A STUDY OF THE UTILIZATION BY OATS OF PHOSPHORUS FROM THE SOIL AND FROM VARIOUS PHOSPHATIC FERTILIZERS AS MEASURED BY TRACER TECHNIQUES

by

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3

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (continued)

LIST OF FIGURES

INTRODUCTION

Phosphorus is applied to soils in any of a number of materials ranging from the manures to highly concentrated commercial fertilizers. The availability to plants of the phosphorus in these is known to vary. It is of considerable economic importance to both fertilizer producer and farmer to have an evaluation of the relative availability to crops of the phosphorus in the various fertilizer materials. The radioactive isotope of phosphorus, P^{32}, has offered a new approach to this problem.

Radioactive phosphorus was first used in soil and fertilizer studies around 1937. However, no really intensive investigations were possible prior to the present post war period because inadequate amounts of P^{32} were available. Following the war, relatively large quantities of P^{32}, produced by the atomic pile, became available for experimentation with growing plants. Since 1946, when the first cooperative study using P^{32} tagged phosphate fertilizers was organized by the New York and North Carolina Agricultural Experiment Stations and the Division of Soils, Fertilizer, and Irrigation of the United States Department of Agriculture, cooperative work with radioactive phosphorus has expanded tremendously. At the present time many of the state agricultural experiment stations are participating, especially on a regional basis.

Other agencies supporting these cooperative field experiments are the Fertilizer Industry Committee on Radioactive and Tagged Element Research, the Atomic Energy Commission, and the Bureau of Plant Industry, Soils, and Agricultural Engineering. The Regional Soil Research Committees are responsible for the overall planning and coordination of the work in each land-grant college region. This is accomplished for the most part, in regional phosphorus work conferences held each fall.

Before the advent of tracer methods, evaluation of the availability of various phosphatic materials depended wholly upon measurements of yield differences and upon comparisons of the total phosphorus content of plants grown on fertilized and unfertilized soils abnormally low in content of soil phosphorus. It was necessary to confine fertilizer availability studies to the relatively infertile soils in order to obtain yield differences sufficiently large to be significant. The validity of applying results obtained on these soils to more fertile soils was, therefore, open to question. The use of radioactive phosphorus makes it possible to measure more exactly fertilizer phosphorus uptake on the more fertile soils, and thereby evaluate the relative availability of phosphate materials under conditions of higher fertility.

The use of the radioactive tracer technique to measure phosphorus availability differences is based on the assumption that the rate and amount of phosphorus uptake from the fertilizer by the plant is a measure of the availability of the fertilizer phosphorus. This assumption is considered valid

whether there is a yield response or not. That is, the tracer technique is considered a somewhat more sensitive method of measuring availability than the yield measurement, although the final test of the value of a phosphorus compound as a fertilizer material should be made under conditions of yield response.

The availability of different phosphorus compounds to plants is usually measured by:

(a) the percentage of plant phosphorus derived from the fertilizer.
(b) the percentage recovery of the fertilizer phosphorus applied.
(c) the yield response attributable to differences in the phosphate carriers.

Using radioactive phosphorus, it is now possible to measure the percentage of plant phosphorus derived from the fertilizer. This overcomes the main weakness of the earlier work on phosphorus availability, which lay in the fact that it was impossible to tell what portion of the phosphorus absorbed by plants was derived from the fertilizer applied at planting time. Knowing the percentage of phosphorus derived from the fertilizer, the yield, and the amount of fertilizer applied to the soil, the percentage recovery of fertilizer phosphorus may be calculated. The yield response is determined in the usual way. For a comprehensive discussion of the basic concepts involved in soil and fertilizer studies with radioactive phosphorus, reference may be made to an article by Hendricks and Dean (5) and to a book by Kamen (7).

The work reported herein was part of a state-federal cooperative project undertaken in Michigan in the Spring of 1950. The primary purpose of this research was to study the utilization by the oat plant of phosphorus derived from different radioactive phosphatic fertilizers and from the soil. To this end, a field plot experiment was laid out in which the six phosphates under investigation were drilled with the oats. Plant samples were taken at intervals during the season and were analyzed for content of total phosphorus and radioactive phosphorus. From the weights of the individual samples, an estimate of yield at the various sampling periods was obtained. From these analytical data, calculations were made which furnished the information desired regarding phosphorus utilization. For the purpose of better characterizing the soil and the phosphates used, several physical and chemical tests were made on them in the laboratory.

There were two secondary purposes of this study. The first was to attempt to explain the differences found in the availability, as measured by the plant, of phosphorus in the various phosphatic materials. The second was to evaluate the relative effectiveness of the various criteria which may be used in measuring availability differences.

REVIEW OF LITERATURE

In the past the recovery of phosphate fertilizer by a crop has generally been determined by a comparison of the uptake of phosphorus by the fertilized and unfertilized crops. The extra phosphorus in the fertilized crop has been taken as the quantity coming from the fertilizer. One of the main weaknesses of the method is the assumption that the phosphorus taken up by the plant was the same phosphorus added in a specific fertilizer treatment. The addition of phosphorus stimulates plant growth and hence it has been considered possible that the increased growth of the fertilized crop will use more soil phosphorus that the unfertilized crop. If this occurs, the increased amount taken up by the fertilized crop would not represent the amount of phosphorus which came from the applied fertilizer.

In an experiment conducted by Spinks and Barber (16) to test this possibility, the recovery of applied phosphorus as measured by the tracer method was compared with the recovery as measured by the "difference" method. It was found that results obtained by the latter method were in error by almost forty percent. It was further found that for light applications more soil phosphorus may be taken up, but for very heavy applications, there may be less. The authors conclude that while the extent of the error may vary with the soil and the season, the old "difference" method of determining fertilizer uptake is unsound and can lead to large errors.

Results of a very different nature were obtained by White, Fried, and Ohlrogge (21). They calculated the percent utilization of applied phosphorus by the two methods and found a very close correlation.

In view of the questionable validity of the results of earlier investigations of phosphorus uptake by plants, this review of the literature is confined to the recent work involving tracer technique. As previously mentioned, most of the work on the utilization of phosphorus employing tracer technique has been done since 1946. The greater part of this work was of the cooperative type described in the introduction. Of the relatively large number of these cooperative experiments that have been undertaken since that time, very few have been published. Instead, the data have been made available to the cooperators in the form of compilations, summaries and progress reports. It is from these sources that most of the following information was obtained. This review is concerned only with those experiments which involved comparison of sources of phosphorus on oats. All of these were field-plot experiments.

In Wisconsin, Starostka, Jackson, and Attoe (19) found that ordinary superphosphate was the most effective source for oats, followed in order of decreasing effectiveness by calcium metaphosphate, alpha-tricalcium phosphate, and dicalcium phosphate.

Jackson, et al. (6), working in Wisconsin, found that the six phosphates compared ranked as follows in order of decreasing yield response: calcium metaphosphate, ordinary superphosphate, monoammonium phosphate = ammoniated superphosphate = alpha-tricalcium phosphate, dicalcium phosphate. The various phosphates ranked as follows in order of decreasing average percentage of total plant phosphorus derived from the fertilizer: monoammonium phosphate, ordinary superphosphate = ammoniated superphosphate, alpha-tricalcium phosphate = dicalcium phosphate, calcium metaphosphate.

Kaufman, Marriott, and Jackson (8), also working in Wisconsin found ordinary superphosphate was far more available to the plant, especially in the early part of the growing season, than calcium metaphosphate, fused tricalcium phosphate, or dicalcium phosphate. Ammoniated superphosphate was slightly more available than ordinary superphosphate. The nitric acid process dicalcium phosphate was nearly as available as the ordinary superphosphate but much more available than dicalcium phosphate with nitrogen or ordinary superphosphate with no nitrogen added. Ammonium phosphate proved to be the most available form of phosphate carrier. The order of availability was summarized as follows:

Ammonium phosphate	>	ammoniated super phos.	≥	superphos. mixed with amm. nitrate	≥	nitric phosphate	>	superphos. without any nitrogen (0-12-12)	>	ca-metaphos. Fused trical-phos. Dical.phos. (+ nitrogen)

In a group of experiments in Iowa, Black (1) determined the relative availabilities of various phosphates on four different soil types. On Clarion loam and Monona silt loam, ordinary superphosphate and calcium metaphosphate were found to be more available than dicalcium phosphate and alpha-tricalcium phosphate. On Marshall silt loam, however, ordinary superphosphate and dicalcium phosphate were superior to calcium metaphosphate and alpha-tricalcium phosphate. The order of availability on Seymour silt loam was also different from that on the Clarion and Monona soils. Here, the materials ranked as follows in decreasing order of availability: dicalcium phosphate, alpha-tricalcium phosphate, ordinary superphosphate, calcium metaphosphate.

Pesek (12) compared these same phosphates on three other Iowa soils and reported that in all cases ordinary superphosphate was the most effective source and fused tricalcium the least effective as measured by yield of total dry matter and uptake of fertilizer phosphorus at the boot and hard dough stages. Calcium metaphosphate and dicalcium phosphate were intermediate. The effectiveness of calcium metaphosphate was greater than that of dicalcium phosphate in the experiments on calcareous Ida silt loam and acid Grundy silt loam but was smaller than that of dicalcium phosphate in the experiment on acid Seymour silt loam. The relative differences between fertilizers as measured in final yield were generally smaller and of a lower level of significance than were the differences in yield of total dry matter and uptake of fertilizer phosphorus at the boot and hard dough stages.

In another experiment by Pesek (13) the following year, various phosphate materials were compared. The order of decreasing availability found was nitric phosphate (12-32-0), concentrated superphosphate, nitric phosphate (17-22-0), calcium metaphosphate (-40 mesh), calcium metaphosphate (-10 mesh), dicalcium phosphate.

Stanford and Nelson (18), also working in Iowa, found that ordinary superphosphate was more available than calcium metaphosphate, dicalcium phosphate, and alpha-tricalcium phosphate.

Lawton, Kawin, and Robertson (9) in an experiment in Michigan compared six different phosphates and found the following order of decreasing availability: ammonium phosphate, ammoniated superphosphate, ordinary superphosphate, dicalcium phosphate, calcium metaphosphate, fused tricalcium phosphate.

EXPERIMENTAL MATERIALS

A. Soil

The soil used in this experiment was a Brookston clay loam (yellow subsoil phase), a type well-suited to the growth of oats when artificially drained.

The Brookston series is described by Veatch (20) as loams and clay loams, with dark-colored plow soil, underlain by wet, mottled gritty clay to depths of several feet. The organic matter content and fertility are high; the clay is highly retentive and is generally moist or wet. These soils are non-acid or only slightly so; the carbonates may be leached out to depths of thirty inches or more. They are found on level plains and in valleys, and are wet or semi-swampy. The original vegetation was hardwood forests consisting of elm, soft maple, ash, shagbark hickory, basswood, swamp white oak, etc. These soils have high value for hay, corn, small grains, beets, beans, and alfalfa when artificially drained.

Several of the physical and chemical properties of this soil are presented in Table I.

B. Phosphates

The six phosphatic fertilizers used in this experiment were materials supplied by the United States Department of Agriculture, Beltsville, Maryland. The kinds used were ordinary superphosphate, calcium metaphosphate, dicalcium

TABLE I

SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE SOIL USED IN THIS EXPERIMENT

Property	Value
Mechanical analysis (hydrometer)	
greater than 50 microns	44.5 %
5 to 50 microns	24.3 %
2 to 5 microns	5.3 %
less than 2 microns	26.0 %
Organic matter content	6.1 %
Cation exchange capacity	24.80 m.e. per 100 gms.
Exchangeable calcium	18.14 m.e. per 100 gms.
Exchangeable magnesium	4.29 m.e. per 100 gms.
Exchangeable potassium	0.46 m.e. per 100 gms.
Calcium: magnesium ratio	4.2:1
pH (glass electrode)	6.58
Available phosphorus	
Spurway, reserve method	137 lbs. P per acre-6 in.
Bray, total available	190 lbs. P per acre-6 in.

phosphate, ammonium phosphate, alpha-tricalcium phosphate, and ammoniated superphosphate. Each of these was furnished in both the radioactive and the non-radioactive form. Except for the presence of the radioactive isotope of phosphorus, P^{32}, each radioactive phosphate was identical with the corresponding non-radioactive phosphate.

The specific activity of each radioactive phosphate was reported as 0.2 millicuries per gram of P_2O_5. The pile date for each material was April 5, 1950.

Data relative to certain physical and chemical characteristics of the various phosphates, furnished by the laboratories of the Bureau of Plant Industry, Soils, and Agricultural Engineering, are given in Table II. The author's data on particle size distribution for these materials are presented in Table III.

TABLE II

SOME PHYSICAL AND CHEMICAL PROPERTIES OF THE PHOSPHATIC FERTILIZERS USED IN THIS EXPERIMENT*

Phosphate form	Lot No.	Fineness, mesh	% NH_3	% Total P_2O_5	Solubility of P, % of Total		
					Water-sol.	Citrate-sol.	Available
Ordinary super-phosphate	2743	-16		20.5	86.2	11.1	97.3
Calcium meta-phosphate	2745-b	-40		64.8	a/	93.0	93.0
Dicalcium phosphate	2761	---		34.1	4.8	95.2	100
Ammonium phosphate	2762	-16	7.6	33.4	100	----	100
Alpha-tricalcium phosphate	2699	-40		28.7	a/	65.7	65.7
Ammoniated super-phosphate	2750	-16	4.13	19.6	42.8	37.3	80.1

* Data supplied by the laboratories of the Bureau of Plant Industry, Soils, and Agricultural Engineering, Beltsville, Md.

a/ The order of 1% or less.

TABLE III

PARTICLE SIZE DISTRIBUTION OF THE PHOSPHATES

Source of phosphate	Greater than 8 mesh	8-20 mesh	20-40 mesh	40-60 mesh	60-80 mesh	80-100 mesh	100-200 mesh	Less than 200 mesh
Ordinary superphosphate	8.1	12.8	9.1	14.7	21.4	6.2	17.9	8.3
Calcium metaphosphate	0.0	0.1	0.4	35.4	13.2	12.4	19.8	17.9
Dicalcium phosphate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Ammonium phosphate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100.0
Alpha-tricalcium phosphate	0.0	0.9	9.4	36.3	12.3	7.9	18.3	13.5
Ammoniated superphosphate	0.1	8.6	25.4	24.2	7.8	7.8	12.4	12.5

EXPERIMENTAL METHODS

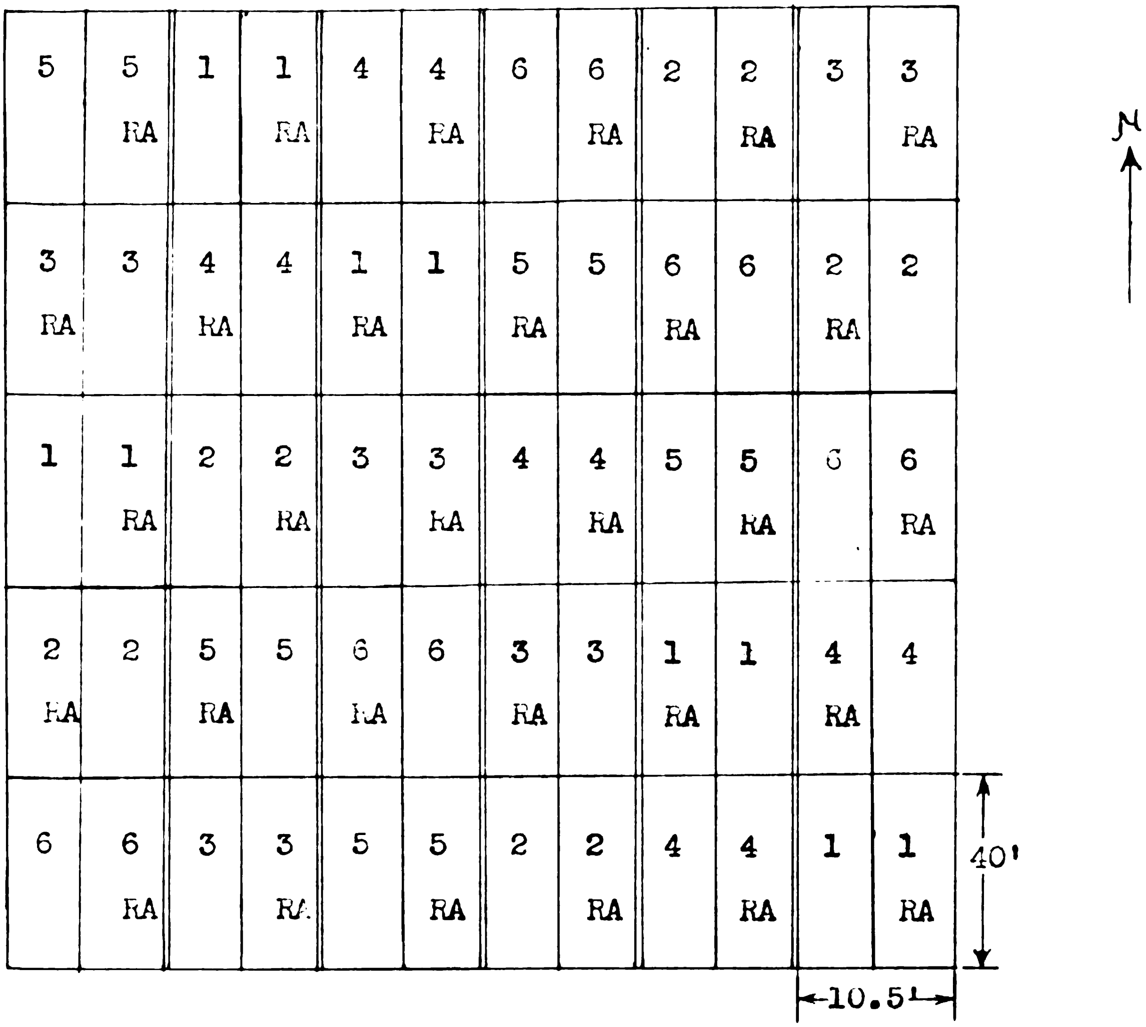
A. Field-plot experiment

This experiment was laid out on plots located on the Lee Ferden farm, Saginaw County, Michigan. These plots occupied about one-third of an acre within the 2.5 acre area whose exact location is given by the legal description NW$\frac{1}{4}$, NW$\frac{1}{4}$, NE$\frac{1}{4}$, NW$\frac{1}{4}$, Sec. 33, T9N, R3E. The plots were drained by means of tile lines and open ditches.

