

This is to certify that the
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A STUDY OF THE BEHAVIOR OF FUSED POTASSIUM
PHOSPHATES IN SOIL

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A STUDY OF THE BEHAVIOR OF FUSED POTASSIUM
PHOSPHATES IN SOIL

by

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AN ABSTRACT

Submitted to the School for Advanced Graduate Studies of
Michigan State University of Agriculture and
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ABSTRACT

Experiments were conducted in the laboratory, greenhouse, and field with various sized particles of potassium-calcium pyrophosphate and potassium metaphosphate to study the behavior of these fused phosphates in soil.

Greenhouse studies involving the effect of different placement and particle size of the fused potassium phosphates on the growth and potassium absorption by field bean and Proso millet plants were conducted in several soils in 1957 and 1958. With Metea sandy loam, there was no significant increase in growth of beans as affected by particle size of the fertilizer or percent water soluble potassium content of the potassium carrier. On Houghton muck soil the application of finely divided potassium metaphosphate in mixed placement resulted in improved growth of bean plants and more plant uptake of potassium.

On Kalamazoo sandy loam soil, application of potassium metaphosphate and potassium pyrophosphate materials produced significantly higher yields of millet than potassium chloride applications. Banding of the potassium sources was more effective than mixed placement the potassium content of plants increased with an increase in water soluble potassium content of the fertilizer and a decrease in particle size. On Houghton muck soil, the yield of millet was found to be highest from soil treated with potassium metaphosphate. With

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this soil, potassium content of plants also increased with an increase in water soluble potassium content of the fertilizer.

In laboratory, particles of fused potassium phosphates were leached with water to study the rate of dissolution and migration of potassium. About three-fourths of the original water soluble potassium present from all particles was leached out with the addition of 40 milliliters of water. The rate of release of potassium increased with decrease in particle size of the fertilizer. The medium sized particles of metaphosphate completely disintegrated, while large fragments became rather soft. After leaching, the large and medium sized particles of pyrophosphate still contained all their original water-insoluble potassium.

When the fused potassium phosphates were placed in soil columns and leached with water, water soluble and exchangeable potassium was found to be concentrated in a layer of soil, 2 inches below the place of application of the fertilizer.

When various sized particles were incubated in moist organic soil, 45.6 percent and 94 percent of the water soluble potassium was released in 24 hours from the -4+14 mesh particles of pyro- and metaphosphate, respectively. For both pyro- and metaphosphates of this particle size,

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the amount of water soluble potassium recoverable remained more or less constant, regardless of an increase in time of incubation.

There was no marked difference in the amount of potassium released as affected by changes in the moisture content of the soil. For potassium pyrophosphate, particle size also did not appreciably influence the release of potassium, although for metaphosphates, more water soluble potassium moved out of the -4+14 mesh particle than from the larger particles at the end of a 24 hour incubation period.

Approximately three-fourths of the potassium released in the incubation studies was recoverable from a volume of soil 2 x 2 x 10 centimeters in the center of which the fertilizer particles were banded. Lateral movement of potassium decreased rapidly with distance from the potassium source. With increase in time of incubation there was an increase in the soluble potassium content of the laterally adjacent volume of soil but very little downward movement of potassium in soil was recorded. The migration and distribution of potassium in Oshtemo sand was similar to that for organic soil.

When the several potash fertilizer particles were left exposed on the soil surface to atmospheric conditions in the field, potassium chloride and -4+14 mesh potassium

metaphosphate particles could not be recovered after 20 days exposure. A short time later, the large particles also had disintegrated. In contrast, potassium pyrophosphate particles were recoverable in unaltered physical form even after 40 days exposure in the field. At the first sampling period, potassium chloride contained about half of its original potassium, and the smaller particles of potassium pyrophosphate and metaphosphate lost 30.7 and 95.8 percent potassium, respectively. However, these materials still contained a large amount of potassium. After 40 days of exposure, the pyrophosphate had lost all water soluble potassium, but still contained most of the original water-insoluble fraction.

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INTRODUCTION

Potassium is one of the most reactive metallic chemical elements. It has an atomic number of 19 and atomic weight of 39.098. Naturally occurring potassium consists of three isotopes of mass numbers 39, 40, and 41, with relative abundance of 93.1, 0.0119, and 6.9 percent, respectively. Potassium belongs to the group of alkali metals and closely resembles other members of this group. It has a single valence electron which is easily removed. The other electrons are tightly held by the nucleus in completely filled orbitals and hence it is very reactive and is a strong reducing agent. Although in the form of simpler chemical compounds potassium is one of the most soluble of elements, in the soil-fertilizer-plant system, potassium exhibits extreme difference in solubility and mobility.

One of the problems faced with the use of potassium in fertilizer practice is the inefficient utilization of this element by plants. Almost all the potash used in mixed fertilizers or as an individual nutrient is potassium chloride, an extremely soluble salt. Part of potassium applied to soil may be lost by leaching, especially in areas of high rainfall, part is fixed by the soil, and part is lost in a sense through luxury consumption by plants. One of the methods that could be used to minimize these losses is the

use of lesser soluble compounds of potassium as potash carriers. In this category belong the fused potassium phosphates developed experimentally by the Tennessee Valley Authority. The Michigan Agricultural Experiment Station entered into cooperative studies with the Soil and Fertilizer Branch of this agency in 1957 to study the behavior of these potassium sources.

The objectives of the present investigation were:

1. To compare the effectiveness of fused potassium phosphates on the yield of and the potassium uptake by plants grown in the greenhouse.
2. To evaluate the effect of leaching of fused potassium phosphates with water to characterize their solubility patterns.
3. To study the dissolution and migration of potassium from the fused potassium phosphates when incubated in soil.
4. To determine the effect of particle size on the behavior of these potassium phosphates.
5. To study the dissolution and disintegration of these fertilizer materials under field conditions.

LITERATURE REVIEW

The benefits of organic and inorganic materials containing potassium were recognized by scientists for some time past, but the significance of this element in crop production was recognized only since the beginning of the nineteenth century. The importance of potassium in plant nutrition was pointed out by such workers as Boussingault, Sprengel, Liebig, and others.

Of the major nutrient elements, potassium is usually the most abundant in soils. Marbut (31) reported that the content of potassium in soil ranges from traces as in Tifton sandy loam to as much as 5 percent or more as in Durham sandy loam. However, the quantity of soil potassium available to plants at any one time is seldom more than 1 to 2 percent of the total present. Even in soils to which potash fertilizer has been applied, the proportion of total potassium held in soluble and exchangeable forms is relatively small. The majority of this element resides in potassium bearing primary minerals of the silt and sand fractions, mainly muscovite, biotite, orthoclase, and microcline. Of the clay minerals, the illite group is considered to be the only one having a substantial potassium content. (22)

Soil potassium is considered to occur in several forms or fractions which have been delineated largely on the basis

of solubility or extractability. First, there is a limited amount of water soluble potassium found in the soil solution. This fraction may be in equilibrium with a larger amount of exchangeable potassium associated with colloidal clay and organic matter. Exchangeable potassium, in turn, is considered to be in equilibrium with less soluble mineral sources, primarily that in clay. It has been convenient to classify these mineral forms as primary sources including the micas and orthoclase feldspars, and secondary sources such as clays of the illite group. Non-replaceable potassium, an arbitrary category, has been defined as that removed by more rigorous means than by leaching with ordinary salt solutions. This form is largely held by clay minerals either as native potassium or as potassium ions fixed within the clay lattice structure.(14)

According to Reitemeier (39), the various forms of soil potassium generally are related to and comprise a system in which an increase in one form occurs at the expense of one or more forms and in which the net movement may occur from less available to more available states, or the reverse, depending on the particular stress. The availability to plants depends on the amount and relative mobility of the different forms, including the rate of replenishment of depleted immediately available forms by reserve supplies. Recently the kinetics of release of potassium from biotite has been established by Mortland.(33)

Potassium is absolutely essential for plants and cannot be replaced entirely by another element. Sodium may be substituted for potassium to a certain degree, but by no means entirely.(8, 32, 19) The plant can absorb from the soil and utilize in its metabolism any soluble inorganic compound of potassium.

The exact roles of potassium in plants are not clearly understood, but some general relationships have been recognized in the physiologic plant processes.(22) It is believed to play a role in carbohydrate synthesis, in the uptake of nitrate ions, the reduction of nitrates, and the synthesis of proteins. Potassium may also play an important role in photosynthesis and cell division. Increased resistance of plants to disease has been attributed to adequate supplies of potassium. Likewise this element is considered essential for the maintainance of turgor in plant tissues.

The most common sources of potassium used in agriculture are the water soluble compounds, potassium chloride and potassium sulphate. When introduced in moist soils, these compounds immediately dissolve. Some of the potassium ions exchange with other cations on the exchange complex, others enter lattice positions of secondary micaceous minerals, and a small fraction remains in solution. Soils possessing low exchange capacities have limited ability for retaining potassium, and in areas of high rainfall, appreciable losses occur by leaching, especially when there is no cover crop.

The use of some of the lesser soluble potassium bearing materials has been investigated for a number of years. As early as 1848, Magnus (30) grew a greenhouse barley crop to maturity using powdered feldspar as the source of potassium. Aitkan compared feldspar with potassium sulphate on peas (1) and found that feldspar was as good a source of potassium for peas as the sulphate salt. DeTurk (13) also found that finely ground potassium bearing minerals increased the yield of buckwheat in peat soils 21 to 35 percent.

Haley (18) compared the dry weight yields of buckwheat grown in nutrient solution with the dry weight of the same plants grown in pots in which potassium was applied as orthoclase. In this experiment a 21 percent higher dry weight yield was obtained from plants grown in pots to which orthoclase was added, even though the potassium content of these plants was lower. However, the majority of workers have concluded that for practical purposes, the orthoclase and mica-like minerals are too insoluble and contain too little potassium. For example, naturally occurring potassium bearing silicate minerals have been compared with potassium chloride for a number of plants including Ladino clover (15), Coastal bermuda grass (20), and pine seedlings.(46) Application of ground feldspar, granite dust, and other resistant minerals generally resulted in significant potassium uptake, but concentrations in plants were well below critical levels, resulting in poor growth.

Lunt and Kwate (28) fused orthoclase feldspar and potassium nitrate or potassium carbonate at 2200°F . and obtained a glass frit containing 36 percent K_2O . When the frit was air quenched, its weathering rate was very high and solubility low. They found that weathering rate could be controlled by alternating the fineness of the grind and by incorporating various impurities in the glass. This frit was found to be a readily available source of potassium to plants and these workers suggested that large applications of frit may be made to plants which will supply potassium over prolonged cropping periods.

Bartholomew and Jacob (4) studied the effects of several phosphates including potassium metaphosphate and potassium pyrophosphate as sources of fertilizer materials. They found that for Sudan grass potassium metaphosphate was 75 percent as effective as monocalcium phosphate-potassium chloride application as far as the growth of the plant was concerned. Potassium pyrophosphate was prepared by heating pure dipotassium phosphate to a constant weight at 1000°C . and it was thus used as a source of potassium to plants. The yield of first cutting of Sudan grass, treated with potassium pyrophosphate was only half as much as that treated with potassium chloride. However, when yield data for three cuttings were combined, the total dry weight of plants treated with potassium metaphosphate and potassium pyrophosphate were equal to that of plants treated with potassium

chloride. Madorsky and Clark (29) also found that potassium metaphosphate could be effectively used as a source of phosphate and potassium.

Chandler (6) compared the effectiveness of potassium metaphosphate as a source of potassium for corn, wheat, alfalfa-orchard grass, soybeans, sudan grass and oats and noted that over a three year period potassium metaphosphate showed a tendency to outyield other carriers. The differences, however, were not statistically significant. In these greenhouse studies with Ladino clover the potassium content of plants was higher when potassium was applied as potassium chloride than when potassium metaphosphate was used as the source of fertilizer potassium. Jones and Rogers also found (21) that potassium metaphosphate was as good a source of potassium as potassium chloride.

Copson, et al. (9) developed a different process for metaphosphate production. Phosphorus was burned with the proper amount of air to maintain a temperature of 1000 to 1050°C. in a combustion chamber. Fine potassium chloride (-14 mesh) was blown in at the top of the reaction chamber at the proper rate to give the desired P_2O_5 - K_2O ratio in the product. The fine potassium chloride was introduced at two diametrically opposite feed holes by means of small air jets which served to distribute it uniformly throughout the reaction chamber. Water was added at the top of the packed tower. The molten product collected in the combustion

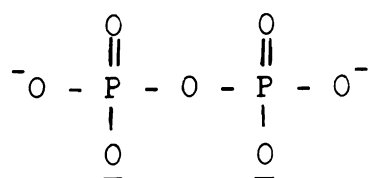
chamber and was tapped from the furnace every two hours into cooled steel pans where it was left to solidify. They found that the product obtained had the following composition:

P_2O_5	K_2O	CaO	SiO_3	Fe_2O_3	Al_2O_3	Cl	Others
54.8%	38.1%	0.3%	1.3%	0.5%	0.6%	3.7%	0.7%

The melt was then ground to give different size fractions.

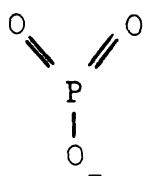
Potassium metaphosphate is now being produced in the same manner in pilot plants by the Fertilizer Development Branch of the Tennessee Valley Authority.(42) Potassium metaphosphate thus obtained varies from 55 to 58 percent P_2O_5 , 35 to 38 percent K_2O , and 1 to 4 percent chlorine. The water soluble potassium content varies from 13 to 20 percent. Potassium-calcium pyrophosphate is produced through the fusion of finely ground phosphate rock, potassium chloride, and phosphorus pentoxide.(40) The degree of solubility of the resulting product is governed largely by the rate of cooling of the melt. This melt is then ground to give various fractions ranging in total potassium content from 24 to 25 percent and water soluble potassium content from 4 to 8 percent.

It is assumed that these thermally prepared pyrophosphate materials are true pyrophosphate having the $P_2O_7^{4-}$ anion with the following structure.

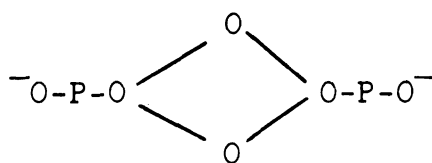


But there is no sound reason for this (45) since it is conceivable that a substance of this composition may be a mixture of ortho- and tri polyphosphates.

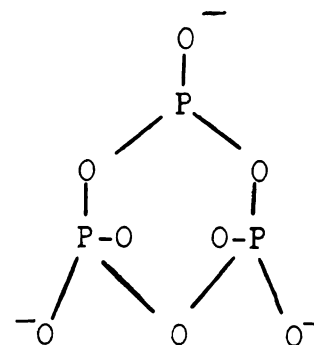
Similarly the crystal structure of the metaphosphates have not been clearly established. Three forms have been suggested including monometa-, dimeta- and trimetaphosphates. Although monometa- and dimetaphosphates have been described in literature, neither of them have been proven to exist. Dimetaphosphates probably can be prepared by low temperature synthesis.(45) Most of the so-called monometa- and dimetaphosphates have been found to be mixtures of chain or ring phosphates. The three suggested forms of metaphosphates have the following structures:



monometaphosphate



dimetaphosphate



trimetaphosphate

Stanford and Hignett (40) reported the results of studies with fused potassium phosphates in the greenhouse. Yield and potassium uptake for three successive crops from a Ruston sandy loam soil treated with potassium metaphosphate, potassium-calcium pyrophosphate, and potassium chloride of -35 mesh size fractions showed there was no significant difference

among potassium sources, notwithstanding the wide range in water solubility. The data indicated that dissolution of these materials occurred rapidly in soils. Apparently the degree of potassium water solubility of these fertilizer materials had little effect on the dry matter production of a crop such as millet. On the other hand, uptake of potassium during the first week of soil-fertilizer contact was proportional to the percent of potassium present in water soluble form. When the fertilizer-soil mixture was incubated for two weeks prior to planting this effect of water solubility was not evident. Also it was observed that with -6+9 mesh materials, leaching losses were less pronounced from fused potassium phosphates than from potassium chloride.

