12-32-0 NP-I	6	7.55	93	96
14-14-14 NP-I	3	6.25	69	89
6-18-0 NP-II	2	8.46	89	94
10-10-10 L-Com.	3	6.13	64	87
10-10-10 H-Com.	3	6.43	76	92
Cucumbers				
12-32-0 NP-I	6	10.47	90	94
14-14-14 NP-I	2	13.73	68	91
6-18-0 NP-II	3	7.24	81	85
10-10-10 L-Com.	4	10.57	84	92
10-10-10 H-Com.	4	10.88	90	95
Potatoes				
12-32-0 NP-I	6	16.25	94	99
14-14-14 NP-I	3	16.95	94	98
6-18-0 NP-II	3	15.09	82	96
10-10-10 L-Com.	3	16.98	95	98
10-10-10 H-Com.	3	16.97	95	98
Sweet Corn				
12-32-0	2	7.72	94	98
14-14-14 NP-I	1	5.81	69	92
6-18-0 NP-II	1	9.50	101	101
10-10-10 L-Com.	1	5.57	53	89
10-10-10 H-Com.	1	6.11	88	97
All crops				
12-32-0 NP-I	20	11.05	92	97
14-14-14 NP-I	9	11.43	82	94
6-18-0 NP-II	9	10.37	85	93
10-10-10 L-Com.	11	10.65	84	94
10-10-10 H-Com.	11	10.89	89	96

Table V. Yields and Relative Yield Increases of Small Grains (Grain Production) in Relation to Soil Treatment with Phosphate Fertilizers

(Data from Alabama, Georgia, Kentucky, North Carolina, Virginia, Colorado, Iowa, New York, and Washington)

Fertilizer	No. of Expts.	Av. Yield Exptl. Fertilizer, Bu./A.	Rel. Yield Increase, % CSP	Rel. Yield, % CSP
12-32-0 NP-I	32	36.8	105	101
17-22-0 NP-I	33	35.5	93	98
14-14-14 NP-I	17	24.6	104	102
11-11-11 NP-II	17	30.5	108	102
12-12-12 NP-III	6	34.2	62	91
10-10-10 L-Com.	17	30.6	98	99
10-10-10 H-Com.	14	31.4	108	102

Table VI. Average Relative Yield and Relative Yield Increases of Legume Crops to Residual Effects of Nitric Phosphates Applied to Previous Row or Grain Crops

(Data from Colorado, New York, Virginia, and Washington)

Fertilizer	No. of Expts.	Av. Rel. Yield Exptl. Fertilizer, % CSP	Rel. Yield Increase, % CSP
12-32-0 NP-I	6	103	118
17-22-0 NP-I	6	106	135
14-14-14 NP-I	3	98	89
11-11-11 NP-II	1	103	110

Legume crops included red clover, clover-grass mixtures, and alfalfa.

water solubility of the contained phosphate.

The yield data for small grains are shown in Table V. The nitric phosphates, with the exception of the 12-12-12 Process III material, compared favorably with concentrated superphosphate and the 10-10-10 commercial-type materials. The phosphate contained in the 12-12-12 fertilizer is 7% water-soluble; phosphate in 14-14-14 is 9% water-soluble. The difference in water solubility, therefore, does not account for the lower crop yields with 12-12-12.

Residual Effects on Legumes A few data were obtained with legumes or legume-grass mixtures the second or third year after soil treatment. The design and conditions of the experiments varied, but the yield response data are similar. The average relative yields and relative yield increases are shown in Table VI. The experiments included red clover in Virginia on soils cropped to corn and wheat the two previous years and treated with fertilizer each year at 30 pounds of phosphorus pentoxide per acre. Alfalfa yields were obtained for 3 years after treatment with 250 and 300 pounds of phosphorus pentoxide per acre in Colorado and Washington, respectively. In New York, yields of a clover and grass mixture were secured the second year following treatment with 30 pounds of phosphorus pentoxide per acre. While the experiments vary in treatment, rate, soils, and crops, the results were similar. The yield response data in Table VI

indicate that the residual benefits from nitric phosphates were closely similar to those from concentrated superphosphate. Yields with 14-14-14 were somewhat lower than with concentrated superphosphate.

Yield Responses on Alkaline Soils

A few field experiments were conducted in Iowa and Colorado on soils varying in pH from 7.4 to 7.8 (Table VII). In all cases, 12-32-0 gave results closely similar to those from concentrated superphosphate. The yields from 17-22-0 were slightly lower, but the differences were not statistically significant. A comparison of these data with those for corn in Table II and small grains in Table V indicates that these two nitric phosphates performed in much the same manner on both acid and alkaline soils.