The statistical design employed was a "split-plot," randomized block design with five replications. One-half of each plot was fertilized with one of the radioactive phosphates and the other half with its non-radioactive counterpart. Plant material from the radioactive half was used in the phosphorus utilization studies; that from the non-radioactive half was used only for yield measurements.

As there were six treatments, each replicated five times, there was a total of thirty radioactive sub-plots and thirty non-radioactive sub-plots. Each sub-plot was 40 feet long by 5.25 feet wide and covered an area of 1/207.5 acre, so that the total area occupied by the plots was 0.2893 acre, an area 200 feet long and 63 feet wide. A diagram of the plot layout is presented in Figure 1.

The plots were plowed and fitted, and on April 20, 1950 they were seeded to Kent oats drilled one inch deep in rows



5	5 RA	1	1 RA	4	4 RA	6	6 RA	2	2 RA	3	3 RA
3 RA	3	4 RA	4	1 RA	1	5 RA	5	6 RA	6	2 RA	2
1	1 RA	2	2 RA	3	3 RA	4	4 RA	5	5 RA	6	6 RA
2 RA	2	5 RA	5	6 RA	6	3 RA	3	1 RA	1	4 RA	4
6	6 RA	3	3 RA	5	5 RA	2	2 RA	4	4 RA	1	1 RA

(Not drawn to scale)

1 Ordinary superphosphate
2 Calcium metaphosphate
3 Dicalcium phosphate
4 Ammonium phosphate
5 Alpha-tricalcium phosphate
6 Ammoniated superphosphate
RA Radioactive

Fig. 1 Statistical arrangement of the experimental plots.

seven inches apart at the rate of 1 1/2 bushels per acre. There were nine rows per sub-plot. The inner seven rows of each radioactive sub-plot were fertilized with one of these radioactive phosphates; the two outer rows were fertilized with the same phosphate material in the non-radioactive form and served as guard rows. All of the rows in a given non-radioactive sub-plot received the same fertilizer treatment.

Both phosphates and supplemental fertilizers were applied with the seed in the drill row. The phosphates were applied at the rate of 60 pounds of total P_2O_5 per acre. Nitrogen was applied as NH_4NO_3 at the rate of 14 pounds nitrogen per acre and potassium as KCl at the rate of 27 pounds K_2O per acre. This was approximately equivalent to the application of 333 pounds of a fertilizer with the analysis 4-18-8.

The radioactive phosphates used in this experiment were weighed and packaged at Beltsville, the exact amount required for one row being placed in an envelope. Altogether 540 such envelopes containing phosphates were required. The weight of each type of phosphate applied per 40 foot row was as follows:

1. 71.6 gms. of ordinary superphosphate
2. 22.6 gms. of calcium metaphosphate
3. 43.1 gms. of dicalcium phosphate
4. 43.9 gms. of ammonium phosphate
5. 51.0 gms. of alpha-tricalcium phosphate
6. 74.9 gms. of ammoniated superphosphate

The weight of P_2O_5 per row supplied by these applications amounted to 0.0323 pounds, so that a total of 6.777 pounds of radioactive P_2O_5 was required, having an initial P^{32} content of 614.5 millicuries. A total of 10.650 pounds of nonradioactive P_2O_5 was used.

The grain drill, loaned by the University of Wisconsin for this experiment, was a 9-hole McCormick-Deering equipped with a special attachment for the distribution of the phosphates. This attachment, designed by the Bureau of Plant Industry, Soils and Agricultural Engineering and assembled at the University of Wisconsin, consisted essentially of three parallel belts, each about 12 inches wide. The upper surface of each belt was divided lengthwise into three equal parts by two Lucite partitions. Preliminary to drilling each plot, the grain drill was stopped and the contents of nine envelopes containing the required form of phosphate were distributed in uniform bands along the entire length of the belts. The belts were geared to the wheels of the grain drill in such a way that the phosphates were deposited evenly in the drill rows as the grain drill moved across the plot.

Amounts of the two supplemental fertilizers sufficient for all of the plots were mixed together and placed in the grain drill fertilizer hopper prior to beginning operations. From this hopper the supplemental mixture was distributed to the drill rows in the usual manner. Drilling was begun in the southwest corner of the plot area.

Samples of the above-ground plant material were obtained from the radioactive sub-plots at four different times during the growing season. At the first sampling period, the sample removed from a sub-plot represented about five percent of the total plant material present, and at each of the three subsequent periods represented approximately three percent.

The method of sampling a sub-plot consisted of removing all of the plants in a more or less randomly chosen meter length section of a row, avoiding those plants near each end of the row. At the first sampling period, the five center rows were sampled in this fashion, the combined plant material representing the sub-plot sample. At each of the later sampling periods, only three of the five center rows in each sub-plot were sampled, usually the central three.

The first sampling period was June 2 at which time the plants were 43 days old and averaged about six inches in height. They were harvested by cutting them off just above the surface of the ground.

At the second sampling on June 22, the plants were 63 days old and averaged about twenty-four inches in height. About one-half of the plants were either headed-out or else had begun to head-out. The plants were harvested at this date by pulling them out of the ground to eliminate the possibility of harvesting regrowth at some later date. The roots and all soil material were then discarded.

At the third sampling on July 4, the plants were 75 days old, were about 42-48 inches tall on the average, and were well headed-out. A few brown leaves were present near the base of many of the plants. Samples were taken by pulling the plants from the ground as before and removing the roots.

At the fourth sampling on July 25, the plants were 96 days old and averaged around 48 inches in height. Most of the plants were yellow at this stage; however, some were still green and others were a mixture of yellow and green. The plants were rather badly lodged, making it very difficult to sample properly. Samples were obtained by cutting the plants with a sickle about three inches above the ground. Since this was the final sampling of the radioactive plots, possible plant regrowth was of no concern.

On August 5, the non-radioactive sub-plots were sampled for measurement of the grain yields. At this time the plants were 107 days old, had all turned yellow, and were rather badly lodged. Incidental to the grain yield measurements, the total dry matter yield was determined for each sub-plot by weighing the sample in the field just prior to threshing. The sample of above ground plant material taken from a sub-plot represented about 28 percent of the material present.

The method of sampling a sub-plot consisted of removing all of the plants from a 20 foot length of each of the five center rows, beginning 10 feet in from each end of the row. The plants were cut with a sickle about three or four inches above the ground. The sheaves from the various plots were shocked together in the field and the heads were covered with cheesecloth to protect them from birds.

On August 14, the samples were threshed in the field using a trailer-mounted thresher constructed especially for use in experimental plot work. Weighings of both the entire sample and the grain were made on a dial-type spring scale.

B. Laboratory investigations

Plant material. As indicated above, plant roots were discarded, only the above-ground portion being used in the analyses. The plant material obtained at the four sampling periods from the radioactive sub-plots was prepared for analysis by drying in a draft oven at 60°C., followed by grinding in a Wiley mill to pass a one millimeter screen. The entire amount of each sample was passed through the Wiley mill and the ground material was mixed thoroughly by rolling diagonally back and forth on a large sheet of paper and weighed. The dry weights of these samples ranged from an average of 33.5 grams at the first harvest to an average of 553 grams at the fourth harvest. The yield of total dry matter in pounds per acre was estimated from the weights of the individual samples.

For the determination of phosphorus in the plants which was taken up from the fertilizer, samples of the plant material were ashed according to a modification of the procedure outlined by Piper (15). This is a wet digestion procedure employing sulfuric, nitric and perchloric acids. Ten grams of material from the first sampling were weighed into a 400 milliliter beaker, and 20 milliliters of a mixture of two parts perchloric acid (70-72%) to one part concentrated sulfuric acid were added from an automatic burette, then 25 milliliters of concentrated nitric acid were added. The beaker was covered with a watch glass, and after the initial violent reaction had subsided, an additional 25 milliliters of concentrated nitric acid were added. The beaker was then placed on a low temperature hot plate for one and one-half hours. At the end of this time, it was removed to a high temperature hot plate and heated until NO_2 fumes and $HClO_4$ fumes were gone and bubbling had ceased. It was further heated for several minutes after the appearance of H_2SO_4 fumes. If the digest contained charred and incompletely oxidized material, a little more nitric acid was added and heated again until excess HNO_3 was removed. This was repeated, if necessary, until the digest was clear.

Since both the specific activity of the phosphates and their concentration in the plant decrease with time, it was found necessary to ash larger amounts of the material taken at subsequent samplings in order to maintain a sufficiently high precision of counting. The sample size was increased to 20 grams of material taken at the second sampling from plots fertilized with calcium metaphosphate, dicalcium phosphate, and alpha-tricalcium phosphate. The ashing procedure was the same as that used with material obtained at the first sampling, the 20 gram sample being ashed as two ten-gram samples, and the digests combined.

It was necessary to ash 50 grams of material obtained at the third and fourth sampling periods. This large amount of material necessitated several changes in the procedure previously used, because of the excessive foaming produced. In order to prevent loss of material by foaming, it was necessary to carry out the digestion in a liter beaker, and to add the sample a little at a time with stirring over a period of about five minutes to a mixture of the three acids. This technique worked very well, apparently because oxidation of each increment of plant material proceded rapidly enough to prevent excessive frothing. The acid mixture used consisted of 30 milliliters of the perchloric acid-sulfuric acid combination described above plus 250 milliliters of concentrated nitric acid. Except for the larger amounts of acid used and the modified technique of mixing plant material and acids, this procedure was essentially the same as was used with the ten gram samples.

The procedure followed in preparing the digest for measurement of the radiophosphorus content was the same for each of the digests. Twenty milliliters of distilled water were added to the beaker to allow the heat of reaction with the sulfuric acid to help disolve and loosen the residue. Then an additional twenty milliliters were added to dilute the acid enough to prevent reaction with the filter paper in the subsequent filtration. Next, the solution was filtered through an 11 cm. Whatman No. 41 filter paper to remove sulfates and silica and was collected in a volumetric flask. The beaker and residue on the filter paper were rinsed several times with a stream of hot water, and the rinsings were added to the volumetric flask to make a total volume of 125 milliliters.

Standard solutions of the six radioactive phosphates were prepared by extracting the phosphorus with dilute sulfuric acid. The quantity of fertilizer used was that amount calculated to give a counting rate of about 200 counts per minute. The fertilizer was weighed into a beaker, dilute acid was added, and the solution was boiled for 15 minutes. Then it was cooled, undissolved material was removed by filtration, and the filtrate was made up to volume in a volumetric flask. The amount of concentrated sulfuric acid present in the solution was made approximately equal to that present in the plant digests. A duplicate set of fertilizer solutions was prepared using five times the amounts of fertilizer and acid previously used. The ratio of counts per minute to phosphorus concentration in this second set of solutions was found to agree very closely with the ratio obtained with the first set, therefore, the average of the two sets of data was used in calculating the fertilizer phosphorus content of the plant material.

Radiation measurements on the solutions of plant ash and on the standard solutions were made with a Tracerlab Auto Scaler - Mark II using a dipping tube. The solution to be measured was poured into a 125 milliliter tall form beaker, and the counter tube was immersed to a depth of approximately four centimeters. To assure absorption thickness sufficient to completely absorb the beta radiation emitted by atoms furthest from the tube, it was necessary to center the tube in the beaker so that there was at least seven-tenths of a centimeter of liquid on all sides. At least three series of 128 counts each were made for each sample. Correction for the background count was made on each average count. A standard solution of ammoniated superphosphate was counted at the beginning and end of each period of counting which usually covered about four hours. The counts were made following the directions outlined in the Auto Scaler manual (4).

Following the radiation measurements, the solutions were diluted and total phosphorus was determined colorimetrically as molybdenum blue. The procedure followed was as outlined by Bray (3) using the Fiske-Subbarow reducing agent which is a mixture of sodium sulfite, sodium bisulfite, and amino-napthol-sulfonic acid. The color was allowed to develop for fifteen minutes and its intensity was then measured with a Lumetron photoelectric colorimeter, Model 400-A, using a 650 millimicron filter. Standards for comparison were prepared from mono-potassium phosphate.

Soil. The mechanical analysis of the soil was made using the hydrometer method as described by Bouyoucos (2).

Organic matter was determined by the rapid titration method of Walkley as modified by Peech and Dean (10).

The cation exchange capacity was measured according to the method proposed by Peech, et al. (11). Neutral normal ammonium acetate was used to saturate the exchange complex with ammonium ions, which were then replaced by means of an acidified 10 percent sodium chloride solution and determined by the Kjeldahl method.

Exchangeable calcium and magnesium determinations were made according to Piper's (14) method. The soil was leached with normal ammonium chloride to remove the exchangeable cations, and an aliquot of the leachate was taken for the determination of calcium and magnesium. Calcium was determined by precipitation as the oxalate, conversion of the oxalate to oxalic acid, and titration with 0.05 N potassium permanganate. Magnesium was determined as magnesium pyrophosphate.

Exchangeable potassium was determined on a portion of the ammonium chloride extract with a Perkin-Elmer flame photometer, Model 52-A, using an acetylene gas flame. The internal standard method was employed. A series of standard solutions for comparison was prepared from potassium chloride.

Measurements of soil reaction values were made with the glass electrode and the Beckman pH meter, Model H-2, using

1:1 soil-water suspensions. The soil-water mixtures were stirred at frequent intervals for fifteen minutes. Each mixture was stirred well just prior to taking a reading.

The available phosphorus level was determined by two rapid test methods, which differed only in the method of extraction used. One procedure was that of Spurway and Lawton (17) for the "reserve" soil phosphorus in which the extracting agent is 0.135 normal HCl. Ten-gram samples of soil were stirred with 40 milliliters of the extracting solution for one minute, filtered, and diluted 1:8. The extracted phosphorus was measured colorimetrically with the Lumetron photoelectric colorimeter.

The second method of extraction used was that of Bray (3) for removal of "total available" soil phosphorus. Five-gram samples of soil were stirred for 40 seconds with 50 milliliters of a solution 0.1 normal with respect to HCl and 0.03 normal in NH_4F, filtered, and diluted 1:5 for colorimetric determination.

All of the above-mentioned soil properties except cation exchange capacity and exchangeable cations were determined in duplicate on each of four samples taken at random from four different locations in the experimental plots. These samples were taken prior to seeding and fertilizing. The analytical data on individual samples agreed very well, indicating that the soil was homogenous across the entire plot area. Measurements of cation exchange capacity and exchangeable cations were made on duplicate weighings of a composite of the four soil samples.

Phosphates. The fixing capacity of the soil for the different forms of phosphate was estimated by adding the calculated amounts to soil samples in beakers in the laboratory and incubating for several days, then extracting with 0.135 normal HCl. The phosphate was added in amounts calculated to simulate 60 and 360 pounds per acre of total P_2O_5. Control samples with no phosphate added were incubated and extracted in the same manner.

The soil used was a composite of the four samples taken from the plots. Fifty gram samples of the composite were used for the 60 pound rate and fifteen gram samples for the 360 pound rate. The dry phosphates were mixed thoroughly with the soil samples, sufficient water was added to give 100 percent moisture content, and the mixture was stirred well. The soils were incubated under laboratory conditions for about one week until they had reached air dryness. The soil was then pulverized and extracted according to the method of Spurway and Lawton, which is described above. Phosphorus in the extract was measured colorimetrically.

The solubility of the various phosphates in different solvents was studied using 0.135 normal HCl, CO_2-free distilled water, and carbonic acid.

The study of solubility in 0.135 normal HCl was undertaken in an attempt to clarify the results of the fixation experiment.

For this reason, the procedures used were designed to simulate the extraction procedures followed in the fixation experiment. Samples of the six phosphates, three times the weight of those used at the 360 pound rate in the fixation experiment were weighed into beakers, larger samples being used for the sake of greater weighing accuracy. This weight would be the equivalent of a 360 pounds of P_2O_5 per acre application if added to 45 grams of soil, therefore, to obtain a 4:1 extraction ratio, 180 milliliters of acid was added. The mixture was stirred for one minute, and then decanted through 11 centimeter number one Whatman paper in an ordinary funnel. The filtrate was diluted, and phosphorus determined colorimetrically.