DeMent and Stanford (11) studied the availability of potassium from a series of fused potassium phosphates, in comparison with potassium chloride and potassium sulphate by short term uptake tests in the greenhouse. In these experiments the availability to corn of potassium from -35 mesh potassium phosphates ranging from 4 to 100 percent water solubility was not related to solubility. The meta and pyro forms of potassium phosphates supplied as much potassium to corn as did potassium chloride and potassium sulphate. Short term uptake by millet during a one week period after application indicated that all the small fertilizer particles had dissolved in soils rapidly and potassium was as available as that in potassium chloride. Potassium phosphates of lower

solubility applied as -6+9 mesh particles, however, were much lower in availability during this same period.

DeMent and Bradford (10) found no difference in availability to corn of -35+60 mesh particles of potassium metaphosphates, potassium pyrophosphates, or potassium chloride mixed throughout the soil in the greenhouse. Placing these finely ground fertilizers on the surface of soil following planting of the crop led to slightly lower potassium uptake from pyrophosphate, but did not appreciably affect the absorption of potassium from potassium metaphosphate and potassium chloride by corn plants.

In this same study, the effect of increasing particle size of the fused phosphates from -35+60 to 1/4 inch mesh resulted in decreased plant availability of potassium. Greater growth of corn plants was obtained from all application rates from 100 to 800 milligrams potassium per pot. There was no evidence of salt injury from any of the materials tested. When similar particle size and placement variables were compared, dry matter yields were usually higher from soils receiving potassium metaphosphate than from those treated with potassium pyrophosphate, except where both were finely ground.

Haiao, et al. (17) found that the availability of potassium from potassium metaphosphosphate and potassium-calcium pyrophosphate was sufficient for good growth of Ladino clover in the greenhouse on a Paxton loam soil, except when -6+14

potassium-calcium pyrophosphate was employed. In addition, a slight reduction in luxury uptake of potassium by Ladino clover from the fused phosphates was noted. Laboratory experiments showed that substantially less leaching of potassium occurred from -6+14 mesh pyrophosphate than from -35 mesh pyrophosphate. In these studies, potassium chloride, used as a standard, was subjected to extensive leaching.

DeMent, et al. (12) studied the coating of fertilizer materials with various substances in an effort to retard the migration of potassium from particles. They found that at the end of a 5 day absorption period, all coatings applied to potassium chloride except floor wax retarded uptake of potassium. Coating with paraffin resulted in least availability of potassium during this period. At the end of two weeks, none of the coatings reduced the availability of potassium appreciably.

The current investigation was undertaken in order to obtain a better understanding of the behavior of these fused potassium phosphates under various soil conditions. Field experiments were conducted in Michigan with alfalfa, corn, sugar beets, and potatoes in 1957 and 1958 using potassium-calcium pyrophosphates, potassium metaphosphate, and potassium chloride as the potassium carriers. (25, 38) Results showed that there was no significant increase in the yield of any of these crops due to the potassium carrier, particle size or placement. Analysis of plant samples of these crops at various

stages of growth indicated that during the initial stages of growth, there was an increase in potassium content of these plants with an increase in water soluble potassium content of the fertilizer applied. However, as the plants reached maturity, no significant differences in the potassium content of plants could be observed.

These studies stimulated interest in obtaining more information as to the nature of these potassium phosphates. To explain differences in their behavior due to potassium water solubility and particle size, detailed experiments were set up in the laboratory and greenhouse using the meta and pyrophosphate forms as potassium carriers.

METHODS AND MATERIALS

In order to study the behavior of potassium fertilizers under various soil conditions, experiments were conducted in the greenhouse and laboratory. The fused potassium phosphates and potassium chloride used in the experiments were produced by the Tennessee Valley Authority. Listed below are the materials used, together with the particle size and water soluble potassium content of each source. There is considerable variability in the water soluble potassium content of different sized fractions of the same fused potassium phosphate. These materials are different mesh size fractions obtained by breaking cooled melts from various chambers and not just size fractions of the same melt.

There was a wide variation in the shape or the smoothness of the particles, therefore, for all studies, fertilizer particles were selected for maximum uniformity.

<u>Fertilizer</u>	<u>Particle Size</u>	<u>Percent K₂O</u>	
		<u>Total</u>	<u>Water Soluble</u>
Potassium pyrophosphate K ₂ CaP ₂ O ₇	-35	25.9	4.8
	-4+14	25.0	5.9
	-3/8+4	24.8	7.5
Potassium metaphosphate KPO ₃	-35	31.0	20.5
	-4+14	33.5	20.6
	-3/8+4	38.9	13.0
Potassium chloride KCl	-35	59.4	59.4
	-6+10	60.6	60.6

In all comparisons of potassium carriers, the quantities of fertilizers used contained equal amounts of potassium based on their content of total potassium.

Greenhouse Studies (1957)

Greenhouse experiments were started in 1957 to study the effect of water solubility of potassium in the fertilizer materials, degree of fineness of the fertilizer particles and method of placement of fertilizer on the yield and potassium uptake of plants.

Soil: Houghton Muck soil from Muck Experimental Station and Metea sandy loam from the University Farms were used in this study.

Fertilizers: Three different potassium carriers, potassium pyrophosphate, potassium metaphosphate, and potassium chloride, of -35 and -6+14 mesh sizes were applied at the rate of one thousand pounds K_2O per acre in both soils. Nitrogen and phosphorus were applied at the rate of one thousand pounds per acre of ammonium nitrate and diammonium hydrogen phosphate, respectively.

Fertilizer placement: In Muck soil all fertilizers were applied as mixed and banded treatments, whereas only the mixed treatment was used in Metea sandy loam soil. In mixed treatments, the fertilizers were thoroughly mixed with the soil, while in banded treatments the fertilizers were applied in circular bands 1 inch deep to the side and below the seeds.

Cultural practices: Two gallon glazed pots were used in the study with four replications per treatment. Eight seeds of Sanilac white pea beans were planted in each pot on May 3, 1957, and on May 29th, the stand of beans was thinned to four plants per pot. Distilled water was added to each pot as required by weighing the pots weekly and applying additional water by estimation between weighing periods. The plants were harvested at the time of flowering. The above ground parts of the plants were removed, dried in an oven at 70°C. and weighed. This material was then ground in a Wiley mill and samples were extracted with a salt solution. Potassium in this extract was evaluated using a flame photometer.

Greenhouse Studies (1958)

Soils: Greenhouse experiments were continued in 1958 on Houghton Muck soil and Kalamazoo sandy loam.

Fertilizers: The potassium carriers used were potassium pyrophosphate, potassium metaphosphate, and potassium chloride. Three particle sizes of -35, -6+14, and -3/8+4 mesh were used with pyro- and metaphosphate materials, whereas only -35 and -6+10 mesh sizes were available for potassium chloride.

Potassium was applied at the rate of 600 pounds K_2O per acre to the organic soil and 300 pounds per acre to the Kalamazoo sandy loam. Nitrogen was added to the mineral soil and organic soil as ammonium sulphate at the rate of 300

pounds and 100 pounds per acre of nitrogen, respectively. Supplemental phosphorus application amounted to 300 pounds P_2O_5 per acre for mineral soil and 600 pounds P_2O_5 for the muck soil, using concentrated superphosphate as the phosphorus source.

Fertilizer placement: All potash fertilizers were applied as mixed and banded treatments. In the former case, fertilizers were mixed with the soil while in the latter they were applied 1 inch below and to the side of the seed. The nitrogen and phosphorus supplements were well mixed with soil for all treatments.

Cultural practices: One gallon glazed pots were used in the study, with three replications per treatment. Fifty seeds of Red Proso variety millet were planted in the pots on June 13, 1958. During growth, the pots were irrigated with measured quantities of distilled water. On July 9th, the stand of millet was thinned to 20 plants per pot. The plants were harvested 15 days later, when they started to head. All above ground plant parts were dried in an oven at $70^{\circ}C.$, weighed, and ground in a Wiley mill. Analyses for potassium were carried out similarly as indicated for samples collected in 1957.

Laboratory Experiments

Experiment 1. To study the rates of dissolution of potassium from the fertilizer granules, a preliminary leaching

experiment was set up in the laboratory. Fertilizers used included -35, -4+14, and -3/8+4 mesh particles of potassium pyrophosphate, potassium metaphosphate, and potassium chloride. Except for the finely divided materials, a specific number of previously weighed particles selected for uniformity were placed in a filter paper in small Buckner funnel and leached with successive 20 milliliter portions of water at a leaching rate of 1 liter per hour. The leachates were collected and analyzed for potassium.

Experiment 2. In order to determine if the leaching characteristics of the partially water soluble fused potassium phosphates incorporated in soil, were similar to those when the fertilizers were leached in funnels, an experiment was conducted to study the distribution of potassium released from these fertilizer materials in a soil column. Tubes, 24 inches tall and 6 inches in diameter were packed uniformly with Kalamazoo sandy loam soil up to 20 inches from the bottom. To the soil in each tube, 2 inches of water was added and the soil mass incubated for four days without loss of moisture. Potassium pyrophosphate, potassium metaphosphate, and potassium chloride, the first two in -35, -4+14, and -3/8+4 mesh sizes and the chloride in -35 and -6+10 mesh sizes were applied at the rate of 500 pounds potassium per acre. The fertilizers were placed uniformly on the surface of soil and covered with another inch of soil. Two more inches of water were then

added to each column and the top of the tubes covered with polyethylene film. After a week, the tubes were opened and the soil column was sliced to give 1 inch thick samples. The samples were dried and analyzed for water soluble potassium.

Experiment 3. An experiment was initiated to study the dissolution and migration of potassium from fertilizer particles placed in a bulk volume of soil. Wooden boxes 4.5 inches long, 4.5 inches wide, and 4.5 inches high were used as containers, the sides of which were provided with grooves horizontally 1 centimeter apart in order to facilitate sampling of soil. The lid and one of the sides were provided with hinges so that the box could be opened and closed from above and from the sides.

The experiment was conducted with two soils, Houghton muck and Oshtemo sand. The soil moisture variable included 50 percent and 100 percent moisture levels for the organic soils and 10 and 20 percent moisture levels for the Oshtemo sand. The soils were incubated with the necessary amount of water for one week so as to enable the soil to reach equilibrium with water. The boxes were packed uniformly with the moist soil to within 2 centimeters from the top.

Potassium pyrophosphate and potassium metaphosphate of -4+14 and -3/8+4 mesh sizes were used in this study. Twenty-five particles of the larger size particles and fifty of the

smaller ones which had been previously weighed, were placed in a band at the center of the box. The boxes were then completely filled with soil and sealed air tight. After 1, 2, 4, 8, 16, and 32 days incubation period one box from each treatment was opened. The first centimeter of soil was removed from the top and the fertilizer particles were recovered from the layer immediately below. Soil samples were taken from the 1-3, 3-5, and 5-7 centimeter depths of the box by introducing steel plates into the grooves. At each depth samples were taken 0-1 (both directions), 1-3, and 3-5 centimeters laterally from the place of application of the fertilizer. The soil samples were analyzed for water soluble potassium.

Experiment 4. Dissolution and diffusion of ions from fertilizers placed in soil are known to be affected by the thickness of the water films. Therefore, an experiment was initiated to study the effect of soil moisture content on the rate of dissolution of the fused potassium phosphates.

Moisture cans 2 inches in diameter were filled with Kalamazoo sandy loam soil at 2, 5, and 12 percent moisture. Ten particles of potassium pyrophosphate of -4+14 mesh size were then placed at the center of the cans. The soil was then incubated and individual cans were opened after 1, 2, 4, 8, 12, 24, 48, and 72 hours incubation period. Concentric samples having diameters of 11, 22, 35, and 50 millimeters

were taken around the center of the fertilizer source. The moisture content was determined in all soil samples taken.

Field experiment. An attempt was made to study the disintegration of potassium fertilizers possessing varying degrees of water solubility and dissolution of potassium therefrom under field conditions. Fertilizer particles were placed on the surface of a Conover loam at the University Farms. Small enclosures were made with wire mesh in order to avoid the loss of granules by rain and wind. Three fertilizer materials, potassium pyrophosphate, potassium metaphosphate, and potassium chloride, the first two as -6+14 and -3/8+4 mesh materials and the last at -6+10 mesh granular particles, were used in the study. Each group of approximately 60 fertilizer particles was selected for uniform size and was weighed before placing the individuals on the soil within the enclosures. Six replications of each fertilizer treatment were laid out in a random arrangement.

At the end of 10, 20, 30, and 40 days all granules were picked up from the plots. They were gently cleaned with a brush to remove all soil particles sticking on them and analyzed for water-soluble and total potassium. During the period of exposure of fertilizer particles in the field, the area received precipitation on the following dates:

May 9	0.07 inches	June 1	1.18 inches
May 18	0.05 inches	June 2	0.42 inches
May 23	0.10 inches	June 8	0.10 inches
May 28	0.05 inches	June 9	0.48 inches
May 31	0.11 inches	June 10	0.17 inches
		June 13	0.51 inches

Laboratory Techniques

The soils for the experiments were analyzed for pH, sand, silt and clay, exchange capacity, and exchangeable bases.

Soil reaction was determined using 1:1 soil-water ratio, by glass electrode.

Percent sand, silt, and clay were determined using the hydrometer procedure of Bouyoucos.(5)

Exchange capacity was determined by the neutral ammonium acetate extraction method of Peech. (36)

Individual bases were determined in the initial ammonium acetate leachate. Analysis of exchangeable potassium was made using a flame photometer. For determining exchangeable calcium and magnesium, a Beckman DU flame photometer was used with the following adjustments:

	<u>Calcium</u>	<u>Magnesium</u>
Wavelength	4227 A°	2582 A°
Phototube resistor	No. 2	No. 2
Selector	0.1	0.1
Slit	0.01	0.06
Sensitivity		
a. Instrument panel	Variable	Variable
b. Photomultiplier	No. 4	Full
Zero suppression	1.0	1.0
Phototube	Blue	Blue

Water soluble potassium in soil was determined by shaking 1 gram soil with 10 milliliters water for 10 minutes, followed by filtration.

For evaluating water soluble potassium in fertilizer, a 1 gram sample was shaken with 50 milliliters water, allowed to remain overnight and then leached with additional water to give a total volume of 200 milliliters.

Total potassium in fertilizer was determined by extracting the material with concentrated hydrochloric acid as described in A.O.A.C. method of analysis. (2)

Potassium in plant samples was determined by extracting the dried, ground plant material with a 2 N ammonium acetate and 0.2 N magnesium acetate solution as described by Attoe. (3)

Potassium extracted from all soil and plant materials was determined using a Perkin Elmer Model 52 A flame photometer or a Coleman Model 21 flame photometer.

RESULTS AND DISCUSSIONS

Greenhouse Studies

The effect of potassium fertilizers with varying water soluble potassium content and particle size was evaluated in terms of dry matter production and potassium uptake by field beans grown on Metea sandy loam and Houghton muck in the greenhouse. The data in Table 2 show that when the potassium carriers were applied in granular form and mixed with this mineral soil, no significant difference was obtained in the yield of beans grown on Metea sandy loam, as a function of water solubility of the fertilizers. Application of potassium pyrophosphate in pulverized form resulted in the same yield as that for granular form. However, bean plants grown in soil treated with pulverized pyrophosphate removed 270.6 milligrams potassium per pot or about 14 percent more than plants grown in pots treated with granular material. This difference is definitely related to the greater surface area presented by the finely divided materials.

However, with potassium metaphosphate treatments, the mixed application of pulverized materials resulted in significantly higher yield of beans than that of granular applications. This could be expected since potassium metaphosphate is more soluble than pyrophosphate and also contains more water

TABLE 1

Some of the chemical and physical properties of the soils used in the study.