Particle Size

Twenty-six experiments were conducted with 11-11-11, in which comparison of effect

of particle size on crop response can be made. In these experiments materials of -12 +50 and -40-mesh particle size were used (Table VIII). The relative yields for the two sizes differed by less than 1%. These data indicate that granulation has not appreciably affected crop growth.

Water Solubility of Phosphorus Pentoxide

The nitric phosphate materials often contain only small amounts of water-soluble phosphorus pentoxide. The nitric phosphates used in any appreciable number of field experiments reported had from 1 to 44% of their available phosphorus pentoxide in a water-soluble form. Concentrated superphosphate and commercial-type 10-10-10 provided materials with higher percentages of water-soluble phosphorus pentoxide. In Figure 1 the average relative yield increases with each fertilizer and crop are plotted against the percentage of phosphorus pentoxide in the fertilizers that are water-soluble.

For all crops and all fertilizers there was no definite relationship between the water solubility of phosphate in fertilizers and the relative increase in crop yields. Experience indicates, however, that water solubility is an important factor in the efficiency of phosphate fertilizers under certain conditions. It is usually most important with crops having restricted root systems growing under conditions in which nutrient supply or rate of crop growth makes it difficult for plants to assimilate phos-

Table VII. Average Relative Yield and Relative Yield Increases of Row and Small Grain Crops Grown on Alkaline Soils (pH 7.4 to 7.8) in Iowa and Colorado

Crop and Fertilizer	No. of Expts.	Av. Rel. Yield Exptl. Fertilizer	Rel. Yield Increase
Row crops ^a			
12-32-0 NP-I	7	101	106
17-22-0 NP-I	5	97	75
Small grains ^b			
12-32-0 NP-I	6	100	100
17-22-0 NP-I	6	95	80

^a Row crops included 4 crops corn, 2 crops sugar beets, 1 crop potatoes.

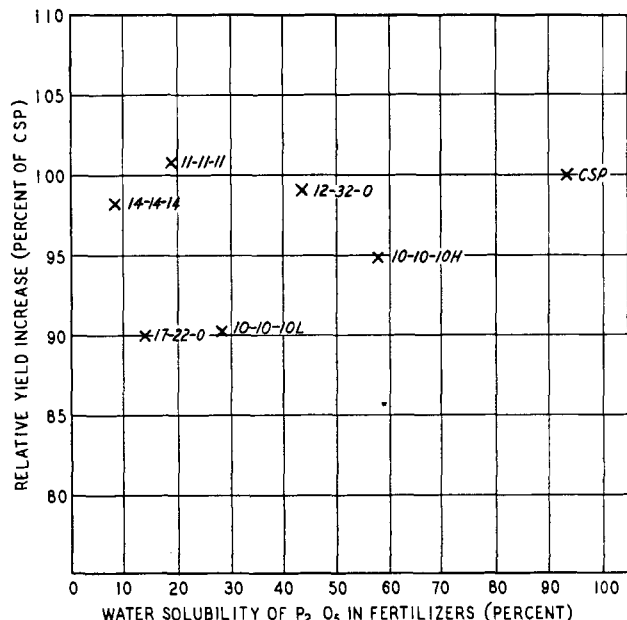
^b Small grain crops included 4 crops barley, 2 crops oats.

phorus fast enough to meet the requirements of growing tissues. Corn, during periods of rapid growth, and vegetable crops, because of limited root systems or short seasons of growth, are the crops employed most nearly meeting these conditions. In Figure 1 there is shown a trend toward greater yield increases for vegetable crops with increased water solubility of the fertilizer phosphate. In the case of corn, there is a less definite trend in this direction. Trends are not apparent for the other crops.

The average relative yield increase for all crops, weighted according to numbers of experiments with each crop, in relation to the degree of water solubility of phosphorus pentoxide in the fertilizer, is shown in Figure 2. The points on this figure and those in Figure 1 indicate that, on an average, the phosphorus in the NP 17-22-0 and in the commercial-type 10-10-10 L was less available to crop plants than that in the other fertilizers.

As 80 field experiments are included in the 17-22-0 average and 61 in the 10-10-10 L average, the lower efficiency of these materials appears to be real. If the lower efficiency of these

Figure 2. Average relative yield increase for all crops in relation to degree of water solubility of P_2O_5 in fertilizers



materials is explained on the basis of the low water solubility of the phosphorus pentoxide, then the satisfactory performance of low water-soluble 14-14-14 and 11-11-11, which also contain only small proportions of water-soluble phosphate, needs a further explanation.