The above experiment was repeated with slight variations in which the solutions were filtered through a Buchner funnel using nine centimeter number 42 Whatman paper. In the second trial, the solution was stirred one minute and filtered. In the third trial, the solution was stirred continuously for 30 minutes and filtered. In the fourth experiment, the phosphates were screened and the 200-270 mesh fraction was stirred for one minute and then filtered.

The solubility of the phosphates in CO_2-free distilled water was measured by adding each fertilizer to the 100 milliliters of water in an Erlenmeyer flask. The phosphates were added in amounts calculated to contain equal quantities of total P_2O_5 and estimated to be sufficient to give solutions

saturated with respect to phosphorus. This was done in an attempt to simulate conditions which may exist in the field in close proximity to the fertilizer. The flasks were shaken intermittently for one hour, then a 10 milliliter aliquot was removed from the supernatant liquid and was filtered, diluted, and the phosphorus content determined colorimetrically by the method described above.

As a check on the degree of phosphorus saturation of the solutions, additional amounts of the phosphates equal to fifty percent of the original weights used were added to the flasks, 10 milliliters of water was added to replace that removed in sampling, and the above process was repeated.

To determine the solubility of the phosphates in carbonic acid, CO_2 was bubbled through the solution for 10 minutes, and the process of filtration, dilution, and phosphorus measurement was again repeated.

The particle size distribution of the different phosphates was measured by means of a nest of sieves of mesh size 8, 20, 40, 60, 80, and 100 fitted to a Cenco-Meinzer sieve shaker. A 50 gram sample was shaken at low speed for five minutes and the residue on each sieve was brushed into a weighing can and weighed.

All of the above-mentioned experiments with phosphates were made with duplicate samples.

RESULTS

A. Yield

Yield measurements were made on samples of above-ground plant material taken from the radioactive sub-plots at four different times during the growing season. Similar measurements were made on larger samples taken at harvest from the non-radioactive sub-plots, and in addition, the grain yields were determined on these samples. The results are presented in Tables IV and V for the radioactive and non-radioactive sub-plots respectively.

Inspection of Table IV shows that there were no significant differences in the yields obtained with the various phosphates at the first, second, and fourth sampling periods. At the third sampling, however, differences significant at the five percent level showed up. Here, the yield with ammonium phosphate was significantly larger than that obtained with either calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. Also, ammoniated superphosphate gave a yield significantly greater than that produced by dicalcium phosphate.

In Table V it is seen that there were no significant differences either in total dry matter yields or in grain yields on the non-radioactive plots at harvest time.

Weather conditions during the growing season are shown

TABLE IV

YIELDS OF TOTAL DRY MATTER FROM RADIOACTIVE PLOTS AT EACH SAMPLING PERIOD

Source of phosphate	Average yield in pounds per acre June 2	June 22	July 4	July 25
Ordinary superphosphate	298	3450	5930	9150
Calcium metaphosphate	310	3230	5710	9040
Dicalcium phosphate	382	3240	5160	8660
Ammonium phosphate	351	3960	7220	9880
Alpha-tricalcium phosphate	312	3710	5670	9730
Ammoniated superphosphate	359	4130	6600	8720
L.S.D. (.05)	N.S.	N.S.	1300	N.S.

TABLE V

YIELDS OF TOTAL DRY MATTER AND GRAIN FROM NON-RADIOACTIVE PLOTS AT HARVEST

Source of phosphate	Average yield expressed as pounds T.D.M./acre	bushels grain/acre
Ordinary superphosphate	6060	72.1
Calcium metaphosphate	5860	64.9
Dicalcium phosphate	6120	68.1
Ammonium phosphate	6640	68.6
Alpha-tricalcium phosphate	6130	69.4
Ammoniated superphosphate	6410	72.7
L.S.D. (.05)	N.S.	N.S.

below:

Month	Rainfall		Air temperature
April	3.57 in.	above normal	below normal
May	1.74 "	far below normal	about "
June	4.15 "	slightly above normal	" "
July	7.91 "	far above normal	" "
August	2.99 "	normal	" "

B. Phosphorus utilization by the plant.

Total phosphorus. The values for total phosphorus composition of the oat plant at various stages, expressed in percent, appear in Table VI and Figure 2. In Table VII the total phosphorus content of the crop is given in pounds per acre which permits the graphical expression of rate of uptake of phosphorus from the fertilizer as shown in Figure 3.

According to Table VI, on June 2 the total phosphorus concentration in plants fertilized with ammonium phosphate was significantly higher at the one percent level than in those which got ordinary superphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. Also, ammonium phosphate gave results significantly higher than those obtained with calcium metaphosphate at the five percent level. Plants fertilized with ammoniated superphosphate were significantly higher in total phosphorus at the five percent level than those fertilized with either dicalcium phosphate or alpha-tricalcium phosphate. At subsequent sampling periods, the differences between treatments were not significant.

During the season, there was a regular decrease in the concentration of total phosphorus in the plant for each of the

TABLE VI

CONCENTRATION OF TOTAL PHOSPHORUS IN DRY PLANT MATERIAL IN PERCENT

Source of phosphate	Average content of elemental phosphorus in percent			
	June 2	June 22	July 4	July 25
Ordinary superphosphate	0.583	0.323	0.235	0.231
Calcium metaphosphate	0.591	0.335	0.248	0.233
Dicalcium phosphate	0.529	0.333	0.244	0.239
Ammonium phosphate	0.703	0.355	0.258	0.237
Alpha-tricalcium phosphate	0.543	0.314	0.243	0.237
Ammoniated superphosphate	0.641	0.362	0.255	0.237
L.S.D. (.05)	0.086	N.S.	N.S.	N.S.
L.S.D. (.01)	0.117			

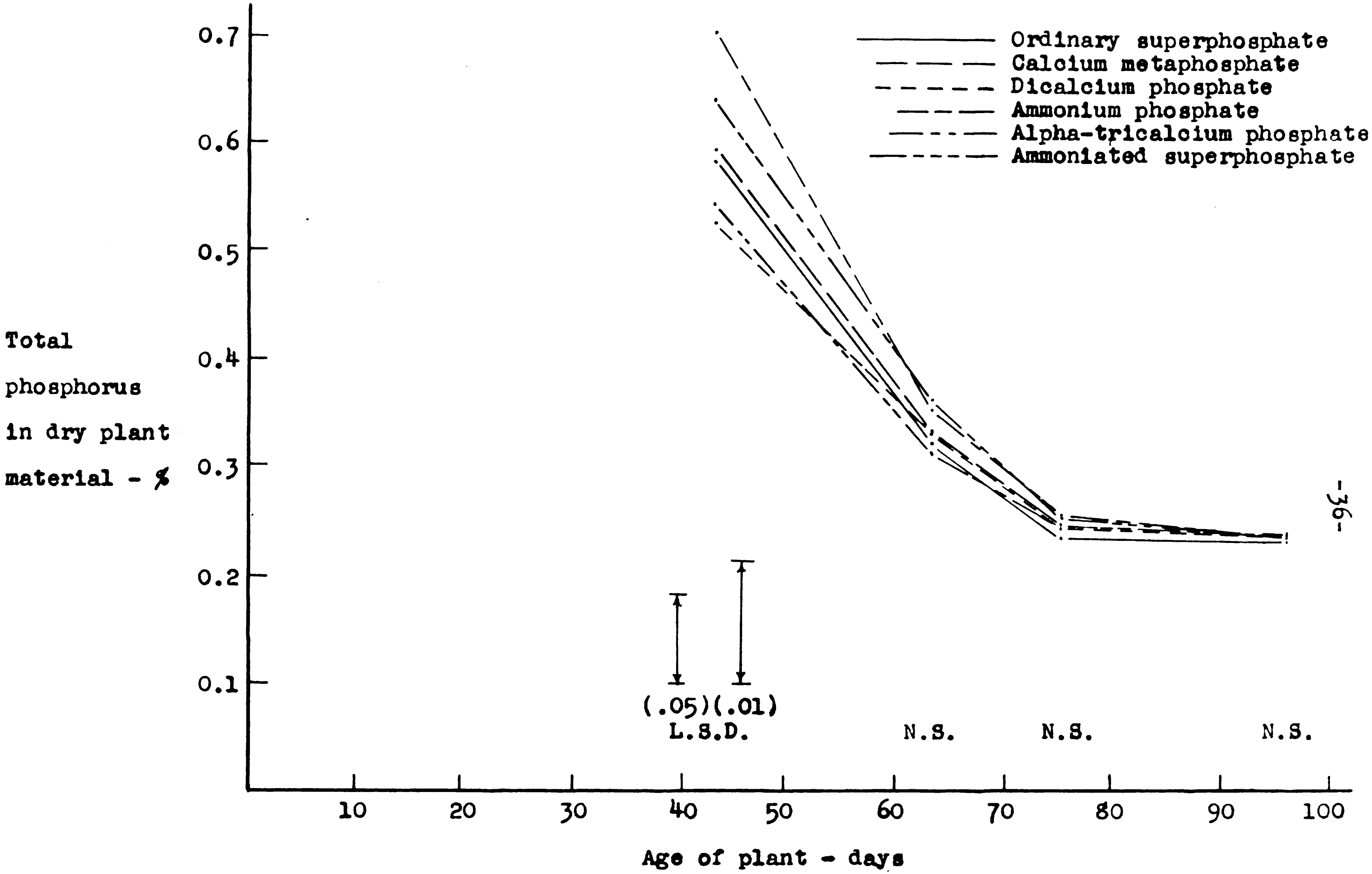


Fig. 2 The effect of source of fertilizer phosphate on the total phosphorus composition of the oat plant.

TABLE VII

CONCENTRATION OF TOTAL PHOSPHORUS IN DRY PLANT MATERIAL IN POUNDS PER ACRE

Source of Phosphate	Average content of elemental phosphorus in pounds per acre*			
	June 2	June 22	July 4	July 25
Ordinary superphosphate	1.74	11.2	14.0	21.1
Calcium metaphosphate	1.79	10.7	14.1	21.0
Dicalcium phosphate	2.03	10.8	12.5	20.6
Ammonium phosphate	2.47	14.1	18.6	23.4
Alpha-tricalcium phosphate	1.73	11.7	13.8	23.1
Ammoniated superphosphate	2.27	14.9	16.8	20.6

* To convert to pounds P_2O_5 per acre, multiply by 2.29.

L.S.D. (.05)	0.52	3.0	3.5	N.S.

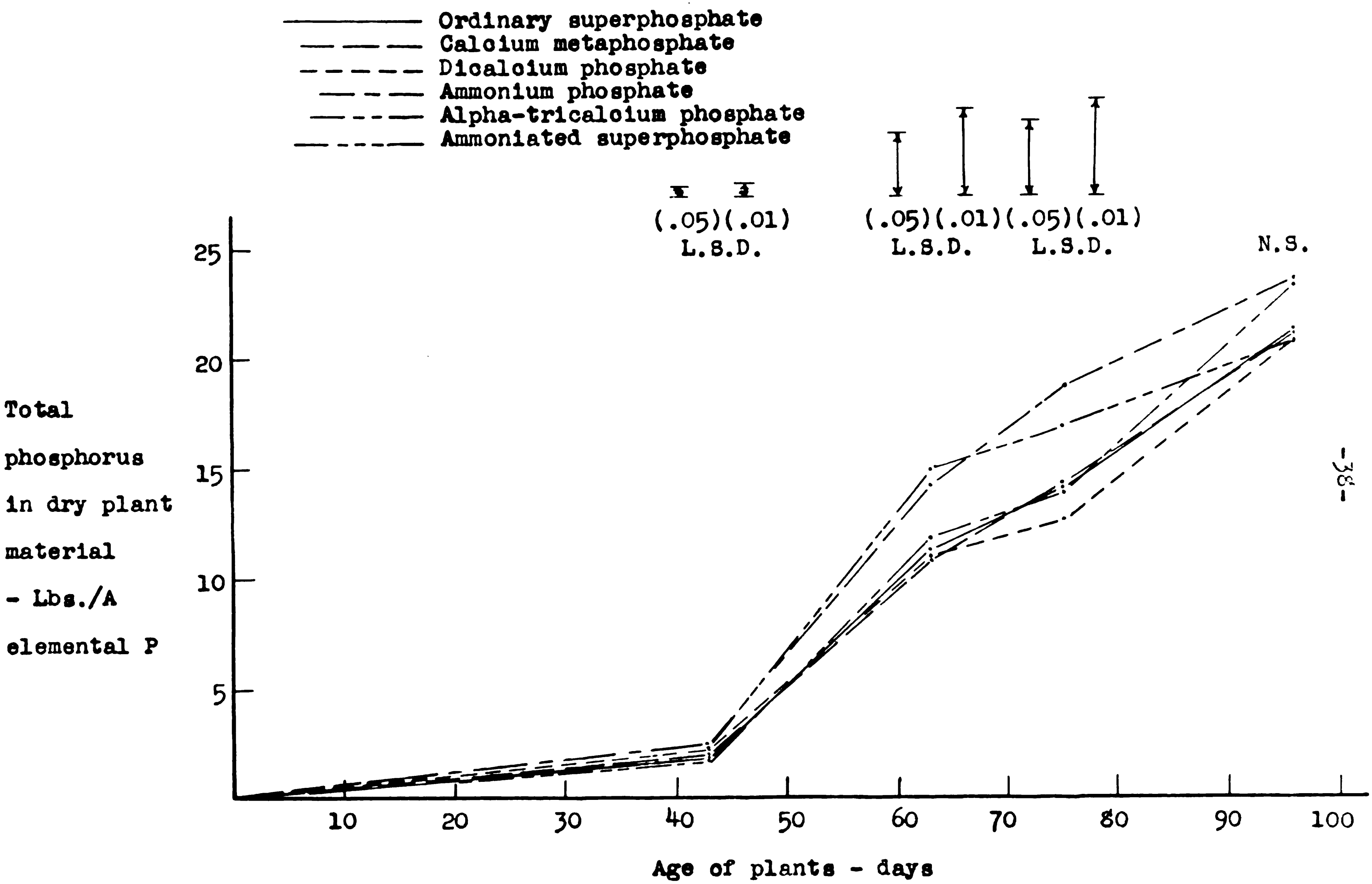


Fig. 3 Rate of uptake of phosphorus by the crop as related to the source of fertilizer phosphate.

phosphate treatments from a high of 0.70 percent on June 2 to a low of 0.23 percent on July 25. By the second sampling period on June 22, the total phosphorus composition of the plant had reached a common value, statistically, for all treatments. By the third sampling on July 4, the total phosphorus level had practically attained a constant value. These trends are illustrated in Figure 2. It is interesting to observe how the curves converge toward a constant value as the differences between treatments continuously decrease with time.

Inspection of the data in Table VII reveals another interesting development. It is seen that when total phosphorus content of the plant was expressed on a pounds per acre basis, significant treatment differences appeared at the first three sampling dates which varied somewhat from those obtained using the criterion of percent composition of total phosphorus. On June 2, ammonium phosphate again ranked above calcium metaphosphate, ordinary superphosphate, and alpha-tricalcium phosphate, but the differences were now significant only at the five percent level. It is further noted that when the results were expressed as pounds per acre, ammonium phosphate no longer ranked higher than dicalcium phosphate. Ammoniated superphosphate was again found to give higher results than alpha-tricalcium phosphate at the five percent level.

On June 22, significant treatment differences for total phosphorus absorption appeared where none were found by the former criterion. Ammonium phosphate gave results higher at the five percent level than either calcium metaphosphate or dicalcium phosphate. Ammoniated superphosphate was higher at the five percent level than either ordinary superphosphate, calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate.

Again on July 4, significant treatment differences were noted which were not found before. Ammonium phosphate was found to be higher at the five percent level than ordinary superphosphate, calcium metaphosphate, dicalcium phosphate, and alpha-tricalcium phosphate. At this time, ammoniated superphosphate was greater than only dicalcium phosphate. There were no significant differences between treatments at the last sampling on July 25.

Although the percent total phosphorus in the plant dropped uniformly throughout the growing season, the amount actually taken up per plant, and therefore, per acre, increased continuously as may be observed in Figure 3. This trend was, of course, due to the rapid increase in size of the plant which greatly overshadows the effect of percentage decrease in phosphorus, and was especially pronounced during the period, between June 2 and June 22, at which time the rate of uptake of total phosphorus was greatest. During this time, the total phosphorus composition decreased to about half its June 2 level, but the total dry weight of the plant increased more than tenfold.

The rate of phosphorus absorption between June 22 and July 4 dropped off in each instance, but it increased during the interval between July 4 and July 25 in all cases but two. The rate of absorption of total phosphorus where ammonium phosphate was used decreased even further, while that with ammoniated superphosphate remained the same. The slowest absorption occurred between planting time on April 20 and the first sampling on June 2.

Phosphorus from fertilizer. The amount of phosphorus in the plants which was derived from the fertilizer was determined, as described in the procedure, by measuring the radiation due to the radioisotope content. These values are presented as percentages in Table VIII and Figure 4, and in terms of pounds per acre in Table IX and Figure 5.