Soil Type	pH	Per- cent Sand	Per- cent Silt	Per- cent Clay	Cation Exchange Capacity m.e./100 grams.	Exchangeable Cations m.e./100 grams.				Water Soluble Potassium m.e./100 grams.
						Ca	Mg	K	Na	
Kalamazoo Sandy Loam	5.8	62.8	20.0	17.6	8.2	6.1	2.0	0.14	0.04	0.05
Metea Sandy Loam	6.0	68.0	23.6	8.4	6.8	4.72	1.11	0.82	0.01	0.07
Oshtemo Sand	5.9	89.2	6.4	4.4	5.0	1.81	1.02	0.18	0.06	0.09
Houghton Muck	6.2	--	--	--	131.0	74.00	22.0	0.62	--	0.10

TABLE 2

Effect of water soluble potassium content of fertilizer on the yield and potassium content of field beans grown on Metea sandy loam in the greenhouse.

Material	Particle Size	Yield gm./pot*	Potassium Content %	Potassium Uptake mgm./pot
Potassium pyrophosphate	Granular	16.7	1.54	257
	Pulverized	16.5	1.64	271
Potassium metaphosphate	Granular	17.6	1.69	297
	Pulverized	23.5	1.43	336
Potassium chloride	Granular	16.5	1.70	289
	Pulverized	16.2	1.50	243
Check (NP)		17.1	1.57	268

*Average of four replications

Summary

Material	Yield gm./pot	Potassium Content %	Potassium Uptake mgm./pot
Potassium pyrophosphate	16.6	1.59	264
Potassium metaphosphate	20.5*	1.56	317
Potassium chloride	16.5	1.60	266
Particle Size			
Granular	17.1	1.64	273
Pulverized	18.6*	1.52	283

*Significantly higher at 5 percent level.

soluble potassium and pulverizing the granules would result in much better contact between soil and fertilizer particles. Additional evidence of the difference in solubility of the meta- and pyrophosphate forms can be seen from the fact that bean plants absorbed 22 percent more potassium from the pulverized metaphosphate treatments than from soil receiving finely divided pyrophosphate. As might be expected, when potassium chloride was used as a source of potassium, there was no difference between the yields of beans grown in soils treated with granular or pulverized materials. Either form dissolves completely in moist soil.

The fact that finely divided metaphosphate produced more growth than potassium chloride suggests that the supplemental phosphate application was not sufficient for maximum growth. In this experiment, when the various potassium carriers were used in Metea sandy loam, pulverized or granular, there was very little difference in yield. This is due to the fact that irrespective of particle sizes, sufficient soluble potassium was available for the plants starting with the seedling stage. Data from Table 6 show that about 2 percent of potassium moved out of pyrophosphate when leached with 20 milliliters of water, whereas 8 percent moved out of metaphosphates of -35 mesh size and 4 percent from -4+14 mesh particles when leached with the same amount of water. In any case, initial supply of potassium from

granules was sufficient to ensure the satisfaction of potassium needs of seedlings.

Examination of the data in Table 3 shows that yield and potassium content of field beans were affected to a much greater extent by the method of fertilizer placement than by the kind of potassium carrier or the particle size. The average effects given in Table 3 indicate that no difference in growth resulted from the use of the highly soluble potassium chloride or the partially soluble fused potassium phosphates. However, potassium content and thereby uptake of this element was directly related to a degree with the water solubility of the fertilizers studied.

Whether the potassium phosphates were applied as large particles or in a fine state of subdivision, had little influence on either yield or potassium content of field beans.

In order to logically explain the marked superiority of mixing versus banding, it must be emphasized that this organic soil as collected had never been fertilized and thereby was very low in available potassium and phosphorus as shown by chemical analysis. It is probable that sufficient potassium was available from each potassium source in banded placement. Though no observations of the root systems were taken, root development was probably restricted to the zone of the fertilizer band. Yield data of the nitrogen-phosphorus treatment indicate that placement had little effect on the

TABLE 3

Effect of water soluble potassium content of fertilizer, particle size, and method of placement on yield and potassium content of field beans on Houghton Muck soil in the Greenhouse.

Material	Particle Size	Place-ment	Yield gms/pot	Potassium Content %	Potassium Uptake mgms/pot*
Potassium pyrophosphate	Granular	Banded	15.5	1.74	270
		Mixed	26.3	1.78	488
	Pulverized	Banded	18.8	1.53	288
		Mixed	28.9	2.28	659
Potassium metaphosphate	Granular	Banded	15.3	1.83	280
		Mixed	28.9	2.30	665
	Pulverized	Banded	18.9	1.42	268
		Mixed	22.2	2.27	504
Potassium chloride	Granular	Banded	16.8	1.78	299
		Mixed	31.5	2.72	857
	Pulverized	Banded	19.4	1.75	340
		Mixed	21.0	2.58	542
Check (NP)		Banded	13.6	1.19	162
		Mixed	12.8	1.18	152

*Average of four replications

Summary			
Materials	Yield gms/pot	Potassium Content %	Potassium Uptake mgms/pot
Potassium pyrophosphate	22.3	1.83	426
Potassium metaphosphate	21.3	1.95	429
Potassium chloride	23.4	2.20	510
Particle Size			
Granular	22.3	2.02	477
Pulverized	22.3	1.96	435
Placement			
Mixed	23.4*	1.99*	
Banded	14.8	1.43	

*Significantly higher at 5 percent level.

growth of beans. In this instance no potassium was present, which in itself limits growth and nutrient absorption. Consequently unless both potassium and phosphorus were well mixed with the soil, maximum plant development could not take place.

This experiment brings out an excellent sample of interaction between nutrient supply and placement in an infertile soil, namely that at moderate to high rates of application, nitrogen and phosphorus must be well mixed with soil to obtain maximum yield and uptake of fertilizer potassium.

The growth of and absorption of potassium by millet grown on a Kalamazoo sandy loam soil as affected by the water soluble potassium content, particle size and placement of several potash fertilizers is presented in Table 4. It is quite evident that potassium water solubility of the fertilizers was not a factor influencing growth since chloride was less effective than either the meta- or the pyrophosphate materials. In fact the data suggest that either the chloride ion concentration was detrimental or that the additional phosphorus applied with the fused potassium phosphates was of benefit.

Variation in yield of millet for the particle size factor within each material make it impossible to draw any conclusions. However, considering all potash sources, the potassium content of millet receiving the finely divided fertilizer was significantly higher for the coarser fertilizers.

The most interesting feature of this experiment is the apparent superiority of banded over mixed placement. In contrast to the greenhouse studies conducted in 1957, the nitrogen

TABLE 4

Effect of water soluble potassium content of fertilizer, particle size, and placement on the yield and potassium content of Proso Millet grown on Kalamazoo sandy loam soil in the greenhouse.

Material	Particle Size	Place-ment	Yield gms/pot*	Potassium Content %*	Potassium Uptake mgms/pot
Potassium pyrophosphate	-35 mesh	Banded	22.7	2.13	484
		Mixed	19.1	2.04	390
	-4+14 mesh	Banded	18.7	2.24	419
		Mixed	18.7	1.89	353
	-3/8+4 mesh	Banded	21.8	2.07	451
		Mixed	15.5	2.07	321
Potassium metaphosphate	-35 mesh	Banded	16.3	2.68	437
		Mixed	17.7	2.53	448
	-4+14 mesh	Banded	20.6	2.28	470
		Mixed	13.4	2.33	312
	-3/8+4 mesh	Banded	21.3	2.51	535
		Mixed	19.7	2.09	412
Potassium chloride	-35 mesh	Banded	17.0	2.40	408
		Mixed	10.1	2.59	262
	-6+10 mesh	Banded	15.3	2.41	369
		Mixed	9.7	2.04	198

*Average of 3 replications.

Summary

Materials	Yield gms/pot	Potassium Content %	Potassium Uptake mgms/pot
Potassium pyrophosphate	19.8*	2.08	403
Potassium metaphosphate	17.8*	2.46*	436
Potassium chloride	13.0	2.36*	309
Particle Size			
-35	17.1	2.40*	
-4+14	16.6	2.20	
-3/8+4	19.6	2.18	
Placement			
Banded	19.2*	2.34	447
Mixed	15.5	2.19	337

*Significantly higher at 5 percent level.

and phosphorus supplements were mixed with this mineral soil regardless of the nature of placement of the potash source. Thus, any benefit ascribed to banding cannot be attributed to greater availability of the supplemental phosphate. Yet, the possibility of additional response arising from the phosphorus combined in the potash carriers cannot be overlooked. In 7 out of 8 comparisons, potassium uptake was greater where the fertilizers were banded, largely as a result of the combination of greater yield and a higher potassium content.

The results of the greenhouse test comparing the effects of the kind, placement and particle size of the potash fertilizer on the growth of millet on an organic soil is given in Table 5. Upon averaging the effects of particle size and placement for each potassium carrier, the potassium metaphosphate was of most benefit, and particularly the finer fractions. Virtually no difference was found between yields of plants receiving the highly soluble chloride and the rather insoluble pyrophosphate. In terms of potassium content, the values are almost twice those for plants from the mineral soil, but the percentage potassium in millet appears to be rather well related to the potassium water solubility of the fertilizer. However, considering the high values of potassium within plants of all treatments, it is unreasonable to assume that potassium was deficient under these conditions.

From the standpoint of dry matter production, neither particle size nor placement had much effect, with the

TABLE 5

Effect of water soluble potassium content of fertilizer, particle size, and placement on the yield and potassium content of Proso Millet grown on Houghton Muck soil in the greenhouse.

Material	Particle Size	Place-ment	Yield gms/pot*	Potassium Content %*	Potassium Uptake mgms/pot*
Potassium pyrophosphate	-35 mesh	Banded	22.5	5.07	1141
		Mixed	23.3	6.13	1428
	-4+14 mesh	Banded	18.2	5.10	928
		Mixed	16.8	5.77	969
	-3/8+4 mesh	Banded	19.0	5.13	975
		Mixed	20.2	5.50	1111
Potassium metaphosphate	-35 mesh	Banded	22.8	5.27	1202
		Mixed	29.0	5.80	1682
	-4+14 mesh	Banded	26.7	5.60	1495
		Mixed	29.8	5.83	1737
	-3/8+4 mesh	Banded	20.3	5.17	1050
		Mixed	18.7	5.00	935
Potassium chloride	-35 mesh	Banded	22.8	6.00	1368
		Mixed	21.8	6.07	1323
	-6+10 mesh	Banded	20.5	5.30	1087
		Mixed	21.7	6.27	1361

*Average of 3 replications.

Summary

Materials	Yield gms/pot	Potassium Content %	Potassium Uptake mgms/pot
Potassium pyrophosphate	20.2	5.52	1092
Potassium metaphosphate	27.1*	5.63	1350
Potassium chloride	21.7	5.91	1285
Particle Size			
-35	23.7	5.72*	
-4+14	22.3	5.64	
-3/8+4	19.0	5.20	
Placement			
Banded	21.6	5.33	
Mixed	22.6	5.78*	

*Significantly higher at 5 percent level.

exception for metaphosphate previously mentioned. As might be expected on the basis of solubility and fertilizer-soil contact relationships, the potassium content of millet was highest where the potash fertilizers were finely divided and mixed well with the soil.

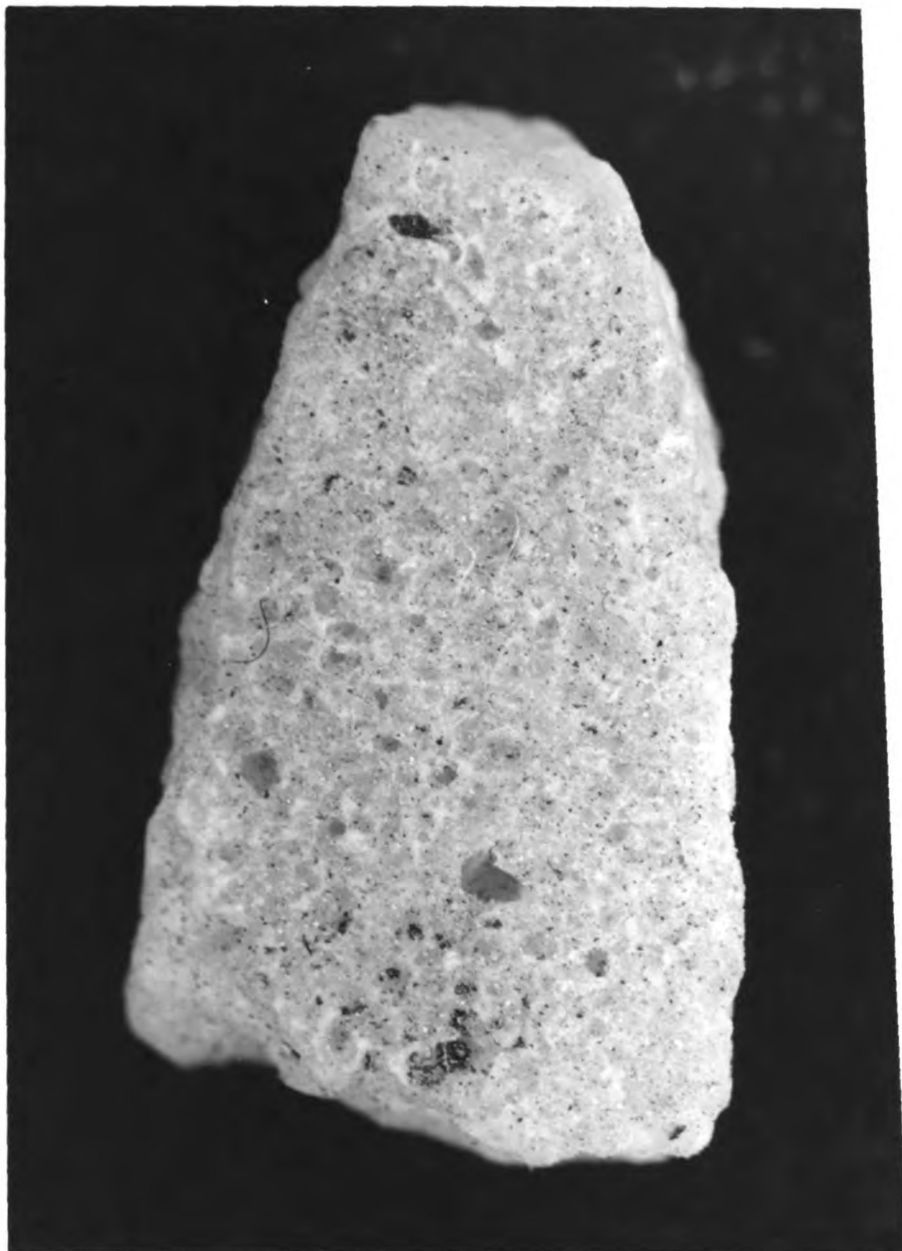


Plate 1. Original -3/8+4 mesh pyrophosphate particle (50x).



Plate 2. Original -3/8+4 mesh metaphosphate particle (50x).

Laboratory Studies

A preliminary test was conducted to determine the rate of dissolution of water soluble fractions of potassium from potassium pyrophosphate, potassium metaphosphate, and potassium chloride. The fertilizers were leached with successive increments of water at a constant leaching rate and the leachates analyzed for potassium.

The data presented in Table 6 show that with potassium pyrophosphate of -35 mesh particle size, 2.85 percent potassium or 59.3 percent of the total water soluble fraction was leached out with the first increment of water. In the next leachate 1.25 percent of potassium or 26.1 percent of the element originally soluble in water was found, accounting for 85.4 percent of this fraction from the two leachates. Addition of 100 milliliters of water practically removed all the existing water soluble potassium from these fine particles. Additional increments of water removed no more potassium.

With -4+14 mesh size particles of pyrophosphate the rate of removal of the water soluble potassium by leaching was slower. Considerable leaching of water soluble potassium occurred after addition of 6 portions of water, or the equivalent of 120 milliliters of water, after which the rate of dissolution decreased. A total of 200 milliliter water was needed to remove all the water soluble fraction of potassium from the intermediate size particles. Further leaching resulted in conversion of only a small fraction of water

TABLE 6

The dissolution of potassium from potassium pyrophosphate fertilizers of different particle size upon leaching with water.