Studies with a polarizing microscope have not suggested any reason for the differences observed. Both 17-22-0 and 14-14-14 contain anhydrous dicalcium phosphate as the major phosphate phase. Apatitelike material is minor in 14-14-14 and 17-22-0; it is more abundant in 11-11-11 and is a major phase in 12-12-12 and 14-11-11.

Discussion

The phosphate in nitric phosphate fertilizers has been shown to be generally as satisfactory for crop production as the phosphate in concentrated superphosphate and commercial-type fertilizer mixtures. In a few instances, some of the nitric phosphates with phosphorus pentoxide of low water solubility appear to be inferior to concentrated superphosphate. But some of the commercial-type mixed fertilizers of low

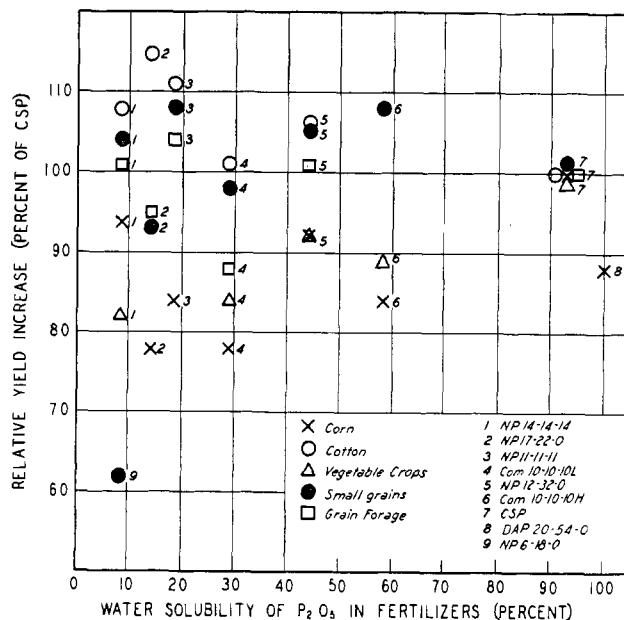


Figure 1. Relative yield increases of five crops (average of all field tests) to various fertilizers as related to degree of water solubility of phosphate

water solubility gave similar poor performances.

General considerations indicate that the inferiority of some nitric phosphates and commercial-type fertilizer mixtures under certain conditions may result from the transformation of large proportions of the contained phosphate to the dicalcium form during the ammoniation process. In the few tests in which a comparison was made, the nitric phosphates and commercial-type mixed fertilizers induced yield increases equal to or greater than those induced by dicalcium phosphate. Since some of the nitric phosphates of low water solubility performed as well as concentrated superphosphate, the phosphate compounds in the various materials may need further investigation. It now seems, therefore, that any final solution of the problem of quality of phosphate in fertilizers must come from a more complete characterization of the compounds of phosphorus involved as well as from crop response.

Acknowledgment

The yield data on which the paper is based were obtained from field experiments conducted under cooperative projects between TVA and state agricultural experiment stations in Alabama, Colorado, Georgia, Iowa, Kentucky, Mississippi, New York, North Carolina, Tennessee, Virginia, and Washington. Microscopic examination of fertilizer materials for principal phosphate compounds was made in the TVA Division of Chemical Development by James R. Lehr.

Literature Cited

- (1) D'Leny, W., *Fertilizer Soc. Engl. Proc.*, No. 24 (1953).
- (2) Hignett, T. P., *Chem. Eng.*, 58, No. 5, 166 (1951).
- (3) Rogers, H. T., *Agron. J.*, 43, 468 (1951).
- (4) Stewart, R., *Bull. doc. assoc. intern. fabr. superphos. (Paris)*, 14, 13 (1953).
- (5) Walthall, J. H., and Houston, E. C., Chap. 12, "Soil and Fertilizer Phosphorus in Crop Nutrition," Vol. IV, *Agronomy Monographs*, Academic Press, New York, 1953.

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Table VIII. Relative Yield of Various Crops as Related to Particle Size of 11-11-11 Fertilizers

Particle Size, U. S. Screen	No. of Expts.	Relative Yield No P 11-11-11	
-12 +50	26	49	102
-40	26	49	102

Crops grown included wheat, oats, corn, and cotton.