In Table VIII, the data show that on June 2 both ammonium phosphate and ammoniated superphosphate produced significantly higher contents of fertilizer phosphorus in the plant at the one percent level than were obtained with either ordinary superphosphate, calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. Ammonium phosphate also gave higher results at the five percent level than did ammoniated superphosphate at this time. Ordinary superphosphate was found to give results significantly higher at the one percent level than those with calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate.

TABLE VIII

CONCENTRATION OF FERTILIZER PHOSPHORUS IN DRY PLANT MATERIAL IN PERCENT

Source of phosphate	Average content of elemental phosphorus in percent			
	June 2	June 22	July 4	July 25
Ordinary superphosphate	0.182	0.062	0.033	0.030
Calcium metaphosphate	0.080	0.030	0.023	0.016
Dicalcium phosphate	0.113	0.042	0.028	0.021
Ammonium phosphate	0.393	0.078	0.063	0.042
Alpha-tricalcium phosphate	0.088	0.031	0.021	0.017
Ammoniated superphosphate	0.340	0.089	0.056	0.037
L.S.D. (.05)	0.050	0.012	0.015	0.012
L.S.D. (.01)	0.068	0.017	0.020	0.016

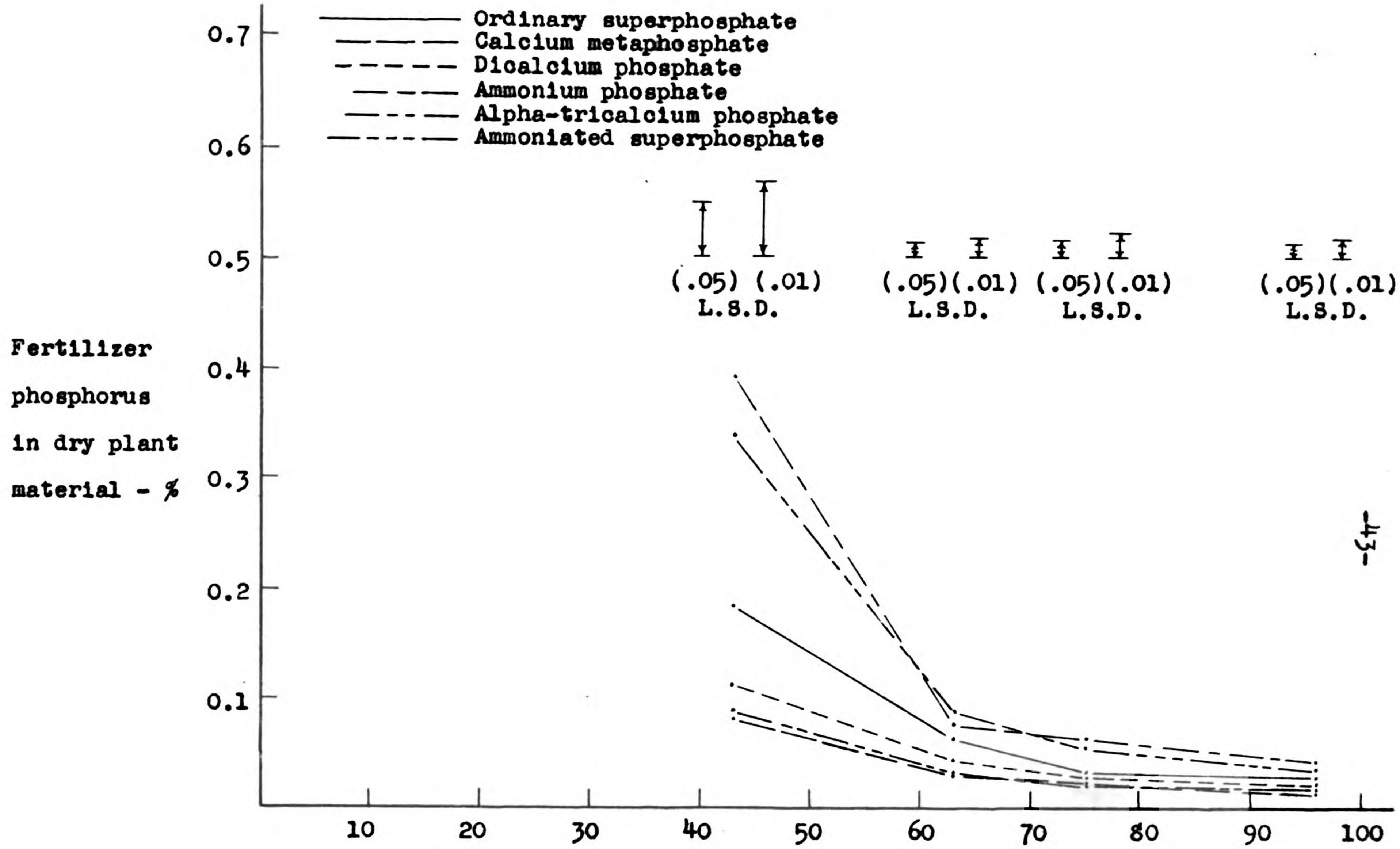


Fig. 4 The effect of source of fertilizer phosphate on the fertilizer phosphorus composition of the oat plant.

TABLE IX

CONCENTRATION OF FERTILIZER PHOSPHORUS IN DRY PLANT MATERIAL IN POUNDS PER ACRE

Source of Phosphate	Average content of elemental phosphorus in pounds per acre*			
	June 2	June 22	July 4	July 25
Ordinary superphosphate	0.55	2.14	1.97	2.78
Calcium metaphosphate	0.26	0.94	1.31	1.42
Dicalcium phosphate	0.43	1.32	1.50	1.80
Ammonium phosphate	1.40	3.04	4.48	4.20
Alpha-tricalcium phosphate	0.27	1.16	1.18	1.66
Ammoniated superphosphate	1.22	3.66	3.72	3.36

*To convert to pounds fertilizer P_2O_5 per acre, multiply by 2.29.

	June 2	June 22	July 4	July 25
L.S.D. (.05)	0.36	0.72	1.09	1.19
L.S.D. (.01)	0.49	0.98	1.48	1.62

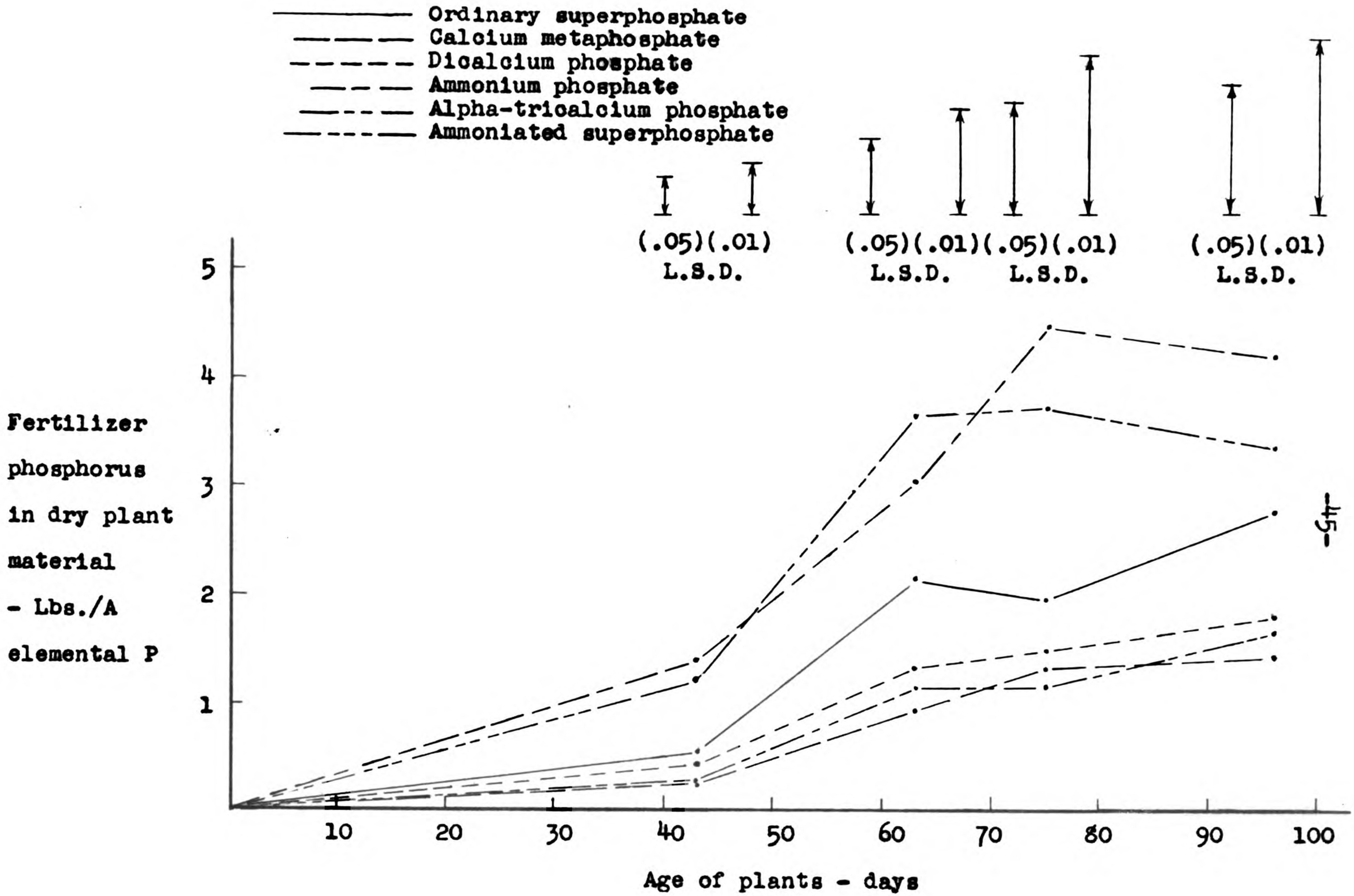


Fig. 5 Rate of uptake of fertilizer phosphorus by the crop as related to the source of fertilizer phosphate.

On June 22, the same situation existed with ordinary superphosphate as on June 2. The situation was also the same as before with ammoniated superphosphate. However, ammonium phosphate, still greater than calcium metaphosphate, dicalcium phosphate, and alpha-tricalcium phosphate at the one percent level, was now higher than ordinary superphosphate only at the five percent level, and was no longer higher than ammoniated superphosphate. It is interesting to note that for the first time dicalcium phosphate gave higher results than did calcium metaphosphate at the five percent level.

On July 4, both ammonium phosphate and ammoniated superphosphate produced higher fertilizer phosphate contents at the one percent level than did ordinary superphosphate, calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate.

On July 25, ammonium phosphate and ammoniated superphosphate gave higher results than calcium metaphosphate, dicalcium phosphate, and alpha-tricalcium phosphate, but were no longer higher than ordinary superphosphate. Ordinary superphosphate at this date ranked higher at the five percent level than calcium metaphosphate and alpha-tricalcium phosphate.

In Figure 4, the change with time in the percent fertilizer phosphorus in the dry plant tissue is shown graphically. Two things especially stand out, the large differences in fertilizer phosphorus composition at the first sampling period produced by the various treatments, and the rapid decrease in the percentage values during the twenty days between the first and second sampling periods. This decrease was especially fast with ammonium phosphate and ammoniated superphosphate. There was a continuous decline in the fertilizer phosphorus composition of the plant in each instance, but it was relatively slow after the second sampling period. The trend appeared to be toward a common value, but this was not very close to attainment even at the last sampling period as there were still differences at the one percent level of significance.

Examination of the data in Table IX shows that at each of the first three sampling periods, the concentration in the plant of fertilizer phosphorus derived from ammonium phosphate and from ammoniated superphosphate was higher at the one percent level than where the phosphorus was supplied as either calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. Ammoniated superphosphate was also higher than ordinary superphosphate at the one percent level at the first three sampling periods, and greater than calcium metaphosphate and alpha-tricalcium phosphate at the one percent level and higher than dicalcium phosphate at the five percent level at the last sampling period. Ammonium phosphate was higher than ordinary superphosphate at the one percent level at the first and third sampling periods and at the five percent level at the second and fourth periods. It was also higher than calcium metaphosphate, dicalcium phosphate, and alpha-tricalcium phosphate at the one percent level at the fourth sampling period.

Ordinary superphosphate was higher than calcium metaphosphate and alpha-tricalcium phosphate at the one percent level and greater than dicalcium phosphate at the five percent level on June 22. Ordinary superphosphate was also significantly greater than calcium metaphosphate at the five percent level on July 25.

The pronounced variations in rate of uptake of phosphorus from each fertilizer during the growing season become evident upon inspection of the curves in Figure 5. In general, the most rapid uptake occurred between June 2 and June 22. The amount of fertilizer phosphorus taken up by the plants increased continuously during the season on the whole. For some reason, however, plants fertilized with ordinary superphosphate showed an apparent loss of fertilizer phosphorus during the twelve days between June 22 and July 4. Plants fertilized with ammoniated superphosphate and ammonium phosphate showed a similar apparent loss during the twenty-one days between July 4 and July 25.

Phosphorus from soil. The amount of phosphorus in the plant which was derived from the soil was determined by subtracting the fertilizer phosphorus content from the total phosphorus content. These values are given as percentages in Table X and Figure 6, and in terms of pounds per acre in Table XI and Figure 7.

At the first sampling on June 2, the data show that there were significant differences between fertilizer treatments in

TABLE X

CONCENTRATION OF SOIL PHOSPHORUS IN DRY PLANT MATERIAL IN PERCENT

Source of Phosphate	Average content of elemental phosphorus in percent			
	June 2	June 22	July 4	July 25
Ordinary superphosphate	0.400	0.260	0.202	0.200
Calcium metaphosphate	0.511	0.305	0.226	0.217
Dicalcium phosphate	0.416	0.291	0.216	0.218
Ammonium phosphate	0.311	0.277	0.195	0.196
Alpha-tricalcium phosphate	0.456	0.283	0.222	0.220
Ammoniated superphosphate	0.301	0.274	0.198	0.198
L.S.D. (.05)	0.090	N.S.	N.S.	N.S.
L.S.D. (.01)	0.123			

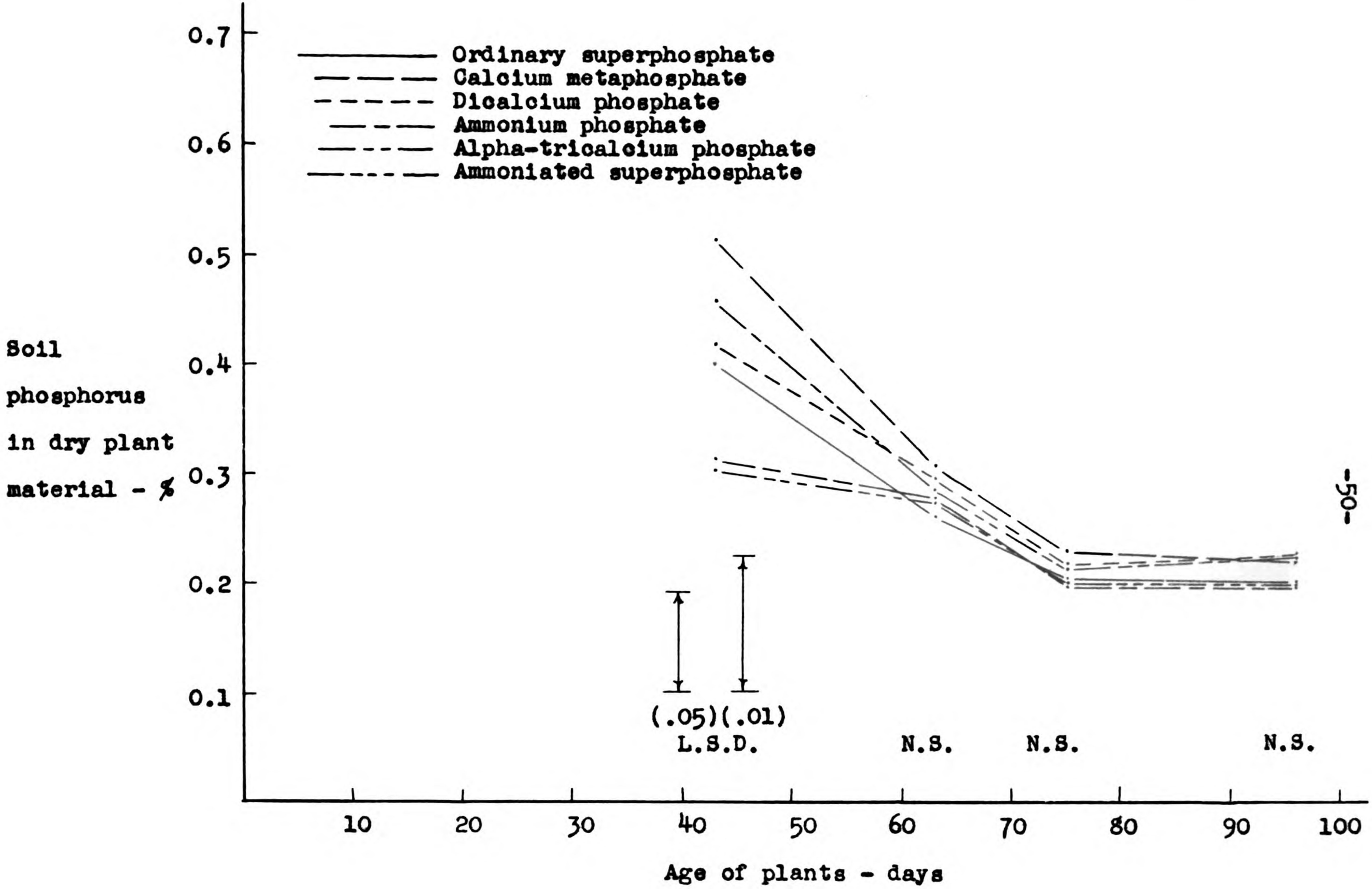


Fig. 6 The effect of source of fertilizer phosphate on the soil phosphorus content of the oat plant.