Amount of Water Added in ccs*	-35 Mesh Size			-4+14 Mesh Size			-3/8+4 Mesh Size		
	% of the % of the		Total K ₂ O	% of the % of the		Total K ₂ O	% of the % of the		Total K ₂ O
	% K ₂ O Released	H ₂ O-Sol. K ₂ O		% K ₂ O Released	H ₂ O-Sol. K ₂ O		% K ₂ O Released	H ₂ O-Sol. K ₂ O	
20	2.85	59.37	11.0	2.04	34.57	8.1	1.98	26.4	7.9
40	4.10	85.41	15.8	3.82	64.74	15.2	3.44	45.8	13.9
60	4.38	91.25	16.9	4.65	78.80	18.6	5.17	68.9	20.8
80	4.64	96.66	17.9	4.87	82.50	19.4	5.73	76.4	23.1
100	4.74	98.75	18.3	5.08	86.10	20.3	5.93	79.0	23.9
120	4.74	98.75	18.3	5.26	89.1	21.0	6.13	81.7	24.7
140	4.74	98.75	18.3	5.40	91.5	21.6	6.19	82.5	24.9
160				5.51	93.3	22.0	6.25	83.3	25.2
180				5.57	94.4	22.2	6.54	87.2	26.3
200				5.66	96.0	22.6	6.80	90.6	27.4
220				5.70	96.6	22.8	6.95	92.6	28.0
240				5.78	97.9	23.1	7.02	93.6	28.3
260				5.86	99.3	23.4	7.14	95.2	28.7
280				5.93	100.5	23.7	7.20	96.0	29.0
300				5.98	101.3	23.7	7.22	96.2	29.0
320				6.04	102.3	23.9	7.30	97.3	
340				6.04	102.3	24.1	7.36	98.1	
360							7.44	99.2	
380							7.45	99.3	
400							7.47	99.6	

*Cumulative

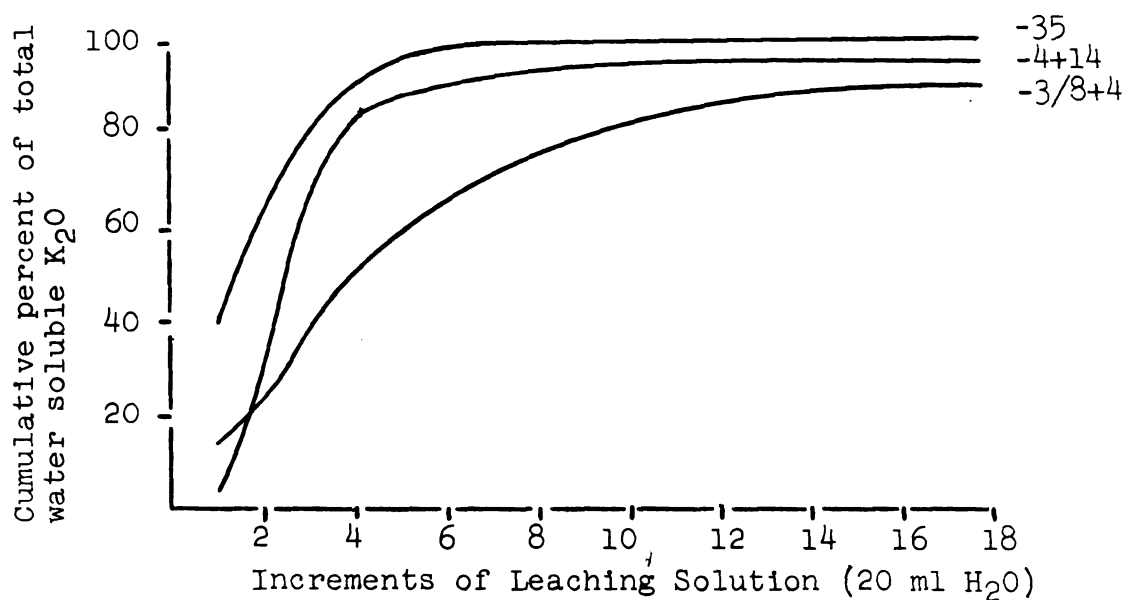


Fig. 2. Dissolution of potassium from potassium metaphosphate upon leaching with water.

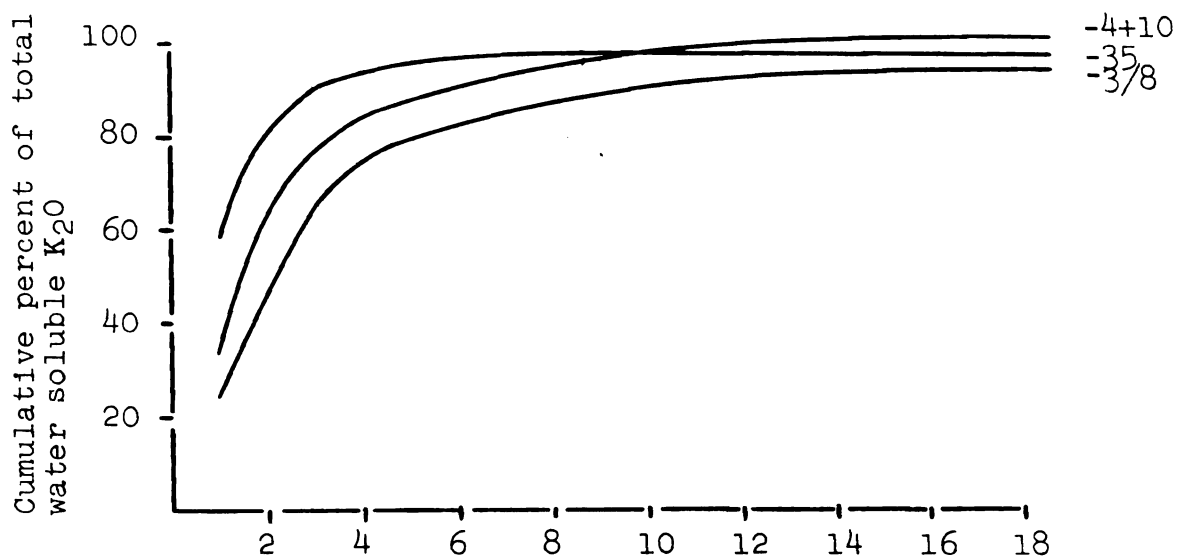


Fig. 1. Dissolution of potassium from Potassium-calcium pyrophosphate upon leaching with water.

insoluble potassium to the water soluble form. With the large particles of potassium pyrophosphate a significant reduction in dissolution of potassium by leaching with water was noted as compared with the smaller size fractions. For example, the first two 20 milliliter portions of water removed only 26.4 percent of the total water soluble potassium, the next portion 19.4 percent of the total, while a total of 60 milliliter water resulted in the removal of about 69 percent of the total water soluble potassium. For this material about 300 milliliter water was needed to leach out most of the water soluble potassium from the particles. A comparison of the dissolution patterns of the three size fractions is given in Figure 1.

There was little change in the appearance of the pyrophosphate fertilizer particles due to leaching with water as noted by optical examination. No physical disintegration was visible, especially in the large size pyrophosphate particles, even though particles appeared to be much more porous and the surface considerably rough after leaching. An enlarged view of the surface of the leached and unleached material is presented in Plates 3 and 4.

With potassium metaphosphate particles, the rate of removal of water soluble potassium from the particles also was dependent on the particle size as noted in Table 7. With the addition of 80 milliliters of water practically all soluble potassium was leached out from the -35 mesh size



Plate 3. Surface of original -3/8+4 mesh pyrophosphate particle (100x).

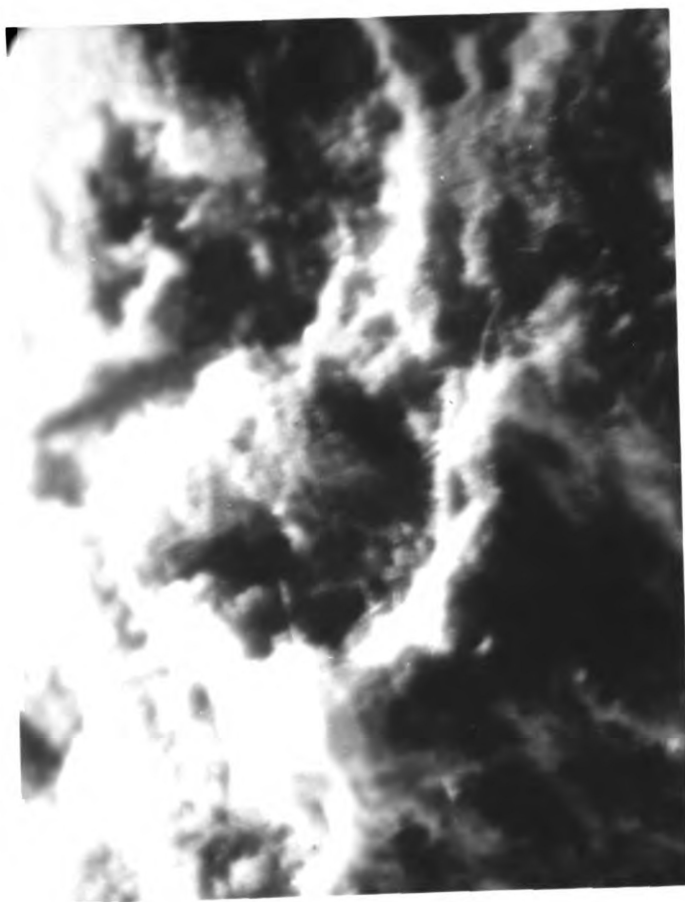


Plate 4. Surface of leached $-3/8+4$ mesh pyrophosphate particle (100x).

particles. The rate of removal of potassium was slower from the $-4+14$ mesh size particles, especially in the early stages of leaching. For instance, only 4.2 percent of the total water soluble potassium was leached out with the first increment of water. Subsequent leaching removed considerably more potassium suggesting that initial dissolution is preceded by an absorption or soaking period. Almost all the water soluble potassium was leached out upon addition of 200 milliliters of water. The release of potassium was still slower from $-3/8+4$ mesh metaphosphate particles. In this case the rate of dissolution was fairly constant for the first four increments of water added. Thereafter potassium apparently dissolved out of the large particles rather slowly.

The appearance of metaphosphate particles was rather altered after leaching. The particles had become soft and the larger particles had started to crumble. Physical disintegration was much more evident here than in the case of smaller particles. A picture of the large metaphosphate particle before and after leaching is given in Plates 5 and 6.

The total amount of potassium leached out from the smaller sized fused potassium phosphates particles is greater than that from the larger ones. This could be expected since the smaller the particle size, more the greater will be the area of direct contact between the fertilizer and the water molecules. An exception is the $-3/8+4$ mesh pyrophosphate

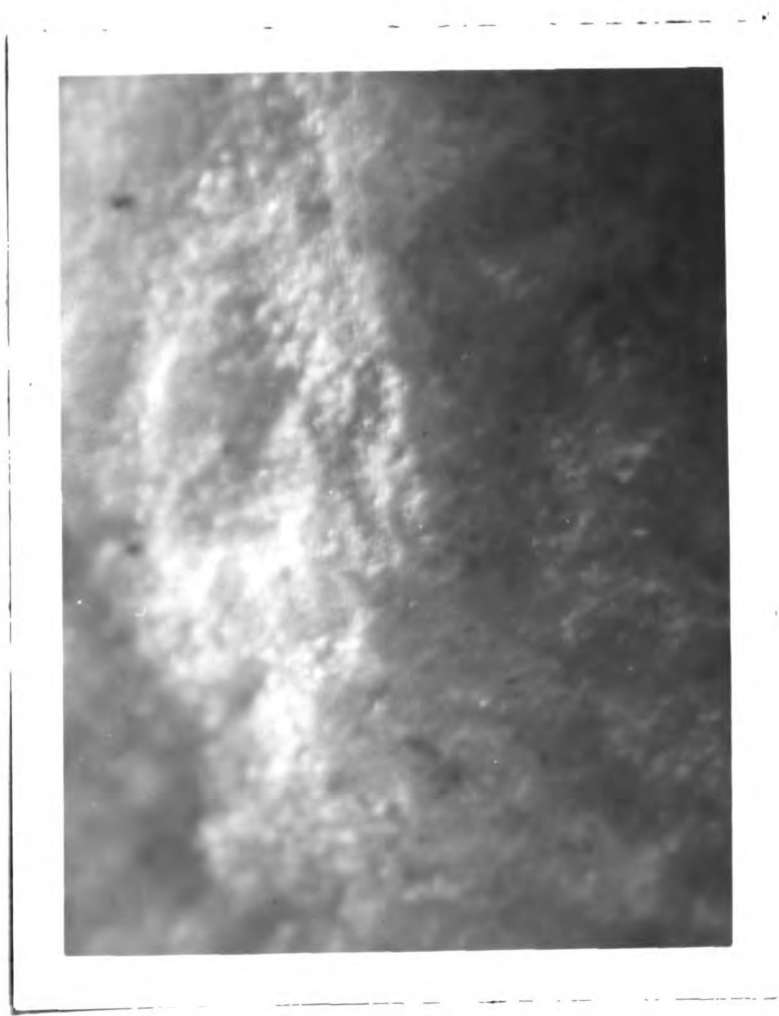


Plate 5. Surface of original -3/8+4 mesh metaphosphate particle (100x).

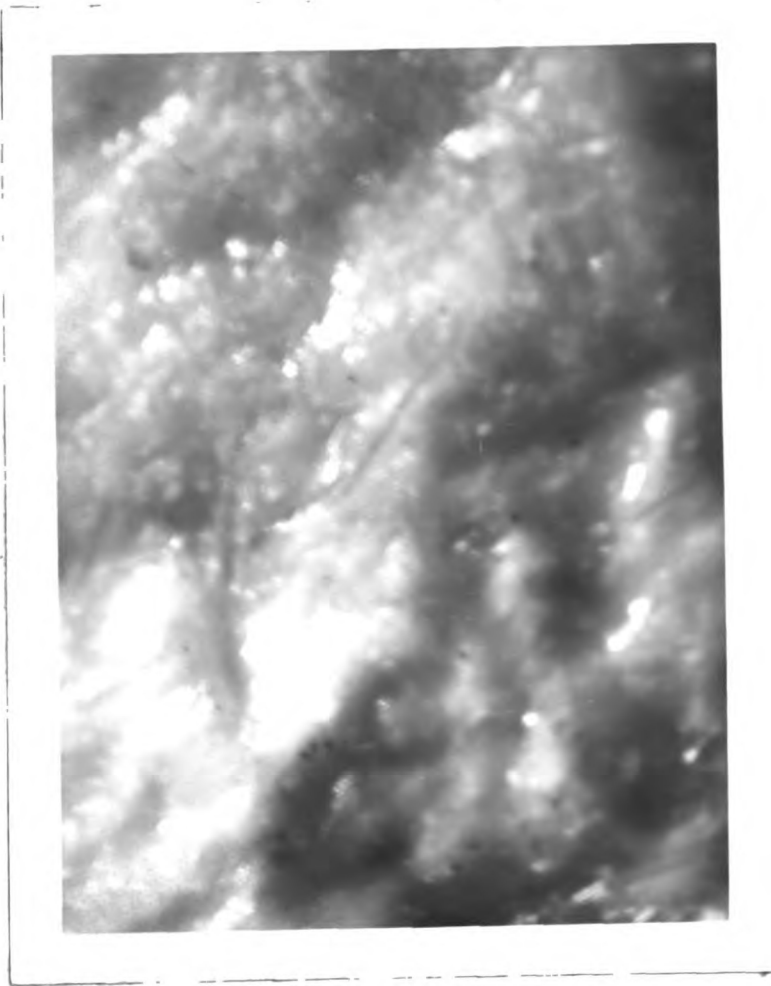


Plate 6. Surface of leached $-3/8+4$ mesh metaphosphate particle (100x).