TABLE XI

CONCENTRATION OF SOIL PHOSPHORUS IN DRY PLANT MATERIAL IN POUNDS PER ACRE

Source of Phosphate	Average content of elemental phosphorus in pounds per acre* June 2	June 22	July 4	July 25
Ordinary superphosphate	1.19	9.05	12.1	18.4
Calcium metaphosphate	1.54	9.75	12.8	19.6
Dicalcium phosphate	1.60	9.49	11.0	18.8
Ammonium phosphate	1.07	11.08	14.2	19.2
Alpha-tricalcium phosphate	1.46	10.52	12.6	21.4
Ammoniated superphosphate	1.05	11.20	13.1	17.3

*To convert to pounds soil P_2O_5 per acre, multiply by 2.29.

	June 2	June 22	July 4	July 25
L.S.D. (.05)	0.31	N.S.	N.S.	N.S.
L.S.D. (.01)	0.42			

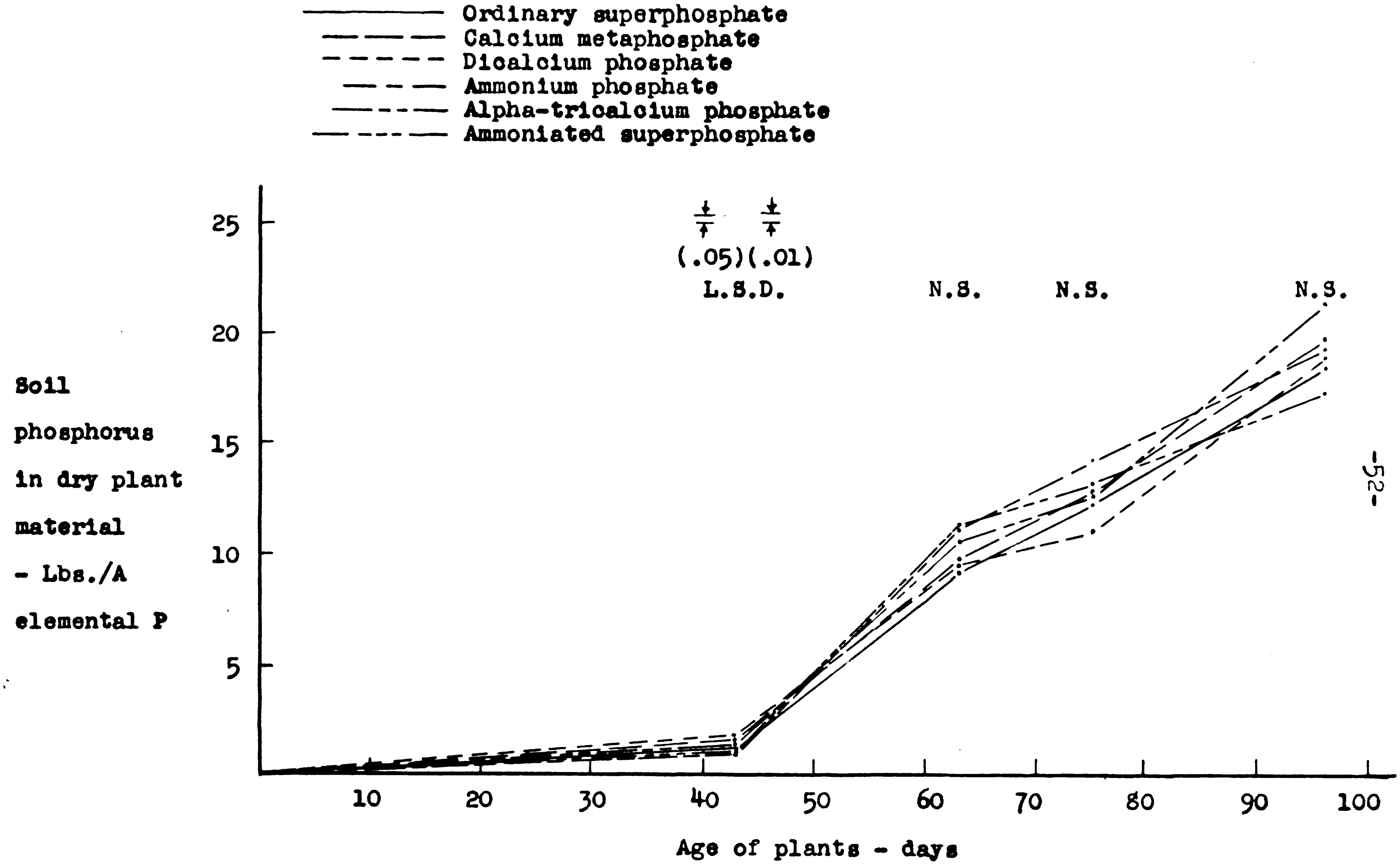


Fig. 7 Rate of uptake of soil phosphorus by the crop as related to the source of fertilizer phosphate.

the amounts of soil phosphorus taken up by the plant. The uptake of phosphorus from the soil was significantly higher at the five percent level where the fertilizer was ordinary superphosphate or dicalcium phosphate. It was higher at the one percent level with calcium metaphosphate on plots where either ammonium phosphate or ammoniated superphosphate was applied.

The uptake of soil phosphorus was higher at the one percent level from plots fertilized with alpha-tricalcium phosphate than from those to which ammonium phosphate or ammoniated superphosphate had been applied. Dicalcium phosphate caused an increase in the soil phosphorus content of plants as compared with those fertilized with ammonium phosphate or ammoniated superphosphate, significant at the five percent level. Ordinary superphosphate gave results higher at the five percent level than where ammoniated superphosphate was used.

At the last three sampling periods, no statistically significant differences were found in the uptake of soil phosphorus from the various plots.

In Figure 6, the curves show that there was a continuous decrease throughout the growing season in the soil phosphorus composition of the plant. With the exception of ammonium phosphate and ammonium phosphate, the most rapid decrease occurred during the period between the first and second samplings. It is interesting to note that with ammonium phosphate and ammoniated superphosphate it took place between the second and third sampling period. By the second sampling period the percent of soil phosphorus in the plant for the different treatments had reached a common value, that is, the results were not statistically different. This held true at the subsequent samplings also. By the third sampling period, the soil phosphorus composition had decreased to a constant value. The data for June 2 given in Table XI show that some of the phosphate treatments caused significant differences in the uptake of soil phosphorus. On plots treated with either calcium metaphosphate or dicalcium phosphate, soil phosphorus was absorbed by the plant at a rate higher at the one percent level than it was from those fertilized with ammonium phosphate or ammoniated superphosphate, and greater at the five percent level than where ordinary superphosphate was applied. Where alpha-tricalcium phosphate was used, soil phosphorus was taken up at a rate greater at the five percent level than from plots where either ammonium phosphate or ammoniated superphosphate were applied. The differences between treatments at the last three samplings were not significant.

The rate of uptake of phosphorus from the soil is illustrated in Figure 7. It may be observed that in general the most rapid absorption occurred between June 22 and July 4. The amount of soil phosphorus in the plant increased throughout the entire season.

Fraction of plant phosphorus derived from fertilizer.

The percent of the phosphorus in the oat plant which was derived from the fertilizer was calculated from the data of tables VI and VIII, and the results are given in Table XII. Examination of these figures shows that the percent of fertilizer-derived phosphorus was highest on June 2. At this time, 55.8 percent of the phosphorus in the plant had come from the fertilizer when the source was ammonium phosphate. At this same period, however, only 13.8 percent of the phosphorus in the plant had come from the fertilizer when the source was calcium metaphosphate. In general, there was a steady drop in the percent of fertilizer phosphorus in the plant for all of the phosphate materials throughout the season, and by the last sampling date on July 25, only 17.70 percent of the plant's phosphorus was fertilizer-derived for ammonium phosphate and only 6.90 percent for calcium metaphosphate, still the highest and lowest respectively.

The trend throughout the growing season of the values presented in Table XII is shown graphically in Figure 8. It may be observed that the most rapid decline in the percent of plant phosphorus derived from fertilizer occurred between June 2 and June 22, the curves for ammonium phosphate and ammoniated superphosphate being especially steep during that time. After June 22, the values dropped off rather slowly on the whole. For some reason, there was an increase for ammonium phosphate and calcium metaphosphate between June 22 and July 4

TABLE XII

PERCENT OF PLANT PHOSPHORUS DERIVED FROM FERTILIZER

Source of phosphate	June 2	June 22	July 4	July 25
Ordinary superphosphate	31.5	19.60	14.20	13.10
Calcium metaphosphate	13.8	8.85	9.23	6.90
Dicalcium phosphate	21.3	12.80	11.80	8.77
Ammonium phosphate	55.8	22.10	24.20	17.70
Alpha-tricalcium phosphate	16.1	9.90	8.51	7.40
Ammoniated superphosphate	53.4	24.30	22.30	16.30
L.S.D. (.05)	7.6	3.34	6.14	5.20
L.S.D. (.01)	10.4	4.56	8.38	7.10

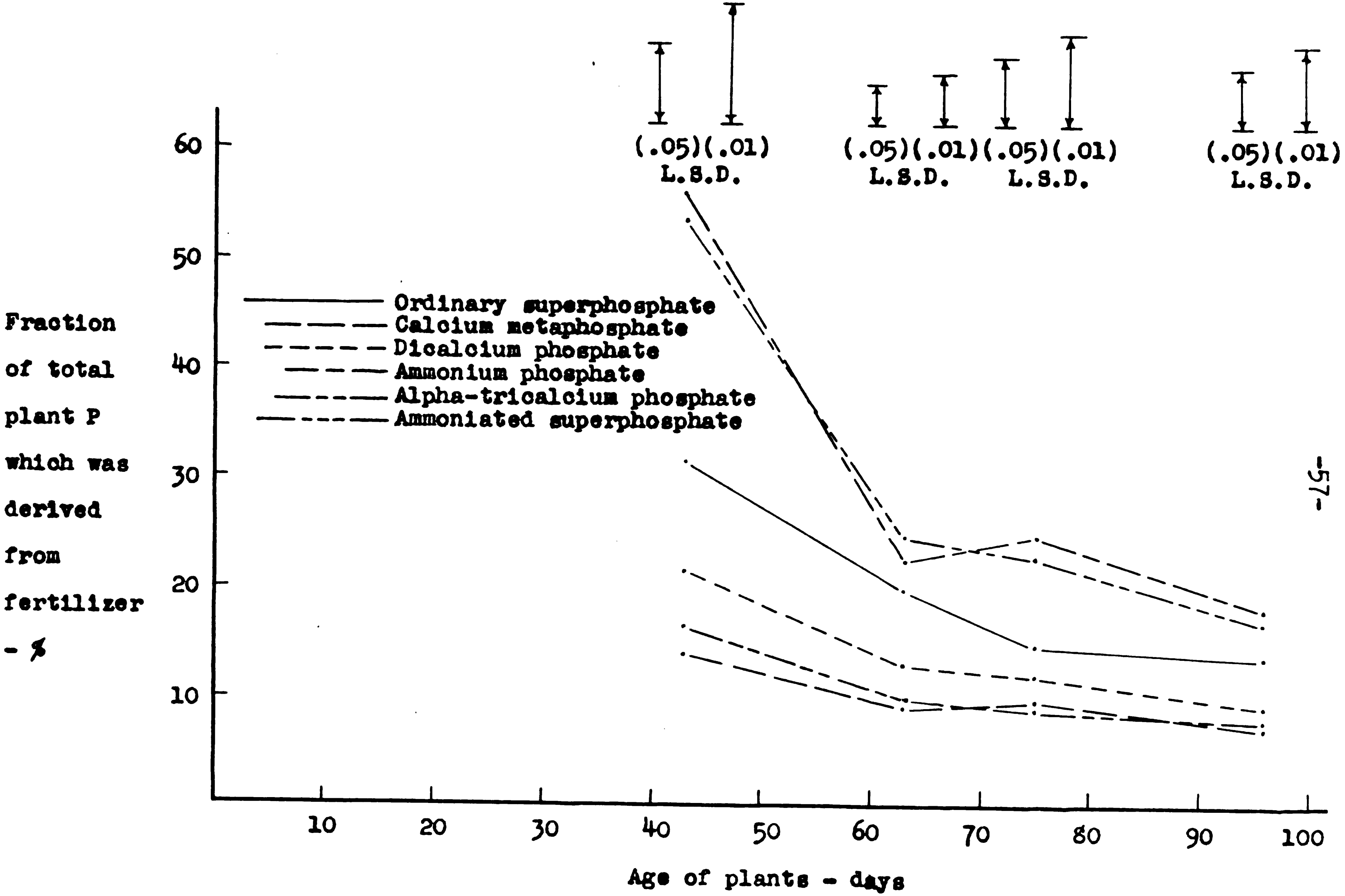


Fig. 8 Relationship between source of fertilizer phosphate and percent of plant phosphorus derived from fertilizer.

in the fraction of total phosphorus which was derived from the fertilizer.

Statistical analysis of the data in Table XII showed significant differences between treatments at each sampling period. At each period it was found that the results with ammonium phosphate and ammoniated superphosphate were higher at the one percent level than with calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. Ammonium phosphate was also higher than ordinary superphosphate at the one percent level on June 2 and July 4. Ammoniated superphosphate was also higher than ordinary superphosphate on June 2 and June 22, and at the five percent level on July 4.

Ordinary superphosphate gave results higher at the one percent level on June 2 and June 22 than were obtained with either calcium metaphosphate or alpha-tricalcium phosphate. It was also higher than dicalcium phosphate at the five percent level on June 2 and at the one percent level on June 22, and higher than either calcium metaphosphate or alpha-tricalcium phosphate at the five percent level on July 25. Dicalcium phosphate was higher than calcium metaphosphate at the five percent level on June 22.

To provide a concise, over-all view of the patterns of phosphorus utilization, the bar graphs shown in Figures 9 and 10 were constructed. The former embodies the data of Tables VI, VIII, X, and XII, and the latter those of Tables

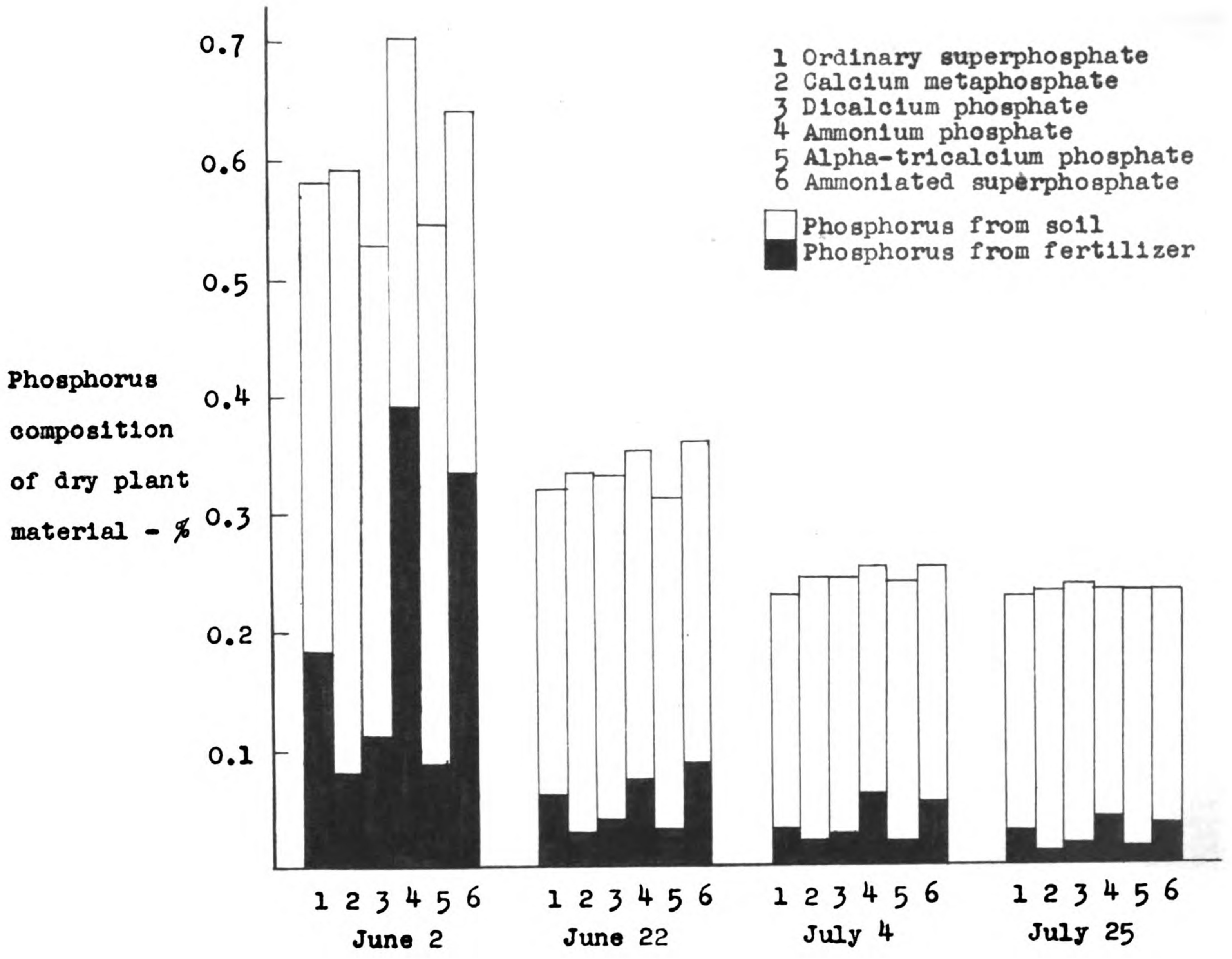


Fig. 9 Composition of plant material and plant phosphorus with respect to source of fertilizer phosphate and age of the plant.

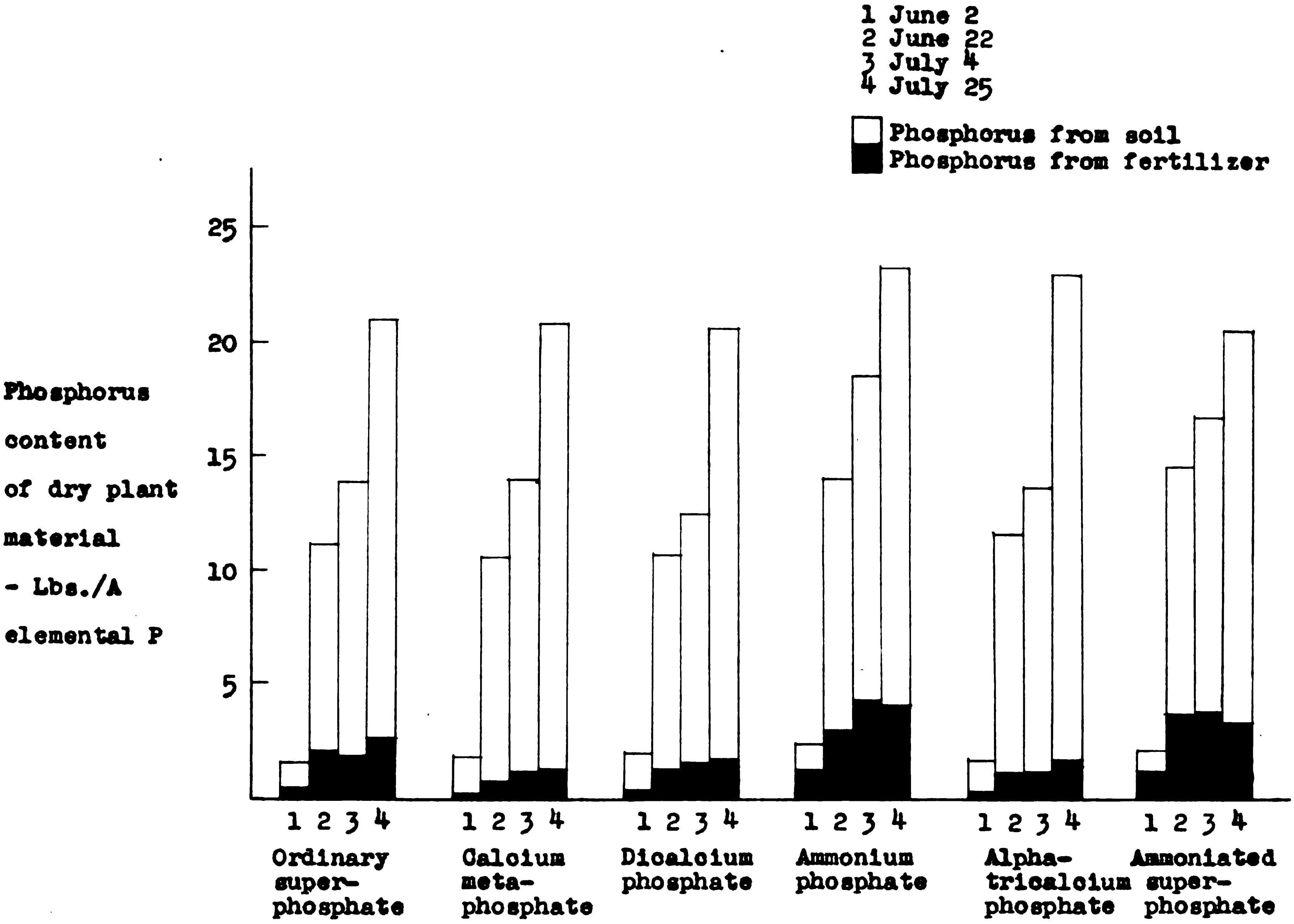


Fig. 10 Phosphorus content of the oat crop with respect to source of fertilizer phosphate and age of the plant.

VII, IX, XI, and XII. There is a fundamental difference between the two in that Figure 9 deals with the phosphorus composition of the plant (the percent of phosphorus in the dry plant material) while Figure 10 in effect deals with the phosphorus content of the plant (the total amount of phosphorus in the entire plant).

From Figures 9 and 10, the following information may be obtained:

(1) Phosphorus composition (content) of the above-ground dry plant material with regard to
  a. total phosphorus
  b. fertilizer phosphorus
  c. soil phosphorus
(2) Relative proportions of soil-derived and fertilizer-derived phosphorus in the plant.
(3) Comparison of phosphatic fertilizers as to their effect on phosphorus composition (content) of plant material with regard to
  a. total phosphorus
  b. fertilizer phosphorus
  c. soil phosphorus
(4) Changes in phosphorus composition (content) of the plant with time with respect to
  a. total phosphorus
  b. fertilizer phosphorus
  c. soil phosphorus

Fraction of applied phosphorus recovered by the crop. The determination of percentage recovery by the crop of the various phosphorus compounds used in the fertilizer is important from the standpoint of economical crop production because the compounds giving the highest recovery are likely to be the most economical to use in fertilizers.

The percent recovery of applied phosphorus was calculated from the data in Table IX, and the results are presented in

Table XIII. Probably the most significant point brought out here is that at best the recovery of phosphorus by the crop was very low. It may be observed that the most efficient source of phosphorus was ammonium phosphate, but even so, only about 17 percent of the phosphorus applied was recovered by the crop. The lowest recovery was from calcium metaphosphate, only 5.40 percent of the applied phosphorus having been recovered at the last sampling period eleven days before harvest. On the whole, the percentage recovery of phosphorus increased more or less regularly throughout the season.

Inspection of the data in Table XIII shows that at each of the first three sampling periods, the percent recovery of phosphorus from both ammonium phosphate and ammoniated superphosphate was higher at the one percent level of significance than from either calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. Ammoniated superphosphate was also higher than ordinary superphosphate at the one percent level at the first three periods, and greater than calcium metaphosphate and alpha-tricalcium phosphate at the one percent level at the last sampling period.

The recovery from ammonium phosphate was greater than from ordinary superphosphate at the one percent level at the first and third sampling periods, and at the five percent level at the second and fourth periods. It was also higher than from calcium metaphosphate, dicalcium phosphate, and

TABLE XIII

PERCENT OF APPLIED PHOSPHORUS RECOVERED BY CROP

Source of phosphate	June 2	June 22	July 4	July 25
Ordinary superphosphate	2.10	8.19	7.53	10.70
Calcium metaphosphate	0.93	3.60	5.01	5.40
Dicalcium phosphate	1.65	5.04	5.72	6.88
Ammonium phosphate	5.33	11.60	17.10	16.10
Alpha-tricalcium phosphate	1.04	4.41	4.49	6.35
Ammoniated superphosphate	4.66	14.00	14.20	12.50
L.S.D. (.05)	1.36	2.76	4.12	4.64
L.S.D. (.01)	1.85	3.76	5.61	6.33

alpha-tricalcium phosphate at the one percent level at the fourth sampling period.

The recovery from ordinary superphosphate was higher than from either calcium metaphosphate or alpha-tricalcium phosphate at the one percent level, and greater than from dicalcium phosphate at the five percent level at the second sampling. The recovery from ordinary superphosphate was also significantly greater than from calcium metaphosphate at the five percent level at the fourth sampling period.

The data of Table XIII are depicted graphically in Figure 11. The greater relative efficiency of certain of the phosphatic materials becomes especially striking when the data are compared in this fashion.

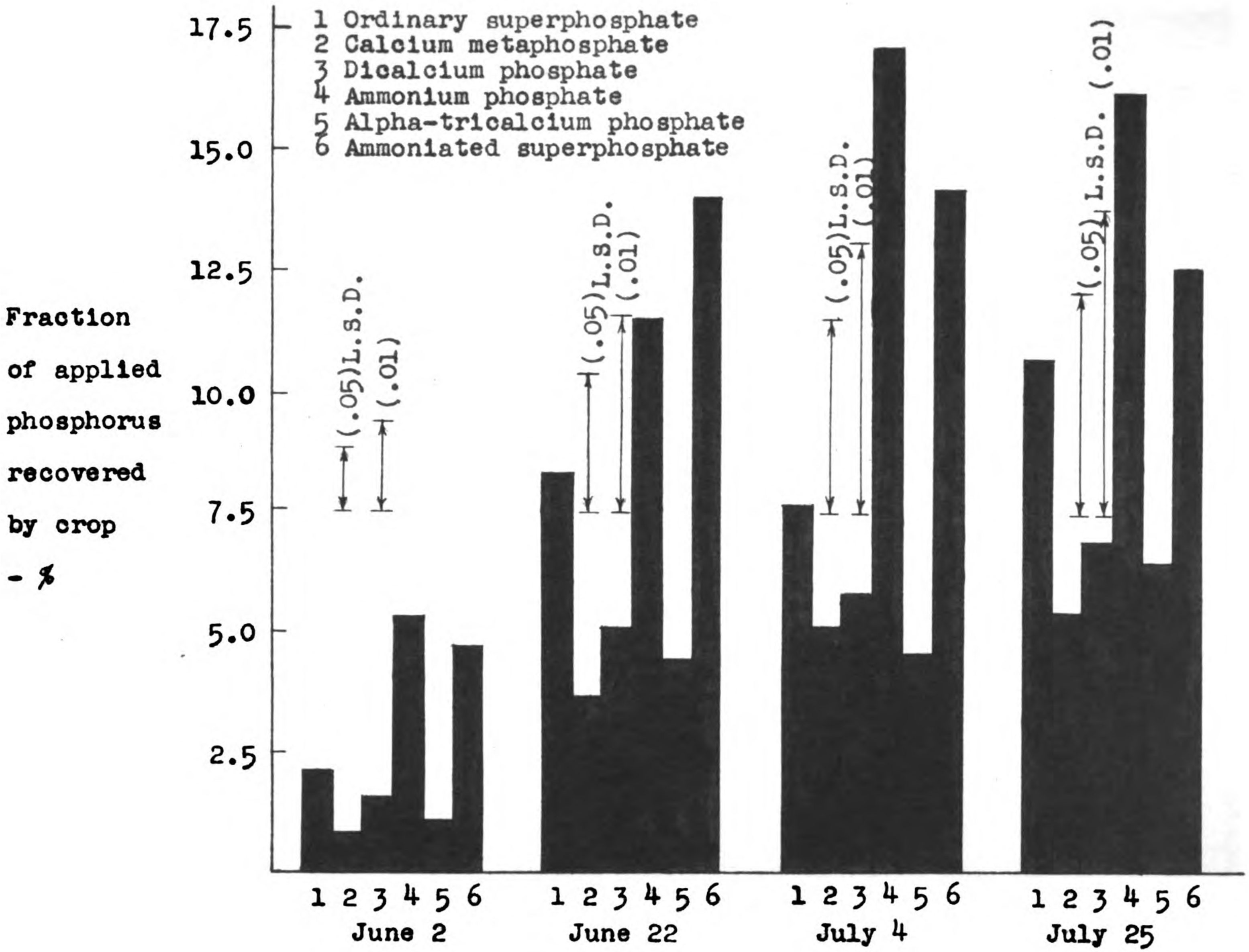


Fig. 11 Relationship between source of fertilizer phosphate and percent of applied phosphorus recovered by the crop.

Summary of statistical evaluations of phosphorus utilization. The utilization of both native and applied phosphorus by the oat plant was measured by various criteria. Interpretation of the data by the statistical method of analysis of variance revealed significant differences in both the rate and degree of utilization of phosphorus from the different phosphatic fertilizers. These treatment differences, discussed above in detail, are presented below in tabular form in Table XIV. Also included here are the "F" values for each criterion and each sampling date.

In this table, treatment differences significant at the one percent level are indicated by a short line under the number; numbers not underlined represent significance at the five percent level. For example, 1 $\underline{2}$, 3, $\underline{5}$, means that treatment 1 gave results significantly higher than either treatment 2 or 5 at the one percent level, and significantly higher than treatment 3 at the five percent level. Treatments which produced results which were not statistically different are shown connected by the equality sign.

Each criterion given in Table XIV could be used to some extent to indicate the relative availability of phosphorus from the different fertilizers. Comparison of the "F" values and treatment differences, however, shows that certain criteria are much more effective than others as indicators of availability. The criterion of percent fertilizer phosphorus in the plant is seen to be the most effective on the whole, as it has the

TABLE XIV

SUMMARY OF STATISTICAL EVALUATIONS OF PHOSPHORUS UTILIZATION BY THE OAT PLANT AS MEASURED BY SEVERAL CRITERIA

Sampling date	Yield T.D.M. R.A. (Lbs./A.)	Yield T.D.M. non-R.A. (Lbs./A.)	Yield grain non-R.A. (Bu./A)	Total P in plant (percent)	Total P in plant (Lbs./A.)
6/2	F=1.57	--	--	F=5.15** $4>\underline{1},2,\underline{3},\underline{5}$ 6>3,5 1=2=3=5, 2=6,4=6	F=3.20* 4>1,2,5 6>1,5 1=2=3=5 2=6,4=6, 3=4
6/22	F=1.68 N.S.	--	--	F=1.55 N.S.	F=3.22* 4>2,3 6>1,2,3,5 1=2=3=5, 4=5,4=6
7/4	F=2.84* 4>2,3,5 6>3 4=1=6, 1=2=3=5, 2=5=6	--	--	F=0.90 N.S.	F=3.78* 4>1,2,3,5 6>3 1=2=3=5, 2=5=6, 4=6
7/25	F=2.12 N.S.	--	--	F=0.24 N.S.	F=1.48 N.S.
Harvest 8/5	--	F=1.13 N.S.	F=0.37 N.S.	--	--

1=ordinary superphosphate, 2=calcium metaphosphate, 3=dicalcium phosphate, 4=ammonium phosphate, 5=alpha-tricalcium phosphate, 6=ammoniated superphosphate.

"F" value required for significance at 5% level = 2.71; at 1% level = 4.10.

TABLE XIV (cont'd.)

SUMMARY OF STATISTICAL EVALUATIONS OF PHOSPHORUS UTILIZATION BY THE OAT PLANT AS MEASURED BY SEVERAL CRITERIA

Sampling date	Fert. P in plant (percent)	Fert. P in plant (Lbs./A.)	Soil P in plant (percent)	Soil P in plant (Lbs./A.)	Plant P derived from fert. (percent)	Fert. recovered by crop (percent)
6/2	F=65.4** $1>\underline{2},\underline{3},\underline{5}$ $4>\underline{1},\underline{2},\underline{3},\underline{5},6$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 2=3=5	F=16.9** $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 1=2=3=5, 4=6	F=7.57** 1>6 $2>1,3,\underline{4},\underline{6}$ 3>4,6 $5>\underline{4},\underline{6}$ 1=3=5,1=4, 1=5,2=5,4=6	F=5.53** $2>1,\underline{4},\underline{6}$ $3>1,\underline{4},\underline{6}$ 5>4,6 1=4=6,1=5, 2=3=5	F=52.6** $1>\underline{2},3,\underline{5}$ $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 2=3=5, 4=6	F=16.9** $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 1=2=3=5, 4=6
6/22	F=35.3** $1>\underline{2},\underline{3},\underline{5}$ 3>2 $4>1,\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 2=5,3=5,4=6	F=20.8** $1>\underline{2},3,\underline{5}$ $4>1,\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 2=3=5,4=6	F=1.29 N.S.	F=1.09 N.S.	F=34.4** $1>\underline{2},\underline{3},\underline{5}$ 3>2 $4>\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 1=4,2=5,3=5, 4=6	F=20.8** $1>\underline{2},3,\underline{5}$ $4>1,\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 2=3=5,4=6
7/4	F=12.9** $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 1=2=3=5,4=6	F=14.8** $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 1=2=3=5, 4=6	F=1.45 N.S.	F=0.90 N.S.	F=10.5** $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>1,\underline{2},\underline{3},\underline{5}$ 1=2=3=5, 4=6	F=14.8** $4>\underline{1},\underline{2},\underline{3},\underline{5}$ $6>\underline{1},\underline{2},\underline{3},\underline{5}$ 1=2=3=5, 4=6
7/25	F=8.08** 1>2,5 $4>\underline{2},\underline{3},\underline{5}$ $6>\underline{2},\underline{3},\underline{5}$ 1=4=6,1=3, 2=3=5	F=7.44** 1>2 $4>1,\underline{2},\underline{3},\underline{5}$ $6>\underline{2},3,\underline{5}$ 1=3=5, 2=3=5,1=6,4=6	F=2.14 N.S.	F=1.73 N.S.	F=7.12** 1>2,5 $4>\underline{2},\underline{3},\underline{5}$ $6>\underline{2},\underline{3},\underline{5}$ 1=4=6,1=3, 2=3=5	F=7.44** 1>2 $4>1,\underline{2},\underline{3},\underline{5}$ $6>\underline{2},3,\underline{5}$ 1=3=5,2=3=5, 1=6,4=6

1=ordinary superphosphate, 2=calcium metaphosphate, 3=dicalcium phosphate, 4=ammonium phosphate, 5=alpha-tricalcium phosphate, 6=ammoniated superphosphate.
"F" value required for significance at 5% level=2.71; at 1% level =4.10.

highest "F" value and reveals the greatest number of availability differences.