TABLE 7

The dissolution of potassium from potassium metaphosphate fertilizers of different particle size upon leaching with water.

Amount of Water Added in ccs*	-35 Mesh Size				-4+14 Mesh Size				-3/8+4 Mesh Size			
	% of the % of the		% of the % of the		% of the % of the		% of the % of the		% of the % of the		% of the % of the	
	% K ₂ O Released	% H ₂ O-Sol. K ₂ O	Total K ₂ O	% of the Total K ₂ O	% K ₂ O Released	% H ₂ O-Sol. K ₂ O	Total K ₂ O	% of the Total K ₂ O	% K ₂ O Released	% H ₂ O-Sol. K ₂ O	Total K ₂ O	% of the Total K ₂ O
20	8.50	41.4	27.4		0.88	4.2	2.6		1.84	14.1	4.65	
40	13.00	63.4	41.9		4.96	24.0	14.8		3.91	30.0	10.00	
60	16.62	81.0	53.6		14.10	68.5	42.0		5.41	41.6	1.90	
80	19.72	96.1	63.0		17.70	86.0	52.9		7.25	55.7	18.60	
100	20.72	101.0	66.8		17.98	87.2	5.6		7.68	59.0	19.70	
120	20.72	101.0	66.8		18.26	88.6	54.5		8.19	63.0	21.00	
140	20.72	101.0	66.8		19.01	92.5	56.8		9.67	74.3	24.80	
160					19.16	93.0	57.0		9.88	76.0	25.30	
180					19.29	93.6	57.5		10.27	79.0	26.40	
200					19.73	95.7	58.8		11.19	86.0	28.70	
220					19.86	96.4	59.2		11.43	87.9	29.30	
240					19.98	96.5	59.3		11.43	87.9		
260					20.00	97.0			11.48	88.3		
280					20.03	97.3			11.61	89.3		
300					20.06	97.6			12.01	92.4		
320					20.16				12.24	94.2		
340					20.24				12.34	94.9		
360					20.29				12.34	95.2		
380					20.32				12.38	95.6		
400					20.35				12.44			

*Cumulative

which is more soluble than the -4+14 mesh size particles. It has to be borne in mind that all these samples are taken from different melts during the manufacturing process. In addition there is little uniformity in the shape or the size of the particles since they are merely pieces of large lumps broken down to give the necessary particle sizes.

Even though the rate of dissolution varied considerably for different sized fractions of the fused potassium phosphates, it is very probable that sufficient potassium would be solubilized during the early contact with soil to supply enough potassium for plant growth.

With potassium chloride particles, addition of 20 milliliters water leached out practically all soluble potassium from both -35 and -6+10 mesh size particles.

Leaching the particles in soil column. To determine the effect of leaching under soil conditions, a soil column study was conducted to evaluate the movement of potassium from several potash fertilizers placed in a layer in moist soil one inch below the surface. After leaching and an incubation period of one week, the tubes were opened and the soil at various depths was analyzed for potassium.

The data presented in Table 8 indicate that in general the dissolution and movement of potassium was rather limited for the two inch application of water. Most of the potassium liberated from the several particle size fractions of both pyrophosphate and metaphosphate was recovered in the first

TABLE 8

Distribution of extractable potassium in soil columns incubated with potassium pyrophosphate, potassium metaphosphate, and potassium chloride of different particle sizes.

Depth of Soil Layer in Inches	Parts per Million Potassium Extracted on Soil Basis*					
	-3/8+4 Mesh Size		-4+14 Mesh Size		-35 Mesh Size**	
	NH ₄ Ac	H ₂ O	NH ₄ Ac	H ₂ O	NH ₄ Ac	H ₂ O
Potassium Pyrophosphate						
0-1	380	90	440	100		
1-2	460	110	440	100	300	60
2-3	220	27	210	27	210	33
3-4	210	27	210	27	210	30
4-5	210	27	210	27	210	30
5-6***	210	27	210	27	210	27
Potassium Metaphosphate						
0-1	460	125	750	230		
1-2	290	45	680	175	680	140
2-3	210	27	210	27	220	27
3-4	210	27	210	27	210	27
4-5	210	27	210	27	210	27
5-6***	210	27	210	27	210	27
Potassium Chloride						
			-6+10 Mesh Size		-35 Mesh Size	
0-1			460	105		
1-2			830	155	330	55
2-3			440	100	830	155
3-4			330	52	520	125
4-5			250	37	380	100
5-6			220	27	210	40
6-7***			210	27	210	35

*Potassium extracted with 1 N. ammonium acetate or distilled water.

**The soil layer containing these particles was disregarded since the individual particles could not be removed prior to extraction.

***No further change in potassium was noted below this depth.

two inches of the soil column. In fact, the sharpness of separation in terms of both exchangeable and water soluble potassium contained in the 1-2 and 2-3 inch layers is rather remarkable. It is believed this phenomenon involves progressive exchange between the leaching potassium ions derived from the fertilizer source and the varied cationic species originally present on the colloidal surfaces of the soil column. If the columns had been subjected to more extensive leaching, it is probable that greater downward movement would have occurred. This supposition is based on the fact that potassium from similar rates of potassium chloride was concentrated in layers sampled to a depth of 5 inches.

The effect of fertilizer particle size on the release and movement of potassium within the soil during and after leaching was not as marked as was expected. For example, values for exchangeable potassium for the pyrophosphate materials listed in Table 8 are quite similar for the large sized particles. However, on the basis of original water soluble potassium contents, a clearer relationship is evident. Though the extent of downward movement of potassium from metaphosphate does not seem to vary for particles of different size, dissolution is apparently considerably greater for the medium sized and very fine fractions. This latter effect is somewhat modified when the lower water soluble potassium content of the coarse particles is taken into account. However, by calculation the quantities of exchangeable potassium from

fertilizer (parts per million in enriched layer--parts per million in lower layers) bear some relationship to quantities of water soluble potassium present in the original fused phosphates. Although, of course, no particles of potassium chloride could be recovered, there is definite evidence of greater movement of this ion in sandy soil from fine particles than from those of -6+10 mesh size.

Movement of potassium in bulk volume of soil. In order to study dissolution and movement of potassium from particles of fused potassium phosphates under moist soil conditions, a laboratory experiment was set up using Metea sandy loam and Houghton muck soil. The rate of movement of potassium from particles incubated in soils previously brought to specific moisture levels was found to vary with the water solubility and particle size of the potassium source and the moisture content of the soil. The data relative to the percent of water soluble and total potassium remaining in fertilizer particles recovered after moist incubation in organic soil held at 50 and 100 percent soil moisture levels are given in Tables 9, 10, 11, and 12. The distribution of potassium in water soluble form with respect to distance from the fertilizer source in the muck soil is presented in Tables 13 and 14.

It is quite evident that a large proportion of the water soluble potassium moved out of potassium pyrophosphate and potassium metaphosphate of both -4+14 and -3/8+4 mesh size particles in a relatively short period of time. Analysis of

TABLE 9

The quantity of water soluble potassium remaining in fertilizer particles after they have been incubated to various lengths of time in muck soil at 50 percent moisture.

Materials	Particle Size	Percent Water Soluble K ₂ O remaining in Particles						Percent Water Soluble K ₂ O Originally Present
		Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	3.21	3.10	2.98	2.99	2.69	2.71	5.9
	-3/8+4 mesh	3.48	3.56	3.41	3.98	4.01	4.06	7.5
Potassium metaphosphate	-4+14 mesh	1.21	1.43	0.98	1.11	1.02	1.10	20.6
	-3/8+4 mesh	4.21	4.00	3.98	4.01	4.12	4.00	13.0

TABLE 10

The quantity of water soluble potassium remaining in fertilizer particles after they have been incubated to various lengths of time in muck soil at 100 percent moisture.

Percent Water Soluble K ₂ O remaining in Particles							Percent Water Soluble K ₂ O Originally Present	
Materials	Particle Size	Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	3.11	2.98	3.12	2.96	2.80	2.69	5.9
	-3/8+4 mesh	3.18	3.00	3.11	2.98	2.91	2.99	7.5
Potassium metaphosphate	-4+14 mesh	1.11	0.98	0.92	0.83	0.71	0.84	20.6
	-3/8+4 mesh	4.01	4.08	3.91	3.86	3.88	3.91	13.0

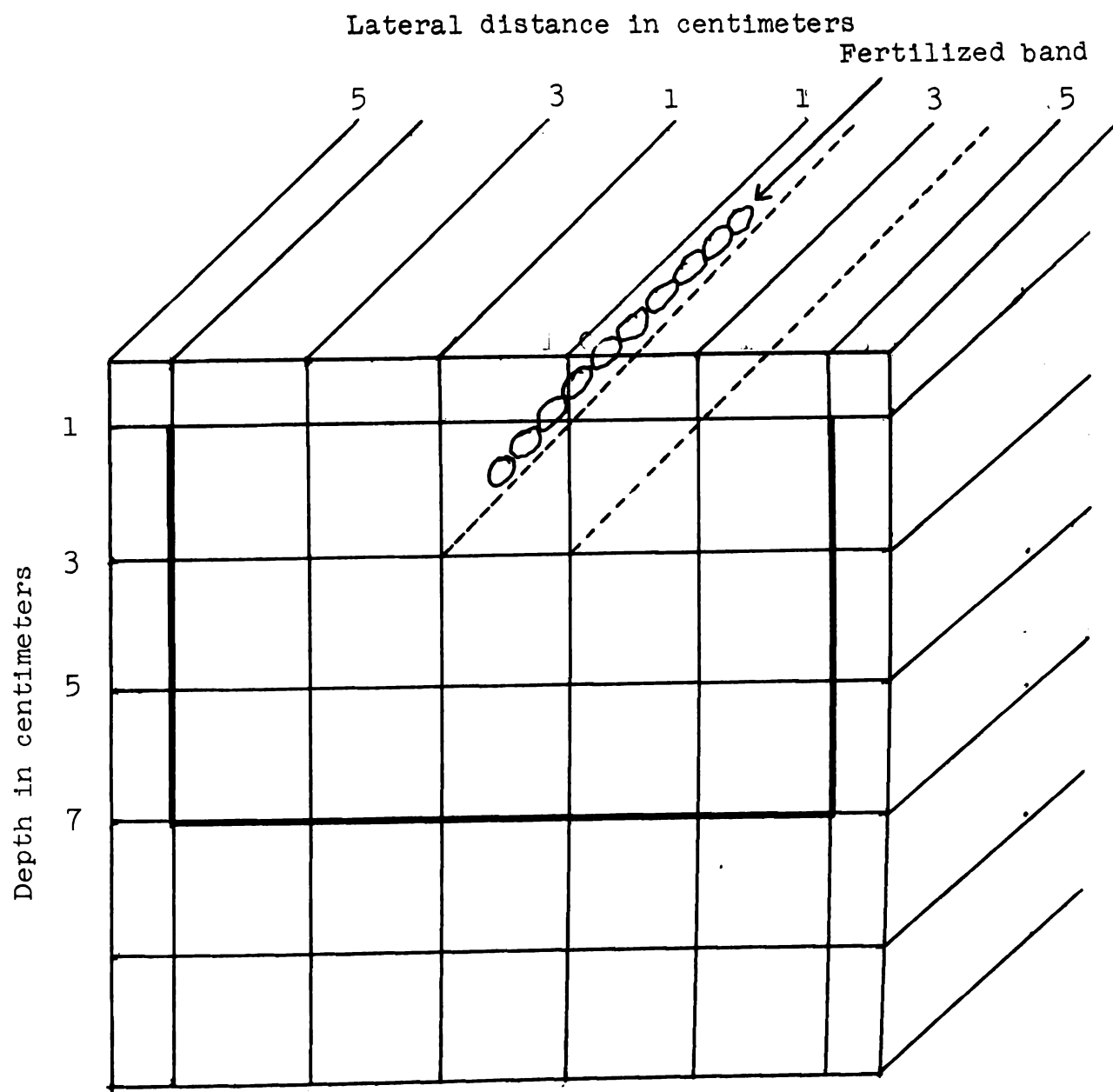


Fig. 3. Diagram of fertilizer placement and sampling volumes relative to the fertilizer band in the laboratory dissolution studies.

recovered particles indicate that 45.6 percent and 94 percent of the total water soluble potassium fraction in -4+14 mesh pyrophosphate and metaphosphate, respectively, was released in a 24 hour period in muck soil containing 50 percent moisture. For both the pyro- and metaphosphates of this particle size, with increase in time of incubation the amount of water soluble potassium recoverable remained more or less constant. This relationship suggests that upon dissolution of the water soluble fraction of potassium, a small part of water insoluble form is converted into water soluble state. It is also quite possible that because of the development of a high concentration of soluble potassium in soil immediately adjacent to the granule, an equilibrium condition exists between potassium ions in the soil solution and that in the porous structure or matrix of the fertilizer particle. This would tend to maintain a constant concentration of water soluble potassium within the particle.

At the high moisture level (100 percent) a similar pattern was evident as shown in Table 10. But in this case, the amount of water soluble potassium remaining was somewhat less than that found in the particles incubated in soils at 50 percent moisture. With potassium pyrophosphates of the smaller particle size 47.6 percent of water soluble potassium was released after the first 24 days of incubation, whereas 95 percent moved out of potassium metaphosphate particles of -4+14 mesh size. During the succeeding 31 days further

TABLE 11

The quantity of total potassium remaining in particles after they have been incubated to various lengths of time in muck soil at 50 percent moisture.

Materials	Particle Size	Percent Total K ₂ O Remaining in Particles						Percent Total K ₂ O Originally Present
		Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	23.12	22.98	22.10	21.91	21.60	21.60	25.00
	-3/8+4 mesh	21.40	21.00	20.64	20.22	20.00	19.00	24.80
Potassium metaphosphate	-4+14 mesh	15.12	14.40	13.91	13.64	13.21	13.20	33.50
	-3/8+4 mesh	30.62	30.12	29.68	29.40	28.21	28.00	38.90

TABLE 12

The quantity of total potassium remaining in particles after they have been incubated to various lengths of time in muck soil at 100 percent moisture.

Materials	Particle Size	Percent Total K ₂ O Remaining in Particles						Percent Total K ₂ O Originally Present
		Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	22.12	22.08	22.10	21.00	20.12	19.98	25.00
	-3/8+4 mesh	21.00	20.91	20.00	19.41	19.21	18.99	24.80
Potassium metaphosphate	-4+14 mesh	13.01	12.98	12.41	12.28	11.98	11.62	33.50
	-3/8+4 mesh	29.01	28.26	28.11	27.91	27.12	26.81	38.90

decreases in water soluble potassium content were rather minor.

In comparing the particle sizes of the two sources for the effect of this factor on the release of potassium, it was noted that for pyrophosphates, the $-3/8+4$ mesh size particles behaved somewhat similar to the smaller particles. For example, in muck soil at 50 percent moisture level, 45.6 percent of the total water soluble potassium moved out of the small particles in one day whereas 53.6 percent of water soluble potassium was released from the larger particles during the same period of time. However, the water soluble potassium contents of the pyrophosphates studied are not exactly the same, and Tennessee Valley Authority reports indicate that the degree of crystallinity of these materials may be somewhat different which could influence rate of release of potassium from the water soluble form.

For metaphosphates the results obtained were substantially different. From data in Tables 9 and 10 it can be calculated that about 95 percent of the water soluble potassium moved out of the $-4+14$ mesh particles within 24 hours time, while from $-3/8+4$ size particles 67-68 percent dissolved out during the same period of time. After a month of moist incubation of the organic soil, this relationship did not change appreciably for either the low or the high soil moisture levels.

The physical appearance of the recovered particles after incubation in moist soil for one month was different for the pyrophosphates and metaphosphate materials. There was practically no change in the appearance of pyrophosphate particles of either the small or large sizes after they were incubated. It was very easy to separate the fertilizer particles from the surrounding soil. But with metaphosphate particles it was very difficult since the particles had become soft and the external surface was completely covered with and cemented to the soil.