The most commonly used criterion for determining relative availability, the percent of the plant phosphorus which was derived from the fertilizer, is seen to be of slightly less value at all sampling periods, as indicated by the consistently lower "F" values. By the former criterion, availability differences are revealed at the first three sampling periods which were not detected by the latter method: On June 2, ammonium phosphate was found to be more available than ammoniated superphosphate at the five percent level; on June 22, ammonium phosphate was seen to be more available than ordinary superphosphate at the five percent level and ordinary superphosphate more available than dicalcium phosphate at the one percent level; and on July 4, ammoniated superphosphate was found to be more available than ordinary superphosphate at the one percent level.

Another frequently used measure of fertilizer phosphorus availability is the percent of applied phosphorus recovered by the crop. Comparison of this data in Table XIV with that for the two previously mentioned criteria shows that at the first two sampling periods this criterion is the least discriminating of the three. At the third and fourth sampling periods the three criteria were of about equal effectiveness.

The "F" values for the pounds of fertilizer phosphorus per acre are the same as those for percent recovery because the latter are based on treatment values of the former criterion divided by a constant--the pounds of phosphorus applied per acre. The former criterion, therefore, is as effective as the latter in availability comparisons.

On soils which give a yield response to phosphorus applications, comparison of yields obtained with different phosphatic materials is a good method of evaluating their availability. In this experiment, however, as previously mentioned, there were no yield differences attributable to fertilizer phosphorus because of the high level of native phosphorus in the soil.

Inspection of the data in Table XIV for the total phosphorus in the plant shows that the "F" values are relatively very low, and there are considerably fewer significant treatment differences than were revealed by the criteria having the highest "F" values. Therefore, it is apparent that the amount of total phosphorus in the plant would not be an adequate measure of fertilizer phosphorus availability.

The percent of fertilizer phosphorus in the plant tissue and the percent of the plant phosphorus which were derived from the fertilizer were shown above to be the best criteria for evaluating the relative availability of fertilizer phosphorus. It is worthwhile to observe how their "F" values decrease steadily throughout the growing season. This trend shows that the availability differences become progressively less pronounced with time. In fact, comparison of the treatment differences for the various sampling dates shows that in several instances they have disappeared altogether by the last sampling date if not before this time.

It is interesting to speculate on availability relationships which might have existed prior to the first sampling date. As indicated by the increasing "F" values, the availability differences became progressively greater between July 25 and June 2 with decreasing age of the plant. If the period of 43 days between planting and the first sampling (June 2) is considered, it is probable that the availability differences were very large during the first few days after seedling emergence. This is significant in view of the well-recognized need of young plants for an adequate supply of quickly soluble phosphate after the reserve in the seed has been used up. At this critical stage, it is possible that the less available phosphates might not be able to meet this need on soils deficient in available native phosphorus.

C. Laboratory experiments with phosphates

Fixation studies. The laboratory extraction procedures used in this experiment to determine the level of available phosphorus in the soil have been found by other workers to correlate well with yield and response measurements. It would appear, therefore, that these procedures could also be used to measure the capacity of soils to fix fertilizer phosphorus in unavailable form.

The reserve extraction method of Spurway and Lawton (17) was used in the present study in an attempt to learn whether the various phosphates differ in the degree of fixation which occurs when they are added to the soil. In addition to the 60 pound rate, fixation was also studied at a 360 pound rate. This higher level was chosen arbitrarily as it was thought that this would more nearly represent the condition existing with band application in the field. The results are presented in Table XV. It should be noted that the values given do not represent percent fixation but rather percent unrecovered phosphorus. This distinction is made as a close study of the data leads to the conclusion that these figures include not only fixed phosphorus but also some undissolved fertilizer phosphorus not recovered by the extractant.

There are several reasons for believing this to be true. First, inspection of the data shows that in every instance the percent of unrecovered phosphorus is greater at the 360 pound rate than at the 60 pound rate. If the figures represented only the phosphorus actually fixed, those for the higher rate of application would be expected to be the same as, or even lower than, the corresponding ones at the lower rate. Second, the data show that in general the percent of unrecovered phosphorus is highest for those phosphates having the lowest percentage of their total P_2O_5 content in the water-soluble form and vice versa. (see Table II, page 13) This is the reverse of what would be expected if fixation only were involved.

TABLE XV

FIXATION OF THE VARIOUS PHOSPHATES BY BROOKSTON SOIL AS MEASURED BY THE SPURWAY RESERVE EXTRACTION METHOD

Source of phosphate	Percent phosphorus not recovered when applied at the rate of	
	60 pounds P_2O_5/A-6"	360 pounds P_2O_5/A-6"
Ordinary superphosphate	46.7	57.0
Calcium metaphosphate	46.7	93.9
Dicalcium phosphate	33.4	50.6
Ammonium phosphate	41.7	44.7
Alpha-tricalcium phosphate	58.4	65.0
Ammoniated superphosphate	33.4	36.6

Since dissolution has to occur before fixation can take place, the more slowly available materials, such as calcium metaphosphate and alpha-tricalcium phosphate would be expected to become fixed less rapidly than the highly available forms such as ammonium phosphate and ammoniated superphosphate.

Phosphorus fixation is thought to be due to physical, chemical, and biological processes which cause the applied phosphorus to become unavailable to plants. Since dissolution of the phosphorus has to occur before these processes can operate, any undissolved phosphorus would not be subject to fixation and could not be considered as fixed even though it would be unavailable to the plant at that time. Therefore, in order to get a "true" measure of fixation it is necessary that the extracting solution recover all of the undissolved phosphorus in addition to any other portion of the phosphorus which was not fixed. Since the data of Table XV indicated that the extractant had not removed all of the undissolved phosphorus, an experiment was set up to check on its ability to do so. The results are given in Table XVI.

Inspection of the data in Table XVI shows that all of the phosphorus from phosphates equivalent to the amounts applied at the 360 pound rate in the fixation experiment was not recovered by the extracting solution. The percent recovery was especially low from alpha-tricalcium phosphate and calcium metaphosphate, only about 55 percent of the phosphorus having been recovered from the former material and about seven percent

TABLE XVI

EXTRACTION OF PHOSPHORUS FROM THE VARIOUS PHOSPHATES BY THE SPURWAY RESERVE METHOD

	Percent recovery of phosphorus			
Source of phosphate	Whole phos. stirred 1 min. gravity filt.	Whole phos. stirred 1 min. vacuum filt.	Whole phos. stirred 30 min. vacuum filt.	200-270 mesh stirred 1 min. vacuum filt.
Ordinary superphosphate	71.2	87.9	92.0	76.8
Calcium metaphosphate	6.62	7.16	7.16	5.63
Dicalcium phosphate	91.6	96.1	100.0	96.2
Ammonium phosphate	106.8	90.0	81.8	63.5
Alpha-tricalcium phosphate	52.8	57.2	88.0	80.9
Ammoniated superphosphate	81.0	79.7	88.0	76.8

from the latter. Since in the fixation experiment a part of the unrecovered phosphorus shown in Table XV was probably truly fixed, the combined quantities of undissolved and unfixed phosphorus subject to removel by the extracting solution were most likely considerably lower in some cases than the amount initially applied. Therefore, the percent recovery of this smaller remaining fraction might have been somewhat higher than is indicated in Table XVI. Nevertheless, it appears unlikely that the recovery was complete in any case in view of the previously discussed evidence in Table XV.

It will be noted in Table XVI that the extractions were carried out under four different sets of conditions. In the first procedure, the whole (unscreened) material was stirred with the extractant for one minute and filtered by gravity. This was the standard procedure used in the fixation experiments. Since the amount of fertilizer and the volume of extractant were three times as large as in the fixation experiments, it was felt that the longer filtration time required might give erroneously high recovery values. To test this possibility, the extraction was repeated on another set of samples, followed by vacuum filtration. For some reason, the recovery was higher rather than lower in most cases, but the difference was not very large.

In the third set of extractions, the object was to determine the effect of longer extraction time on the percent recovery. It was found that thirty minutes extraction gave a considerable increase in recovery with all materials but ammonium phosphate and calcium metaphosphate. The former material showed a decrease in recovery, probably attributable to experimental error, and the latter only a slight increase. Even this long extraction, however, failed to completely recover all of the phosphorus. The one exception to this was dicalcium phosphate, from which the recovery was apparently complete.

In the fourth set of extractions, the phosphates were screened to obtain fractions of equal particle size. The purpose was to eliminate the particle size variable in order to attempt to evaluate the effect of inherent solubility of the various materials on the percent recovery. Comparison of these results with those for the second set of extractions in which the unscreened material was used shows that the results are quite inconsistent. This may have been due to a difference in the phosphorus content of the fine particle size fraction as compared with that of the unscreened material.

The incomplete recovery evidenced by the data of Table XVI furnishes the third reason for believing that the figures in Table XV include undissolved phosphorus in addition to fixed phosphorus. Since it isn't possible to determine how much of the unrecovered phosphorus in Table XV was actually fixed, it is impossible to evaluate differences in the degree of fixation of the various phosphatic materials.

On the basis of the relatively high recovery values for ammonium phosphate and ammoniated superphosphate shown in Table XVI and the fact that the percent of unrecovered phosphorus at the two rates agreed rather closely as shown in Table XV, it appears likely that these values in Table XV for the two ammoniated phosphates represent the approximate amount of actual fixation. Therefore, it is probable that the percent fixation for the less soluble materials was somewhat lower than 33 percent.

Solubility studies. The purpose of these studies was to determine the relative solubility of the different phosphatic fertilizers in water and carbonic acid. As previously described in the section on experimental procedures, phosphates were added to the flasks on an equivalent total P_2O_5 basis in amounts estimated to be sufficient to give saturated solutions. This was done in an attempt to simulate conditions which may exist in the field in close proximity to the bands of fertilizer. The relative solubility of the different materials was determined by measuring the phosphorus concentration of the solutions and comparing the values obtained. The results are shown in Table XVII.

The most significant point brought out by these data is that the phosphate materials fall into two distinctly different groups on the basis of solubility in water and carbonic acid. Ordinary superphosphate, ammonium phosphate, and ammoniated superphosphate were highly soluble while calcium metaphosphate

TABLE XVII

COMPARISON OF SOLUBILITY OF THE PHOSPHATES IN DIFFERENT SOLVENTS AS MEASURED BY PHOSPHORUS CONTENT OF THE SOLUTIONS

Source of phosphate	Concentration in parts per million elemental phosphorus Water (A)	Water (B)*	Carbonic Acid**
Ordinary superphosphate	22,500	40,000	37,500
Calcium metaphosphate	28.0	67.5	153
Dicalcium phosphate	150	160	320
Ammonium phosphate	36,000	48,000	56,000
Alpha-tricalcium phosphate	18.4	18.4	89.6
Ammoniated superphosphate	10,400	14,400	14,000

* 50 percent more phosphate added to solution (A)
**CO_2 bubbled through solution (B) for 10 minutes

dicalcium phosphate, and alpha-tricalcium phosphate were only slightly soluble. The order of decreasing solubility in the highly soluble group was ammonium phosphate, ordinary superphosphate, ammoniated superphosphate; in the slightly soluble group it was dicalcium phosphate,calcium metaphosphate, alpha-tricalcium phosphate.

Comparison of these results with the data for water-soluble phosphorus in Table II (page 13) shows that the order of solubility is the same in both cases as would be expected.

DISCUSSION

It was shown in Table V that there were no significant differences either in the total dry matter yields or in the grain yields produced by the various phosphate materials. In Table IV, the data showed that the only significant differences between fertilizers in dry matter yields produced occurred at the third sampling period. This almost complete lack of differential yield response to the various phosphates was undoubtedly due to the high level of available native phosphorus in the soil. This, as may be seen in Table I, amounted to 137 pounds of elemental phosphorus per acre as determined by the Spurway reserve method. With this test, according to workers at the Michigan Experiment Station, the critical level on slightly acid heavy-textured soils such as was used in this experiment is believed to be about 70 pounds per acre. Soils containing less than this amount of acid extractable phosphorus can be expected to respond to fertilization, while those containing more usually do not.

Table I also gives the available phosphorus content of the soil as measured by Bray's method for measuring "total available" phosphorus. This is seen to be equal to 190 pounds of elemental phosphorus per acre. Data reported by Bray (3) indicate that a soil containing 54-61 pounds per acre of "total available" phosphorus should be capable of a yield equal to 98 percent of that possible with adequate phosphate. This means that if the soil contained more than 61 pounds per acre, little or no response to phosphorus fertilization could be expected.

Since the soil used in this experiment was found to contain levels of available phosphorus two to three times higher than the critical amounts indicated above, it is obvious that yield differences due to differential utilization of phosphorus from the various fertilizers would not be expected. The significant differences noted in yields at the third sampling period were, therefore, probably due directly to the extra nitrogen supplied by the two phosphates containing ammonia rather than to the phosphorus they contained. Furthermore, an additional indication that the effect was due to ammonia is that ammonium phosphate, containing 7.6 percent NH_3, gave a higher yield than ammoniated superphosphate, containing 4.13 percent.

As mentioned above, more fertilizer ammonia was supplied to the plants fertilized with the ammonium phosphate and ammoniated superphosphate than to plants receiving the other phosphate materials. This was due to the fact that no allowance was made for the ammonia contained in the ammoniated phosphates when applying supplemental nitrogen to the plots, ammonium sulfate being applied in equal quantities to all plots. Apparently because of this extra ammonia, the two ammoniated phosphates gave significantly higher yields at the third sampling period. It seems possible, also, that the higher availability and greater utilization of phosphorus from these materials was at least partly due to the combined direct and indirect effects of the extra ammonia. Such an indirect effect might be to increase the solubility of the phosphate and thereby increase its availability; and a direct effect would well be upon yield and thereby upon degree of utilization, because of the nutrient effect of the extra nitrogen.

Consideration of the above thoughts leads to the question of whether the amount of ammonium sulfate applied to the plots fertilized with the ammoniated phosphates should have been reduced sufficiently to give equal ammonia levels for all plots. At first glance, it might seem that this would obviously be the proper procedure, and in accord with the scientific method of eliminating all the variables but one. Apparently this is the line of reasoning of some workers, at least, on this question. In some of the work on comparison of sources which was reviewed in which the ammoniated forms were studied, the authors stated that they had made due allowance for the ammonia in the ammoniated materials and had reduced the application of supplemental ammonia accordingly. In the majority of the reports, it was not stated whether this had been done.

In support of the procedure followed in this experiment, it seems to the author that it would be both illogical and inconsistent to equalize the ammonia applications. The ammonium ion is an integral part of the fertilizer as much as is the calcium ion, the sulfate ion, and any of the other ions present in the different materials. No attempt is, or should be, made to equalize the amounts of these other ions to produce the equivalent of fertilizers differing only in the availability of the phosphate ion because the availability would be changed in so doing. If the ammonia applications were equalized, the effect would be that of comparing only a part of the ammoniated phosphates with the other materials as the influence of the ammonia in the ammoniated materials on availability and utilization would be removed, or rather, masked. In a comparison of sources, the purpose is to compare the effect of the entire phosphate fertilizer on yield and utilization, not just the effect of some specific part of the material. On the basis of the above reasoning the procedure followed seems justified.

With regard to the data of Table XII for the percent of plant phosphorus derived from the fertilizer, it will be observed that the values decreased continuously during the growing season. It is of interest to consider the factors which might have caused this trend.

The percent of fertilizer-derived phosphorus in the plant at any given time would depend on the relative rates of uptake of soil-derived and fertilizer-derived phosphorus which existed prior to that time. Therefore, the factors determining the percent of fertilizer phosphorus in the plant would be those affecting the rate of uptake from both the fertilizer and the soil.

Several factors which would affect the rate of uptake from the fertilizer are the following:

1. Amount of fertilizer applied.
2. Availability of the material.
3. Degree of fixation.
4. Total area of functional root surfaces per unit quantity of fertilizer.
5. Amount of available phosphorus in the soil.

Several factors affecting the rate of uptake of soil phosphorus are:

1. Amount of available phosphorus in the soil
2. Total area of functional root surfaces per unit volume of soil
3. Total volume of soil from which the roots are absorbing.

All of the above-mentioned factors are dynamic and in general would operate in the following way to cause a more or less continuous decrease in the percent of fertilizer-derived phosphorus in the plant. Early in the season the root system of the plant is small and is more or less restricted to the fertilizer zone. Because of this, the proportion of fertilizer phosphorus taken up by the plant is relatively very high. Also, at this time relatively little fixation has taken place. As plant growth progresses the root system expands and increasing amounts of soil phosphorus become accessible to the plant and are absorbed. Since there is a limit to the total amount of phosphorus which the plant will absorb in a given length of time, an increase in the amount of soil phosphorus absorbed would cause a proportional depression in the absorption of phosphorus from the fertilizer. This would lead to a progressive decrease in the percent of the plant phosphorus which was derived from fertilizer.

The degree of phosphorus fixation has been shown to be a function of time, several months sometimes being required for the maximum to be attained. This, together with the fact that the quantity of phosphorus remaining in the fertilizer is inversely related to the amount which has been absorbed from it, means that as the season progresses a continuously decreasing amount of fertilizer phosphorus will be available for plant use. This, also, would operate to cause a progressive decrease in the percent of the plant phosphorus which was derived from the fertilizer.

The effects of the above-mentioned factors in operation are well-illustrated by the data in Tables IX and XI and by Figures 5 and 7. Comparison of the data in Table IX with those in Table XI shows that the absorption of phosphorus from the soil by the plant proceeded at a much faster rate than from the fertilizer. This, as previously mentioned, caused the progressive decrease in the percent of the plant phosphorus derived from the fertilizer.

The primary objective of this investigation was to obtain quantitative information regarding the utilization of phosphorus derived from the soil and from various phosphatic fertilizers. A secondary objective was to attempt to explain the differences found in the availability and degree of uptake of phosphorus from these fertilizers. Only a very limited amount of experimental data was obtained for this latter purpose as extensive investigation of the reasons for the differences observed was beyond the scope of this experiment. Experimental data were obtained relating to solubility studies and fixation studies. As will be shown below, the solubility results seem to correlate rather well with availability data. The fixation data, however, for reasons previously discussed, are of no value for this purpose. Because of the lack of other data to help explain the availability differences observed, several hypotheses will be offered later which may be of some value.

As may be observed in Table XIV, availability relationships fluctuated considerably during the season. This is, of course, to be expected because of the wide differences in the composition and properties of the various phosphates, and the fact that the availability of the phosphorus in a fertilizer is not a fixed quantity but changes continuously after it is applied to the soil. On the whole, however, the availability relationships in this experiment were sufficiently constant to permit generalized ranking as to order of availability.

The phosphatic materials were found to rank in order of decreasing availability as follows: ammonium phosphate = ammoniated superphosphate > ordinary superphosphate > dicalcium phosphate = alpha-tricalcium phosphate = calcium metaphosphate. Ammonium phosphate, ammoniated superphosphate, and ordinary superphosphate were found to be highly available, while dicalcium phosphate, alpha-tricalcium phosphate, and calcium metaphosphate presented a much lower availability. The last three phosphates were of equal availability statistically. There was, however, a definite trend below the level of significance toward decreasing availability in the order given above. As the season progressed, the availability differences between all the materials became less and less pronounced.

From a study of the data of Table II and XVII, it was shown previously that on the basis of water-solubility, the phosphates may be divided into two groups. Ammonium phosphate, ordinary superphosphate, and ammoniated superphosphate, listed in order of decreasing water-solubility, were all highly soluble; dicalcium phosphate, calcium metaphosphate, and alpha-tricalcium phosphate, in decreasing order, were all only slightly soluble.

To facilitate comparison of the relationship between water-solubility and availability,the materials are classified below on the basis of decreasing solubility and availability.

Water-solubility		Availability	
High	Low	High	Low
Ammonium phosphate	Dicalcium phosphate	Ammonium phosphate	Dicalcium phosphate
Ordinary superphosphate	Calcium metaphosphate	Ammoniated superphosphate	Alpha-tricalcium phosphate
Ammoniated superphosphate	Alpha-tricalcium phosphate	Ordinary superphosphate	Calcium metaphosphate

It may readily be seen from the above classification that, as a group, the phosphates with the high water-solubility were also the most available as measured by the plant. Likewise, the group which were only slightly water-soluble were the least available. It appears, therefore, that there is a definite positive correlation between water-solubility and availability in a broad way in this experiment.

It might appear that this would be expected in this, and any similar, experiment. Jackson, et al. (6), working with corn and oats in Wisconsin, obtained results in which the order of relative availability of these materials was quite similar to that reported here. On the other hand, Starostka, Jackson, and Attoe (19), also in Wisconsin, working with the same crops and fertilizers the previous year found calcium metaphosphate to have the highest availability to the plant. Apparently, the degree of water-solubility of a phosphate material is not a dependable criterion for predicting its availability to the plant.

Although in this experiment good correlation was found between water-solubility and availability as measured by the plant when the materials were compared as groups, the correlation for individual fertilizers was not so good. For example, inspection of the above classification shows that ammoniated superphosphate (42.8% H_2O-sol.), the least soluble material in the high solubility group, was more available than the more soluble ordinary superphosphate (86.2% H_2O-sol.). A possible explanation for this situation is that the water-soluble fraction of the ordinary superphosphate is super-available leading to excessive fixation. Yet, if this is so, it is difficult to explain why the even more highly water-soluble ammonium phosphate (100% H_2O-sol.) was also found to be the most available.

Since the phosphate materials studied also contain widely differing amounts of the citrate-soluble and citrate-insoluble fractions which may become available to the plant at varying rates during the season, it seems unreasonable to expect a consistent correlation between water-soluble phosphorus and availability, except, perhaps, early in the season.

If, as is commonly believed, the $-H_2PO_4$ ion is the only phosphate ion which plants utilize, the relative availability of a phosphate fertilizer would apparently depend upon the rate at which it was able to furnish this ion in optimum amounts, consistent with fixation effects and plant requirements, throughout the growing season. There are a number of dynamic factors operating simultaneously in the soil which would affect the rate of conversion of the various phosphate ions to the $-H_2PO_4$ ion, as well as affecting the rate of fixation. Therefore, explanation of availability and utilization differences observed in any particular experiment would appear to be very difficult in view of the complex interrelationships involved in the soil and the extreme difficulty of experimentally evaluating the individual factors involved.

SUMMARY

1. The data from this experiment show that there were distinct differences in the percent utilization of phosphorus by oats from the six different phosphate materials studied. Oat plants receiving ammonium phosphate and ammoniated superphosphate had the highest percent absorption from the phosphate applied, while oats receiving calcium metaphosphate and alpha-tricalcium phosphate showed the lowest percent absorption. The percent utilization values obtained using ordinary superphosphate and dicalcium phosphate were intermediate with the latter source giving a somewhat lower utilization figure.

2. Availability relationships were determined from the utilization values obtained during the growing season. The relative availability of a phosphate material, as measured by the plant, was found to fluctuate somewhat during the season. However, in general the materials were found to rank in decreasing order of availability as follows: ammonium phosphate = ammoniated superphosphate > ordinary superphosphate > dicalcium phosphate = alpha-tricalcium phosphate = calcium metaphosphate. Ammoniated phosphate and ammoniated superphosphate were more available than dicalcium phosphate, alpha-tricalcium phosphate, and calcium metaphosphate at the one

percent level of significance, and were more available than ordinary superphosphate at the five percent level on the whole. Ordinary superphosphate was more available than dicalcium phosphate, alpha-tricalcium phosphate, and calcium metaphosphate at the five percent level in general. The last three phosphates were of equal availability statistically. There was, however, a definite trend below the level of significance toward decreasing availability in the order given above.

3. The percent recovery of applied phosphorus was very low. At the last sampling period, 11 days before harvest, the highest recovery was from ammonium phosphate and the lowest from calcium metaphosphate. These recovery values were 16.1 and 5.4 percent respectively.

4. There was a continuous decrease in the phosphorus composition of the plant during the growing season. The total phosphorus composition decreased from a high of 0.70 percent to a low of 0.23 percent, the fertilizer-derived phosphorus from 0.39 percent to 0.16 percent, and the soil-derived phosphorus from 0.51 percent to 0.20 percent.

5. Statistically significant differences between the various phosphate materials were found with regard to their effect on the percent composition and rate of uptake of total, fertilizer, and soil phosphorus by the oat plant.

6. There was a pronounced inverse relationship early in the growing season between the rates of uptake of phosphorus from

the fertilizer and from the soil. The relatively rapid uptake from the more available phosphates caused a correspondingly slower uptake from the soil. Conversely, the relatively slow uptake from the less available phosphates permitted a correspondingly greater rate of uptake from the soil. During the latter part of the season the rate of uptake of phosphorus from the fertilizer had no effect on the rate of uptake of soil phosphorus. A similar pronounced inverse relationship also was found early in the season between percent of fertilizer-derived and soil-derived phosphorus in the plant. This inverse relationship persisted throughout the season, but below the level of significance during the latter part of the season.

7. At the first sampling date, 43 days after planting, 55.8 percent of the phosphorus in the plant was found to be fertilizer-derived for those plants receiving ammonium phosphate, the most available material. At this time, only 13.8 percent of the plant phosphorus was fertilizer-derived for those plants receiving calcium metaphosphate, the least available material. The percentage values for all of the phosphates declined steadily during the growing season, and at the last sampling date, 11 days before harvest, the values for ammonium phosphate and calcium metaphosphate were only 17.7 and 6.9 percent respectively. Percentage values for the other phosphates were intermediate at all sampling dates. Significant differences existed throughout the season between the more available

materials and those less available with regard to the percent of plant phosphorus derived from the fertilizer.

8. Grain yields for the various treatments were not significantly different. Total dry matter yields differed significantly only at the third sampling period, at which time the yield with ammonium phosphate was higher than that produced by either calcium metaphosphate, dicalcium phosphate, or alpha-tricalcium phosphate. The yield with ammoniated superphosphate was higher than that produced by dicalcium phosphate. In all cases, the yield differences were significant at the five percent level. There were indications that the differential yield responses observed were caused by the direct effect of the extra nitrogen supplied by the two ammoniated phosphates, rather than by the phosphorus in these materials. One reason for believeing this to be true is that the level of native phosphorus in the soil was so very high, yield response to fertilizer phosphorus would not be expected.

9. Differences in yield response and phosphorus utilization obtained with the different materials were used as criteria for evaluating phosphate availability differences. It was found that certain criteria were much more effective than others in revealing availability differences. The percent of fertilizer-derived phosphorus in the plant (percent of the total dry matter) was shown to be the best criterion, being slightly more effective than the percent of the total plant

phosphorus which was derived from the fertilizer, the most commonly used criterion. Yield values and the percent total phosphorus in the plant were found to be the least effective criteria. It was suggested that under conditions of yield response, the percent recovery of applied phosphate would probably be the most effective criterion.

10. Differences in availability to the plant of phosphorus from the various phosphates became progressively less pronounced during the growing season.

11. Phosphorus availability as measured by plant utilization data appeared to be positively correlated, in a broad way, with water-solubility of the phosphates. Ammonium phosphate, ammoniated superphosphate, and ordinary superphosphate, shown by utilization data to be the most available, were also found to have the highest water solubility. Dicalcium phosphate, alpha-tricalcium phosphate, and calcium metaphosphate, shown to be the least available, were found to have the lowest water solubility. This correlation existed only when the materials were compared as high and low solubility groups. There was apparently little correlation of availability with water solubility for individual phosphates.

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APPENDIX

SUMMARY OF ANALYSIS OF VARIANCE DATA

Data	Tot. SS	Bk. SS	Treat. SS	Error SS	Treat. MS	Error MS	Treat. F	(.05) L.S.D.	(.01) L.S.D.
Yield T.D.M. R.A. (Lbs./A.)									
6/2	120,572	21,097	28,108	71,457	5,604	3,573	1.57 (N.S.)	--	--
6/22	15,505,947	3,599,880	3,520,707	8,385,360	704,141	419,268	1.68 (N.S.)	--	--
7/4	35,501,097	2,526,413	13,705,177	19,269,507	2,741,035	963,475	2.84*	1300	--
7/25	28,030,830	9,305,350	6,485,240	12,240,240	1,297,048	612,012	2.12 (N.S.)	--	--
Yield T.D.M. Non-R.A. (Lbs./A.)									
8/5	12,693,897	4,013,313	1,913,457	6,767,127	382,691	388,356	1.13 (N.S.)	--	--
Yield grain Non-R.A. (Bu./A.)									
8/5	5,141.55	2,745.39	204.95	2,191.21	40.99	109.56	0.37 (N.S.)	--	--
Total P (percent)									
6/2	0.1934	0.0051	0.1054	0.0829	0.0211	0.0041	5.15**	0.086	0.117
6/22	0.0345	0.0047	0.0087	0.0211	0.0017	0.0011	1.55 (N.S.)	--	--
7/4	0.0108	0.0010	0.0018	0.0080	0.0036	0.00040	0.90 (N.S.)	--	--
7/25	0.0047	0.0012	0.0002	0.0033	0.00004	0.00017	0.24 (N.S.)	--	--
Total P (Lbs./A.)									
6/2	6.10	0.68	2.40	3.02	0.480	0.151	3.20*	0.52	--
6/22	252.49	70.94	81.01	100.54	16.20	5.027	3.22*	3.0	--
7/4	294.13	27.73	129.43	136.97	25.89	6.849	3.78*	3.5	--
7/25	168.51	23.18	39.18	106.15	7.84	5.308	1.48 (N.S.)	--	--
Fert. P. (percent)									
6/2	0.4892	0.0029	0.4581	0.0282	0.09162	0.00141	65.4**	0.050	0.068
6/22	0.01810	0.00091	0.01544	0.00175	0.00309	0.0000875	35.3**	0.012	0.017
7/4	0.01141	0.00078	0.00812	0.00251	0.00162	0.000126	12.9**	0.015	0.020
7/25	0.00464	0.00005	0.00307	0.00152	0.00061	0.000076	8.08*	0.012	0.016

Tot. DF = 29, Bk. DF = 4, Treat. DF = 5, Error DF = 20.
"F" value required for significance at 5% level = 2.71; at 1% level = 4.10.

SUMMARY OF ANALYSIS OF VARIANCE DATA (Cont'd.)

Data	Tot. SS	Bk. SS	Treat. SS	Error SS	Treat. MS	Error MS	Treat. F	(.05) L.S.D.	(.01) L.S.D
Fert. P (Lbs./A.)									
6/2	7.665	0.021	6.184	1.460	1.237	0.0730	16.94**	0.36	0.49
6/22	38.949	2.387	30.672	5.890	6.134	0.295	20.79**	0.72	0.98
7/4	64.17	2.46	48.54	13.17	9.71	0.658	14.75**	1.09	1.48
7/25	48.05	1.55	30.23	16.27	6.05	0.813	7.44**	1.19	1.62
Soil P (percent)									
6/2	0.2608	0.0071	0.1664	0.0873	0.0333	0.0044	7.57**	0.090	0.123
6/22	0.0320	0.0074	0.0060	0.0186	0.0012	0.00093	1.29 (N.S.)	--	--
7/4	0.0168	0.0011	0.0042	0.0115	0.00084	0.00058	1.45 (N.S.)	--	--
7/25	0.0100	0.0012	0.0031	0.0057	0.00062	0.00029	2.14 (N.S.)	--	--
Soil P (Lbs./A.)									
6/2	3.10	0.55	1.48	1.07	0.296	0.0535	5.53**	0.31	0.42
6/22	154.00	63.36	19.45	71.19	3.89	3.56	1.09 (N.S.)	--	--
7/4	175.98	26.61	27.43	121.94	5.49	6.10	0.90 (N.S.)	--	--
7/25	172.36	14.39	47.71	110.26	9.54	5.51	1.73 (N.S.)	--	--
Plant P from fert. (percent)									
6/2	9,344.71	80.89	8,609.48	654.34	1,721.90	32.72	52.63**	7.6	10.4
6/22	1,331.78	113.57	1,091.16	127.05	218.23	6.35	34.37**	3.34	4.56
7/4	1,676.89	123.62	1,125.65	427.62	225.13	21.38	10.53**	6.14	8.38
7/25	863.86	11.83	545.54	306.49	109.11	15.32	7.12**	5.20	7.10
Fert.P Recovery (percent)									
6/2	111.72	0.27	90.27	21.18	17.96	1.06	16.94**	1.36	1.85
6/22	571.22	35.08	448.69	87.45	89.74	4.37	20.79**	2.76	3.76
7/4	934.43	36.34	705.55	192.54	141.11	9.63	14.75**	4.12	5.61
7/25	704.32	26.46	434.60	243.26	86.92	12.16	7.44**	4.64	6.33

Tot. DF = 29, Bk. DF = 4, Treat. DF = 5, Error DF = 20.
"F" value required for significance at 5% level = 2.71; at 1% level = 4.10.