Evaluation of data in Table 11 indicate that 1.88 percent or 7.5 percent of the original potassium, was lost from -4+14 mesh pyrophosphate granules during the first 24 hours incubation in organic soil at 50 percent moisture. From the larger -3/8+4 mesh particles, 3.4 percent or 13.7 percent of the total potassium was lost during the same period. The greater loss from the larger particles can be accounted for in part by the fact that they originally contained more water soluble potassium. After the first 24 hours incubation there was a gradual migration of potassium from both groups of pyrophosphates resulting in a further reduction of 7 to 8 percent of the original potassium content of this fused potassium phosphate.

In contrast, about 55 percent of the total potassium was lost from the -4+14 mesh size metaphosphate during the first day of incubation assuming there was no physical

sloughing of the softened particle surface. During the next 31 days a gradual dissolution of potassium occurred, so that at this time, 60.0 percent of the original potassium had migrated from the small metaphosphate particles. With respect to $-3/8+4$ mesh size particles of metaphosphate it was found that only 21.3 percent of the original potassium was released during the first 24 hours incubation at 50 percent soil moisture level. At the end of 32 days 72 percent of the total potassium or 28 percent K_2O remained within the particles. Upon subtracting the water soluble potassium content of pyrophosphate and metaphosphate materials from the values for total potassium and comparing the results with potassium content of particles recovered after full incubation, it is noted that they are quite similar. This agreement is considered as evidence of the release of water soluble potassium with only slight loss of this element from water insoluble form.

With the particles incubated at the 100 percent moisture level, the results obtained were similar as noted in Table 12. Here again the amount of potassium lost during incubation was slightly greater than that released from granules at 50 percent moisture.

The distribution of water-extractable potassium with respect to the position of the fertilizer source in moist organic soil with time is presented in Tables 13 and 14. The water soluble potassium content of the original muck soil was

TABLE 13

Distribution of potassium at various distances and depths from the place of application with time in muck soil at 50 percent moisture.

		Percent of Total Water Soluble Potassium Diffused Out									
Materials	Particle Size	Days Of Incuba- tion	Depth 1-3 cms			Depth 3-5 cms			Depth 5-7 cms		
			Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms
Potassium pyrophosphate	-4+14 mesh	1	76.42	12.24	1.41	3.12	1.69	1.02	2.11	1.01	0.98
		2	71.01	14.61	3.11	4.28	1.71	1.05	2.22	1.01	1.00
		4	62.25	15.48	4.38	6.29	2.11	2.00	3.86	2.06	1.59
		8	61.29	15.55	4.82	7.44	2.11	2.53	3.77	1.48	1.11
		16	59.11	12.21	5.11	8.29	2.61	2.11	4.68	3.11	2.78
		32	56.01	12.41	5.62	15.21	2.81	2.15	3.21	1.98	0.70
	-3/8+4 mesh	1	76.10	8.91	1.61	2.12	2.16	1.83	2.11	2.18	2.98
		2	60.12	18.97	3.14	4.61	3.21	1.91	3.13	2.50	2.41
		4	59.21	22.05	1.81	5.96	3.41	1.62	3.11	1.60	1.23
		8	55.11	24.91	2.00	6.91	4.10	1.01	3.18	1.81	0.97
		16	54.21	26.12	2.62	7.29	3.97	1.61	3.11	1.00	0.07
		32	50.19	24.21	3.61	7.94	4.21	2.10	4.86	1.88	1.00
Potassium metaphosphate	-4+14 mesh	1	72.01	9.24	2.41	4.88	2.44	1.96	3.21	1.98	1.87
		2	71.06	10.41	3.61	4.91	2.81	2.00	3.10	1.10	1.00
		4	68.41	12.21	3.01	5.11	2.30	2.05	3.26	1.67	1.98
		8	61.21	10.42	4.62	6.00	2.48	2.15	5.32	4.35	3.25
		16	57.10	10.61	5.91	8.21	6.48	2.15	6.11	3.01	1.41
		32	51.01	11.96	6.00	8.68	6.11	3.42	6.10	4.21	2.51
	-3/8+4 mesh	1	81.01	8.21	1.21	2.11	1.01	0.98	1.98	2.48	1.41
		2	76.21	14.21	2.01	2.46	1.08	0.98	1.21		
		4	71.00	14.68	2.91	3.21	2.00	1.12	2.08	2.10	1.00
		8	69.82	12.09	3.21	5.11	2.01	1.64	3.98	2.21	0.83
		16	64.52	12.00	5.11	6.86	3.00	1.62	3.91	1.98	1.00
		32	--	12.00	--	--	--	--	--	--	--

TABLE 14

Distribution of potassium at various distances and depths from the place of application with time in muck soil at 100 percent moisture.

		Percent of Total Water Soluble Potassium Diffused Out									
Materials	Particle Size	Days of Incubation	Depth 1-3 cms			Depth 3-5 cms			Depth 5-7 cms		
			Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms
Potassium pyrophosphate	-4+14 mesh	1	71.01	14.11	1.86	3.26	4.21	1.21	2.61	2.62	0.99
		2	69.82	11.21	2.11	4.61	4.20	1.04	3.11	2.69	1.21
		4	66.41	10.00	3.40	6.98	5.10	1.92	3.86	2.10	1.21
		8	64.21	11.11	3.48	6.90	4.30	1.86	3.92	2.59	0.89
		16	58.01	12.20	4.21	8.21	5.70	2.01	4.64	3.10	2.11
		32	54.02	12.20	5.00	12.31	6.10	2.01	4.71	2.90	1.00
	-3/8+4 mesh	1	76.80	11.33	1.20	2.10	1.98	1.08	2.01	2.20	1.21
		2	61.98	20.63	2.98	3.98	3.11	1.91	2.81	2.60	1.00
		4	59.46	17.36	3.11	5.62	5.14	2.11	3.11	2.11	1.98
		8	54.21	20.16	3.04	6.49	5.81	2.01	3.00	2.41	2.01
		16	50.90	21.43	4.00	7.21	8.00	2.01	2.98	2.58	0.89
		32	48.02	20.59	4.21	7.89	9.21	2.88	3.11	3.00	1.00
Potassium metaphosphate	-4+14 mesh	1	70.91	12.90	1.29	3.01	2.11	1.81	4.01	1.98	1.98
		2	68.26	14.30	2.41	4.86	4.00	1.07	2.98	1.10	0.82
		4	66.41	13.47	3.61	5.62	3.12	1.99	3.10	1.67	1.01
		8	61.02	14.73	3.61	6.21	5.84	2.11	3.41	1.81	1.26
		16	59.01	13.58	4.91	8.21	3.99	2.89	4.21	2.00	1.20
		32	51.98	13.59	4.62	8.68	6.21	3.01	6.21	4.41	1.29
	-3/8+4 mesh	1	80.67	5.96	1.33	2.86	2.21	1.98	2.00	1.91	1.08
		2	75.21	10.04	2.41	3.11	2.86	1.21	1.98	1.26	1.92
		4	69.26	15.85	2.86	3.26	3.00	2.01	1.20	1.10	1.46
		8	67.21	14.47	3.11	5.61	3.42	1.12	1.99	1.46	1.41
		16	65.00	14.58	3.42	6.98	4.21	1.64	2.08	1.21	1.21
		32	58.23	14.25	3.30	9.26	6.86	2.01	3.11	1.49	1.49

extremely low as indicated in Table 1. However, this quantity of potassium present in the soil has been subtracted from the values obtained after incubation and so the values given in the table essentially represent the amount of water soluble potassium released from the fertilizer particles.

Approximately three-fourths of the potassium leached from the fertilizer source was recovered after one day in the 2 x 2 x 10 centimeter volume of organic soil (low moisture level) in the center of which the fertilizer band was placed. Lateral movement of potassium decreased rapidly with distance from the potassium source. For instance, for the -4+14 mesh pyrophosphate in the 2 x 2 x 10 centimeter volume of soil immediately to the side of the first sampling volume, 12.2 percent of the leached potassium was found, whereas 3-5 centimeter away from the fertilizer band only 1.4 percent of the water soluble potassium was recovered. Directly below the fertilizer band, values of 3.1 and 2.1 percent were recorded for depths of 3-5 and 5-7 centimeters. As further indication of limited migration at the 50 percent moisture level, only 1.7 percent of the leached potassium was found 3-5 centimeters below the second sampling volume as shown in Table 13. The downward movement of potassium from a position 3-5 centimeters laterally from the place of application of fertilizer was very small with only 1 percent of potassium having been recovered at 3-5 and 5-7 centimeter depths.

Incubating the soil for 4 days resulted in similar trends in the amounts of water soluble potassium diffusing away from the potassium pyrophosphate in organic soil at low moisture content. The concentration of potassium in the 2 x 2 x 10 centimeter volume of soil in the center of which the fertilizer band was placed continued to decrease, while the lateral movement of potassium increased. A total of 15.5 and 4.5 percent of the total water soluble potassium dissolved from this fertilizer was recovered from the two lateral sampling volumes adjacent to the first sampling volume. The downward movement of potassium also increased as shown by the fact that immediately below the fertilizer band after four days incubation the amount of potassium increased to 6.6 percent of the total recovered, whereas at the two lateral samples at this depth 2.1 and 2.0 percent of the diffusible water soluble fraction were found. Downward and lateral migration of potassium also continued in the slice of soil 4 centimeters below the place of application of fertilizer for the period of 2 to 4 day incubation period.

The distribution of water soluble potassium from fertilizer for the 32 day incubation period can be more clearly seen in Figure 4. For example, after approximately one month incubation the potassium level in soil around the fertilizer dropped to 56 percent of that leached out, while 1-3 centimeters to the side, the percentage did not change. As might be expected in the area 3-5 centimeters to the side of the

fertilizer band, an increase of from 1.4 to 5.6 was recorded. Although there are minor irregularities with time for potassium distribution, migration of potassium away from the fertilizer source in both lateral and vertical directions in organic soil was noted.

With potassium pyrophosphate, with one exception there was no marked difference in the behavior of particles of different sizes with respect to the movement of potassium from the water soluble fraction. For the $-3/8+4$ mesh pyrophosphate, values for the soil volume 1-3 centimeters away and at the same level as the fertilizer band were exceptionally high after the 24 hour incubation period. For instance, the water soluble potassium moved out after two days increased from 8.9 to approximately 19 percent, to 22 percent after 4 days and to about 25 percent after 8 days incubation. After 32 days, 24 percent of the diffusable potassium was still located in this volume of soil. No explanation can be offered for the behavior of the soluble potassium within this zone, other than that mentioned previously in dissolution studies.

With potassium metaphosphates the results obtained for movement of water soluble potassium with time were similar to those for pyrophosphate. With the smaller sized particles incubated in muck soil at 50 percent moisture, 72 percent of the water soluble potassium was concentrated in the zone of soil $2 \times 2 \times 10$ centimeters in the center of which the

fertilizer was placed. The amount of soluble potassium within this volume of soil decreased with an increase in incubation time. After 2 days 71 percent of this diffusible fraction was found in this zone, decreasing to about 68, 61, 57, and 51 percent of the total potassium moved out after 4, 8, 16, and 32 days incubation, respectively. In the laterally adjacent soil volume after 1 day incubation, 9.2 percent of the diffusible water soluble potassium remained in the $-4+14$ mesh metaphosphate particles. Here there was only slight change in the amount of soluble potassium with an increase in time of incubation. However, there was a significant increase in concentration of water soluble potassium 3-5 centimeters away from the place of application of fertilizer with time, ranging from 2.4 percent after 1 day to 6.0 percent after 32 days incubation. Some effect of particle size on a reduction in migration is evident in data in Table 13 for the metaphosphate sources. In all probability this is in reality an expression of a decrease in rates of dissolution. However, no proof for this is available from these data since all calculations have been made on basis of 100 percent. It can be noted from Figure 4 that downward as well as lateral movement of potassium ions occurred with time. An interesting point of these migration studies is that especially in the early stages of incubation, a considerably higher proportion of the diffusible potassium was found in the laterally adjacent zone rather than in the vertically adjacent volume. This phenomenon was less

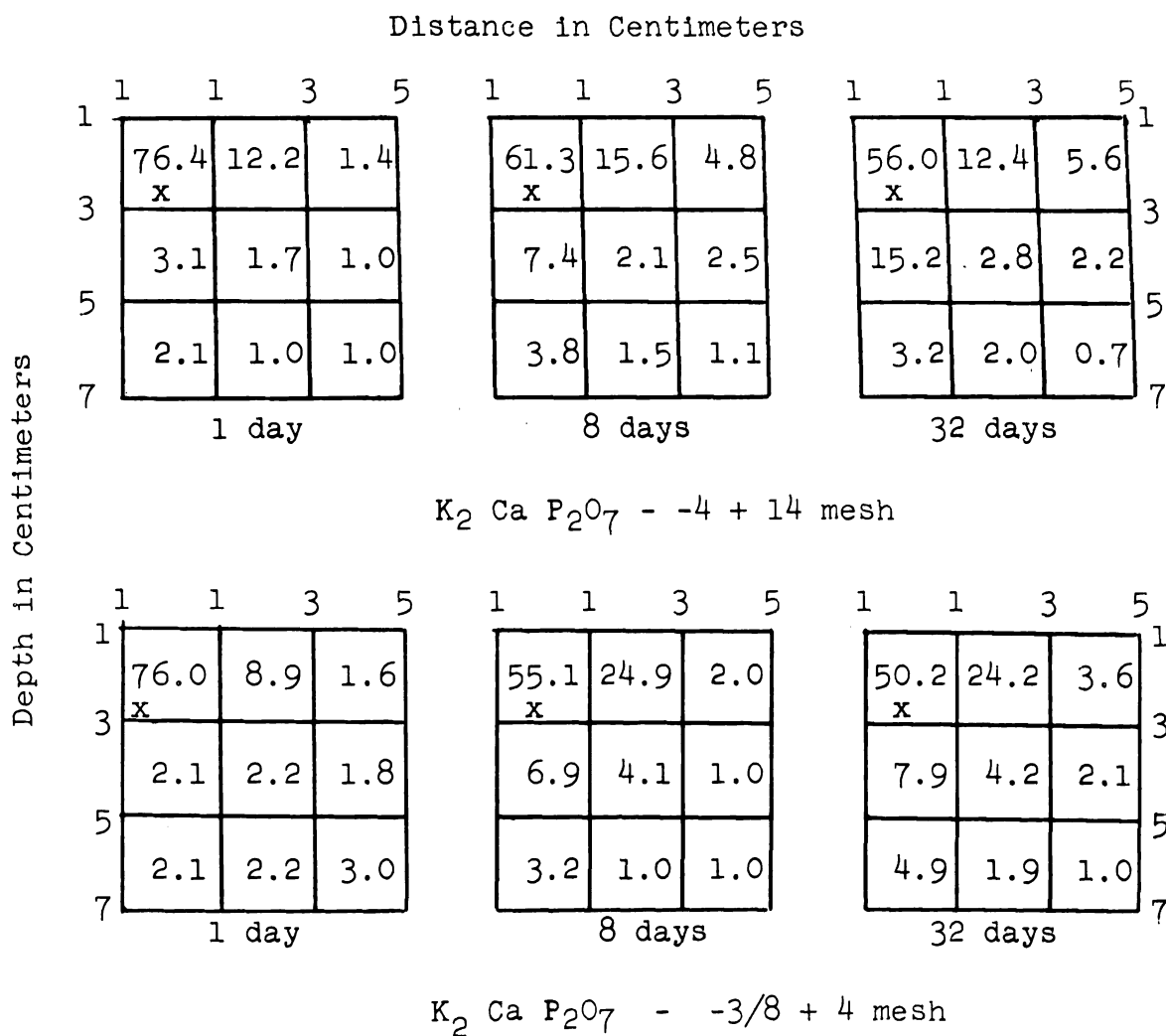
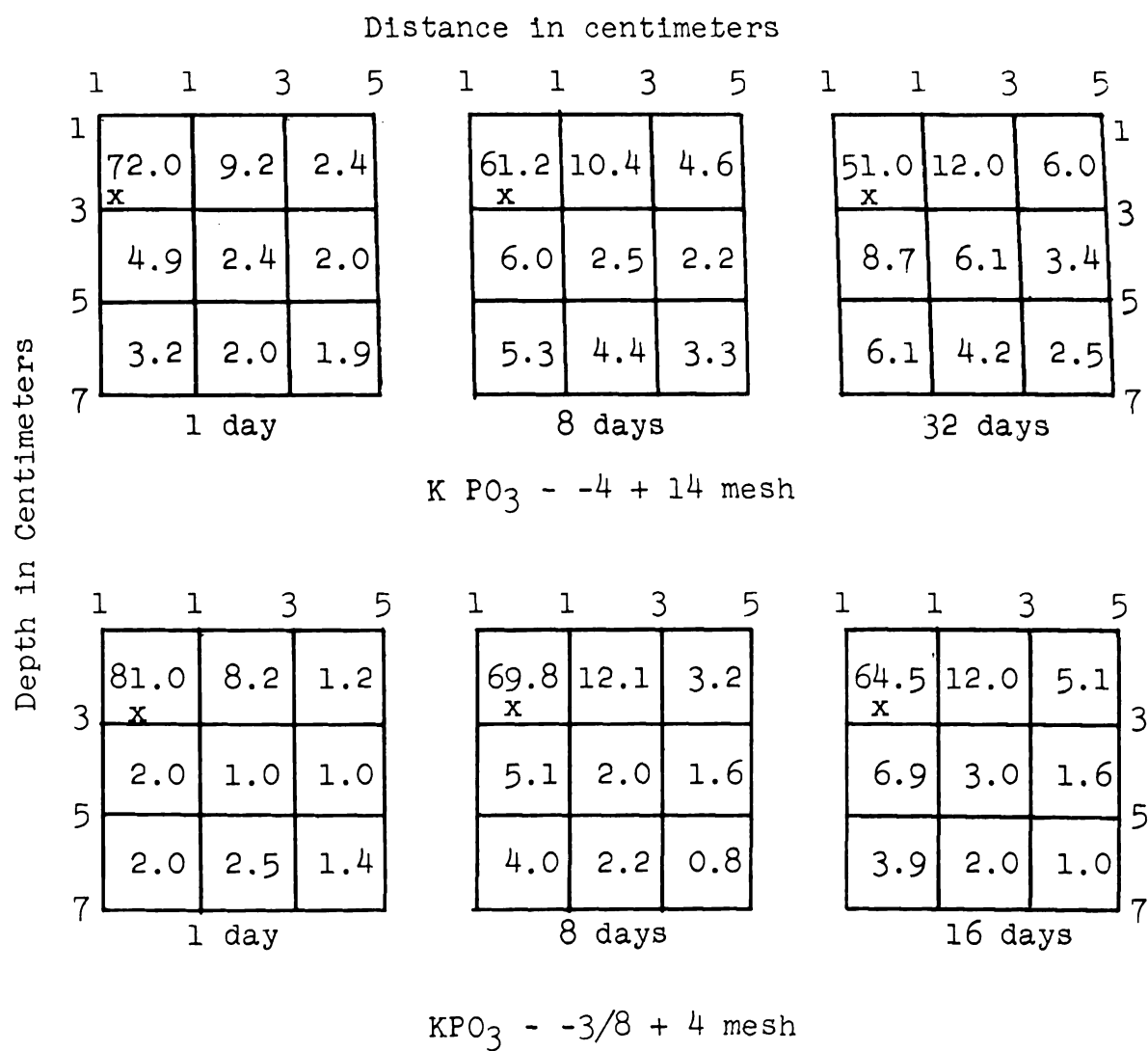


Fig. 4. Cross-section distribution of potassium at various distances and depths from place of fertilizer application (x) with time in muck soil at 50% moisture, expressed as percent of total water soluble potassium released.

Fig. 4. Continued

marked at the end of the incubation period, but only for the smaller sized fused potassium phosphates.

A comparison of data in Tables 13 and 14 on the effect of soil moisture level on migration of soluble potassium indicates that doubling the percent moisture from 50 percent to 100 percent had very little effect on the outward movement of potassium from the fertilizer source.

A dissolution-migration study similar to that discussed for organic soil was conducted using Oshtemo sandy soil. Except for a few variations the quantities of potassium remaining in soluble form in recovered pyrophosphate and metaphosphate particles were similar to those found for comparable materials recovered from the organic soil. The discrepancies in question involve the fact that no water soluble potassium was found in either -3/8+4 mesh pyrophosphate or -4+14 mesh metaphosphate particles at the end of the incubation period in Oshtemo sand with a high water content. However, moisture characteristics of the two soils and fertilizer dissolution data point to the fact that there is more available moisture in Oshtemo sand containing 20 percent moisture than there is in Houghton muck at 100 percent moisture. Thus, maximum dissolution of soluble fertilizer potassium should occur with the sandy soil system.

The loss of total potassium from the two types of fertilizers is presented in Tables 15 and 16. Actual dissolution with time was similar to the patterns already

TABLE 15

The quantity of water soluble potassium remaining in fertilizer particles after they have been incubated to various lengths of time in Oshtemo sand at 5 percent moisture.

Materials	Particle Size	Percent Water Soluble K ₂ O Remaining in Particles						Percent Water Soluble K ₂ O Originally Present
		Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	3.84	3.11	3.14	3.16	3.38	3.45	5.90
	-3/8+4 mesh	3.87	3.09	3.72	4.61	4.29	4.60	7.50
Potassium metaphosphate	-4+14 mesh	1.43	0.98	1.15	1.20	1.20	1.22	20.60
	-3/8+4 mesh	4.55	4.59	5.02	4.60	4.60	4.10	13.00

TABLE 16

The quantity of water soluble potassium remaining in fertilizer particles after they have been incubated to various lengths of time in Oshtemo sand at 20 percent moisture.

Materials	Particle Size	Percent Water Soluble K ₂ O Remaining in Particles						Percent Water Soluble K ₂ O Originally Present
		Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	3.85	2.51	2.77	2.08	2.12	2.88	5.90
	-3/8+4 mesh	3.79	3.79	3.20	2.27	0.77	0.00	7.50
Potassium metaphosphate	-4+14 mesh	1.05	1.23	0.73	0.57	0.18	0.00	20.60
	-3/8+4 mesh	4.10	4.39	3.81	4.48	4.25	3.60	13.00

TABLE 17

The quantity of total potassium remaining in particles after they have been incubated to various lengths of time in Oshtemo sand at 5 percent moisture.

Materials	Particle Size	Percent Total K ₂ O Remaining in Particles						Percent Total K ₂ O	
		Days of Incubation						Originally	Present
		1	2	4	8	16	32		
Potassium pyrophosphate	-4+14 mesh	22.95	22.98	22.90	22.84	22.79	22.32	25.00	
	-3/8+4 mesh	21.39	20.97	20.86	20.11	19.99	18.82	24.80	
Potassium metaphosphate	-4+14 mesh	14.43	13.98	13.15	13.20	13.20	13.20	33.50	
	-3/8+4 mesh	30.46	29.70	29.75	29.44	28.85	28.03	38.90	

TABLE 18

The quantity of total potassium remaining in particles after they have been incubated to various lengths of time in Oshtemo sand at 20 percent moisture.

Materials	Particle Size	Percent Total K ₂ O Remaining in Particles						Percent Total K ₂ O Originally Present
		Days of Incubation						
		1	2	4	8	16	32	
Potassium pyrophosphate	-4+14 mesh	22.19	22.21	22.20	21.48	20.27	20.11	25.00
	-3/8+4 mesh	21.12	21.11	20.49	20.05	20.03	19.00	24.80
Potassium metaphosphate	-4+14 mesh	14.07	14.06	12.95	12.72	12.42	12.21	33.50
	-3/8+4 mesh	29.04	28.19	28.18	27.84	27.84	27.64	38.90

described for organic soils. The large particle of potassium pyrophosphate again lost more potassium than the smaller ones while the reverse was true for the metaphosphates. From these data it is evident that the release of total potassium from the two types of fused phosphates was not appreciably different for a wide variation in soil moisture level, although a minor exception would be -4+14 mesh pyrophosphate.

It is interesting to compare the actual loss of total potassium from the fertilizer particles with that representing the difference between the water soluble fractions before and after in the recovered particles. In general, the loss based on total analysis are larger by values up to 2.7 percent. This suggests that during incubation some of the less soluble potassium within the particle was changed to a water soluble state, which would be evaluated as a higher percent of water soluble potassium remaining in the fertilizer. The one exception to this trend is the erratic behavior of the -3/8+4 mesh pyrophosphate particles.

When the several fertilizer materials were placed in moist sandy soil, the distribution pattern of water soluble potassium from soil at different distances from the fertilizer band was quite similar to that found for organic soil. With potassium pyrophosphate of smaller size, a large amount of potassium was concentrated around and below the place of application of the fertilizer. From Figure 5 it can be seen that in a volume of soil 2 x 2 x 10 centimeters in the center

TABLE 19

Distribution of potassium at various distances and depths from the place of application with time in Oshtemo sand at 5 percent moisture.

Percent of Total Water Soluble Potassium Diffused Out											
Materials	Particle Size	Days of Incubation	Depth 1-3 cms			Depth 3-5 cms			Depth 5-7 cms		
			Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms
Potassium pyrophosphate	-4+14 mesh	1	--	--	--	--	--	--	--	--	--
		2	78.68	10.78	1.45	2.41	1.86	1.31	0.87	1.01	1.60
		4	71.19	12.20	4.80	2.31	3.58	2.64	0.61	1.26	1.31
		8	69.22	15.82	3.16	1.83	1.81	1.87	2.57	1.81	1.06
		16	60.11	30.67	0.83	2.57	2.45	1.25	0.58	0.70	0.82
		32	64.93	9.24	1.62	3.71	8.20	4.35	3.33	2.64	1.91
	-3/8+4 mesh	1	80.10	6.21	2.74	1.63	1.83	1.76	2.02	2.02	2.11
		2	62.22	22.70	1.09	7.86	1.44	1.00	1.39	1.39	0.87
		4	61.40	26.06	4.16	3.66	2.15	3.16	0.57	1.15	1.20
		8	57.60	27.89	4.39	3.00	4.29	1.60	0.77	1.66	1.66
		16	57.90	24.52	5.58	4.43	5.33	0.55	0.28	0.71	0.55
		32	55.45	23.33	6.71	5.18	5.73	2.41	2.52	0.52	0.41
Potassium metaphosphate	-4+14 mesh	1	74.50	8.67	2.42	2.42	2.42	2.65	2.42	2.42	2.08
		2	71.73	20.23	1.08	1.29	1.33	1.08	1.08	1.00	1.10
		4	67.42	22.07	1.78	1.80	1.78	0.71	0.89	0.71	2.83
		8	57.92	28.02	2.76	3.66	1.79	1.79	1.64	0.89	1.49
		16	51.91	26.91	2.13	2.72	2.73	2.89	3.89	2.51	2.45
		32	50.60	22.68	4.01	4.22	4.01	3.58	4.32	2.58	1.58
	-3/8+4 mesh	1	91.50	4.70	0.64	0.59	0.47	0.79	0.29	0.38	0.57
		2	78.90	16.23	0.81	1.20	0.68	0.58	0.58	0.36	0.38
		4	74.90	18.66	0.38	2.37	0.47	0.68	0.87	0.87	0.82
		8	74.70	19.60	0.81	2.03	1.18	0.50	0.28	0.32	0.46
		16	61.50	28.80	1.03	6.23	0.77	0.51	0.30	0.50	0.42
		32	--	--	--	--	--	--	--	--	--

TABLE 20

Distribution of Potassium at various distances and depths from the place of application with time in Oshtemo sand at 20 percent moisture.

Percent of Total Water Soluble Potassium Diffused Out											
Materials	Particle Size	Days of Incubation	Depth 1-3 cms			Depth 3-5 cms			Depth 5-7 cms		
			Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms	Center	1-3 cms	3-5 cms
Potassium pyrophosphate	-4+14 mesh	1	65.07	19.68	1.33	3.24	2.53	2.73	2.44	0.92	2.03
		2	57.70	18.13	0.98	12.95	5.88	0.82	1.10	1.10	1.31
		4	45.00	21.92	2.30	21.92	3.76	2.15	0.80	0.96	1.19
		8	55.77	19.90	4.53	5.33	5.41	2.30	1.99	2.54	2.22
		16	52.81	14.23	7.46	5.39	7.46	3.68	4.36	2.41	2.24
		32	43.60	14.73	6.80	9.29	8.04	5.21	5.81	3.96	2.38
Potassium metaphosphate	-3/8+4 mesh	1	65.00	27.08	3.19	0.81	1.73	1.46	0.86	0.78	0.78
		2	51.36	31.41	1.69	6.46	4.04	1.26	1.51	0.75	1.51
		4	58.80	18.98	4.66	23.59	4.44	2.11	1.54	1.08	0.59
		8	50.17	17.30	7.26	11.07	5.74	4.32	3.11	0.86	1.74
		16	51.19	12.23	11.98	10.08	6.99	2.47	1.64	1.41	1.04
		32	47.10	14.34	9.06	13.59	7.17	2.18	2.59	2.22	1.73
Potassium metaphosphate	-4+14 mesh	1	46.87	6.53	5.96	7.10	5.96	5.96	5.53	14.20	4.69
		2	70.98	15.17	1.41	3.54	3.03	1.89	1.62	1.49	1.06
		4	71.36	16.78	2.01	3.61	2.51	0.92	0.46	0.83	1.46
		8	60.59	17.15	2.76	4.08	3.43	1.93	7.73	1.07	1.22
		16	61.98	19.46	4.71	4.95	3.99	1.34	1.07	1.46	0.99
		32	--	--	--	--	--	--	--	--	--
Potassium metaphosphate	-3/8+4 mesh	1	60.50	27.10	1.29	5.21	1.87	0.91	1.21	0.75	1.04
		2	44.00	18.22	2.00	5.14	5.46	0.94	2.15	1.25	0.72
		4	64.60	26.90	1.93	1.60	0.96	1.31	1.11	1.11	0.39
		8	49.50	22.50	11.65	2.33	8.01	0.67	2.50	1.60	1.08
		16	32.39	21.20	13.71	12.61	9.70	5.58	1.45	1.94	1.37
		32	--	--	--	--	--	--	--	--	--

of which the fertilizer material was banded, almost 80 percent of potassium was concentrated, and during 32 days of incubation only 16 percent of this moved out. To a distance of 1-3 centimeters from the fertilizer band about 10 percent of the water soluble potassium moved out during the first day of incubation. In this area there was a gradual increase of potassium with time. After 16 days incubation as much as 30 percent of the water soluble potassium released was concentrated in this zone. But 3-5 centimeters from the first sampling area, the amount of potassium recovered was very small. Below 2 centimeters from the place of application of the fertilizer there was very little movement of potassium laterally or vertically.

With pyrophosphate of $-3/8+4$ mesh particle size, about 80 percent of the migrated potassium was concentrated on the first day in a volume of soil $2 \times 2 \times 10$ centimeters in the center of which the fertilizer was banded. After 8 days this was reduced to about 58 percent after which further migration was slight. Here again there was very little downward movement of potassium below the fertilizer source. The puzzling feature of the migration pattern is the concentration of soluble potassium in the first sampling volume adjacent to that enclosing the band of fertilizer. At this period approximately 28 per cent of the total water soluble potassium migrated was concentrated in this $2 \times 2 \times 10$ centimeter zone as compared to only 3 percent immediately below the potassium pyrophosphate particles.

From a theoretical standpoint, potassium ions from a fertilizer source should diffuse outward in equal concentration for all directions in a soil mass of uniform moisture content. However, in these studies movement in the upward direction is soon limited by the presence of the soil surface. Assuming these ions concentrate near the surface, they would then migrate laterally in perhaps the upper half centimeter of soil to the adjacent sampling volume.

In soil supplied with smaller sized potassium metaphosphate, 74 percent of the diffusible water soluble potassium was concentrated in a volume of soil 2 x 2 x 10 centimeters in the center of which the fertilizer was banded. There was a gradual reduction in the amount of water soluble potassium in this area till at the end of 32 day period only 50 percent of potassium dissolved from the fertilizer was located in this zone. In the sampling volume immediately below this position the potassium concentration increased from 2.4 percent after one day incubation to 4.2 percent at the end of the study. However, in the first layer of soil 2 centimeters away from the place of application of the fertilizer, the concentration of water soluble potassium increased from 8 percent of the total moved out in 1 day to almost 23 percent in 32 days. This again is considered to be a reflection of position of the fertilizer band relative to the respective sampling volumes of soil.

With the metaphosphate particles of larger size, slightly more than 91 percent of the total water soluble potassium dissolved was concentrated in the volume of soil in which the fertilizer was banded after 24 hours of moist incubation. Thirty-two days later, 61 percent was still located in this position. In the laterally adjacent volume, the concentration of water soluble potassium increased from 4 to 28 percent in 32 days time. Yet there was very little change in the potassium content of soil below or to the side of this volume of soil.

Similar migration patterns for potassium were obtained with the fused potassium phosphate incubated in Oshtemo sandy loam at the higher moisture level as shown in Table 20. In all cases, the concentration of potassium in the volume of soil in which the fertilizer was located was less on the first day, whereas more potassium was located in the volume of soil next to this. Slightly more downward movement of potassium was also noted here.

In all cases studied, a large portion of the water soluble potassium moved out in relatively short period of time. Apparently, these fertilizer particles are hygroscopic. As soon as they are placed in moist soil, they start absorbing moisture from the surrounding medium.

Data presented in Table 21 show that when potassium metaphosphate particles of -4+14 mesh size were incubated in Kalamazoo sandy loam containing 2.1 percent moisture, the percent water in an area immediately surrounding the particles

increased. In 12 hours time in this zone there was 3.8 percent moisture and in 24 hours time the moisture content increased to 4.6 percent. Similarly when the soil mass contained 5.2 percent moisture, within 24 hours time there was an increase of moisture to 6.1 percent in the soil adjacent to the fertilizer particle. This effect is similar to that reported by Lawton and Vomocil (26) for superphosphate granules.

Close examination of unweathered particles of pyrophosphate and metaphosphate under a microscope show that they contain rather rough or uneven surfaces, often with the presence of pores or crevices. Some surfaces of potassium-calcium-pyrophosphate particles appear quite dense with few cavities, while others are extremely uneven with a multitude of crevices and needle-like crystals bridging the pockets. The metaphosphate particles generally exhibit a more solid, though rough surface with few visible pores. Many small elongated crystals can be found in the minor depressions. These observations indicate that water should be able to dissolve and penetrate these materials with relative ease.

It is believed that moisture movement to the fertilizer particles is controlled by vapor diffusion as proposed by Lehr, et al. (27) for granules of monocalcium phosphate placed in moist soil.

With the entry of water into the particles the soluble substances contained therein dissolve. This results in the

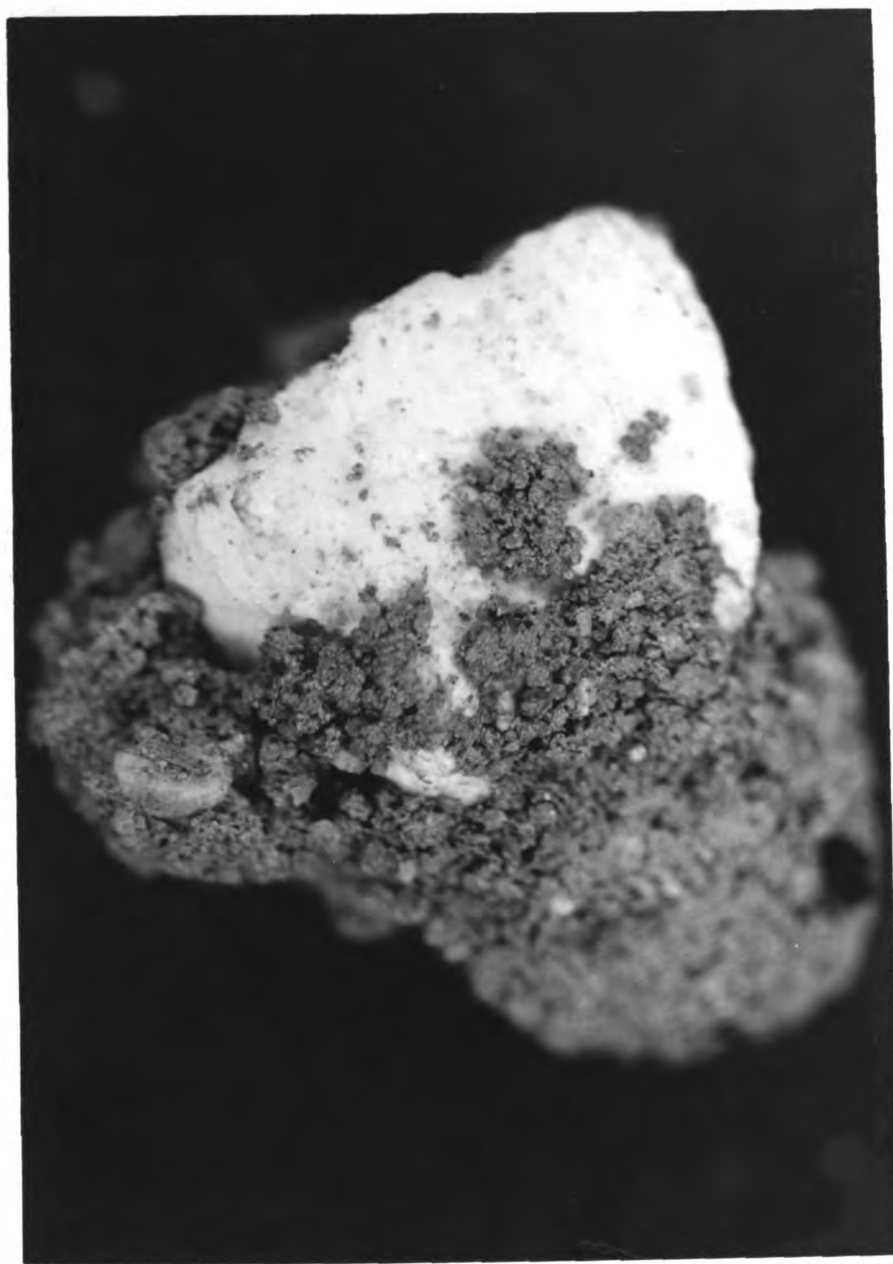


Plate 7. Soil particles adhering to the fertilizer particle after it is incubated in moist soil (50x).

TABLE 21

Moisture content of soil surrounding potassium metaphosphate particles incubated in Kalamazoo sandy loam at various moisture levels.

Percent Moisture in Soil Adjacent to Particle*						
0	1	Time of Incubation in Hours				
		2	4	8	12	24
2.1	2.1	2.6	2.8	3.0	3.8	4.6
5.2	5.2	5.2	5.4	5.8	6.0	6.1
12.0	12.0	12.0	12.4	12.8	13.6	14.0

*Sampling volume represented by a cylinder 20 millimeters in diameter and 20 millimeters in length.

formation of a very highly concentrated solution in and closely surrounding the fertilizer particles. Since water has a very high dielectric constant, the electrical properties of the solvent weakens bonding forces between ions and molecules resulting in the rapid dissolution of the particles. In the case of the pyrophosphate, the matrix of the particle remain relatively stable because of resistant P-O-P bonding, whereas solubility of metaphosphate proceeds to completion upon exposure to moisture.

The relationships between solubility and particle size of compounds such as fertilizers is well known. If the solvent comes in contact with a greater surface it will be able to dissolve the solid more rapidly. In addition to increasing the rate of solubility, the particle size also influences actual solubility. The smaller the size, greater would be the solubility.

The difference in concentration of the solution inside and outside results in a diffusion process. In an ideal system, the osmotic pressure causes the ions or molecules of the stronger solution to be transferred to the weaker solution until the osmotic pressures are equalized, when equilibrium is attained. In other words, the strong solution gradually becomes more dilute, so that the existence of osmotic pressure causes the progressive dilution by the entry of water. In an ideal solid-liquid or liquid-liquid system, with time, equilibrium is reached whereby the concentration

of the solutions becomes the same. But this is unlikely to occur in a soil-water-fertilizer system. First of all water may act as a limiting factor here. Free movement of dissolved ions of a solid can take place only if there is a continuous water film outward from the dissolving solid. With a relatively low water content in moist soil, water is drawn as it were, from the surrounding soil towards the fertilizer particles. This results in zones of progressively diminishing moisture contents from the particles towards the outer mass of soil. As a result the potassium released from the particles tend to be concentrated in areas adjoining the fertilizer source. Also the lack of continuity of capillary pores may impede outward diffusion of dissolved salts. Equilibrium between the solution within the fertilizer particles and that in the surrounding soil may be difficult to establish due to continued fixation of potassium by soil minerals, though in this zone, fixation is probably overshadowed by an extremely high concentration of potassium ions in solution.

Dissolution of particles of potash fertilizers under field conditions. In another experiment an attempt was made to study the dissolution and disintegration of fertilizer particles placed on the soil surface under field conditions. During the 40 day period which the particles were exposed in the field, the area received a total of 3.84 inches of precipitation.

During the first 10 days, only 0.12 inches of rain fell and particles of all materials were recovered. However, after 20 days exposure during which several light showers occurred, the potassium chloride granules had dissolved and in addition it was impossible to recover the -4+14 mesh metaphosphate particles. The next exposure period included heavy rains of 1.6 inches on June 1 and 2. After the beating action of these rains, many of the fertilizer particles were embedded in the soil surface, but it was still possible to recover the large metaphosphate particles as well as both large and small pyrophosphate materials. After 40 days exposure to the elements, all particles of potassium metaphosphate had disintegrated partly due to the physical action of an additional 1.26 inches of rain. Particles of pyrophosphate could be easily recovered, but they appeared to have undergone solvent action and some physical disintegration.

The analysis of fertilizers after varying exposure periods to field conditions are listed in Table 22. At the first sampling date potassium chloride particles contained 50.7 percent of the original potassium, while the -4+14 mesh pyrophosphate and metaphosphate had lost 31.7 and 95.8 percent of their water soluble potassium, respectively. The larger particles of fused potassium phosphates retained about the same percent of their water soluble potassium content. After 20 days exposure, about 70 percent of the water soluble potassium from pyrophosphate particles of both sizes had been

TABLE 22

The quantity of water soluble potassium remaining in fused potassium phosphate particles after they have been left in the field for various lengths of time.

Material		Potassium Remaining in Particles											
		Time in Days During Which the Particles were Left in the Field				30				40			
Particle Size		10		20		30		40		50		60	
		% of the Total H ₂ O-Sol. K ₂ O	% K ₂ O Remaining	% of the Total H ₂ O-Sol. K ₂ O	% K ₂ O Remaining	% of the Total H ₂ O-Sol. K ₂ O	% K ₂ O Remaining	% of the Total H ₂ O-Sol. K ₂ O	% K ₂ O Remaining	% of the Total H ₂ O-Sol. K ₂ O	% K ₂ O Remaining	% of the Total H ₂ O-Sol. K ₂ O	% K ₂ O Remaining
Potassium pyrophosphate	-4+14 mesh	4.03	68.30	1.81	30.6	0.57	9.9	0.0	0.0	0.0	0.0	0.0	0.0
	-3/8+4 mesh	3.46	46.98	2.17	28.9	0.37	4.9	0.0	0.0	0.0	0.0	0.0	0.0
Potassium metaphosphate	-4+14 mesh	0.94	4.23	--	--	--	--	--	--	--	--	--	--
	-3/8+4 mesh	5.78	39.93	3.14	24.2	1.35	10.3	--	--	--	--	--	--
Potassium chloride	-6+10 mesh	50.73	83.78	--	--	--	--	--	--	--	--	--	--

*Mean of six replications.

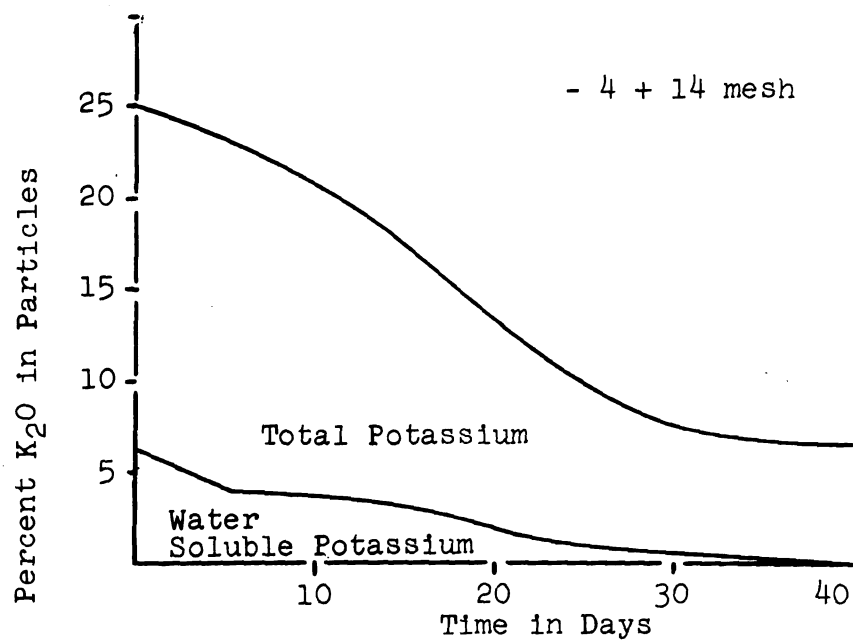
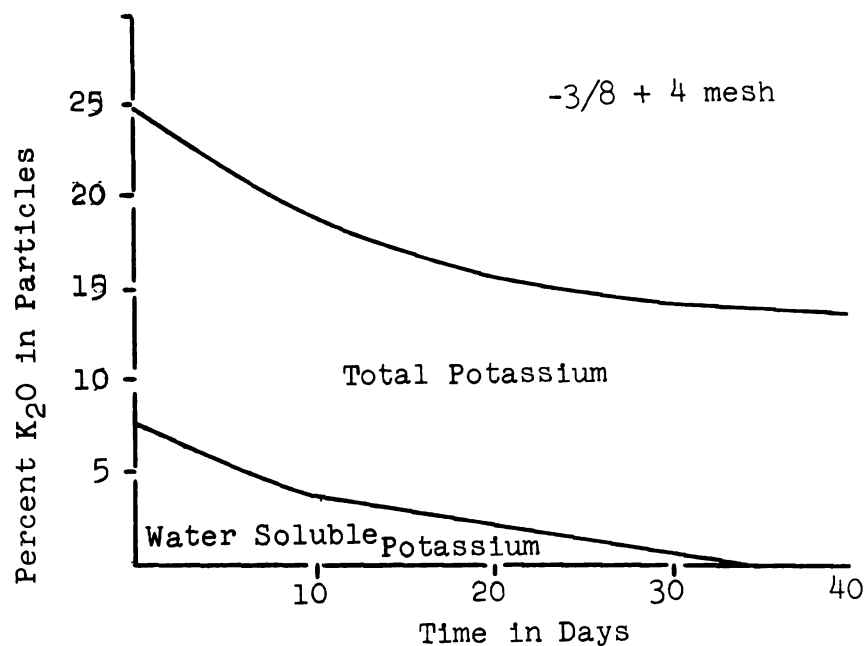


Fig. 6. Potassium remaining in potassium pyrophosphate particles after exposure in the field for varying lengths of time.

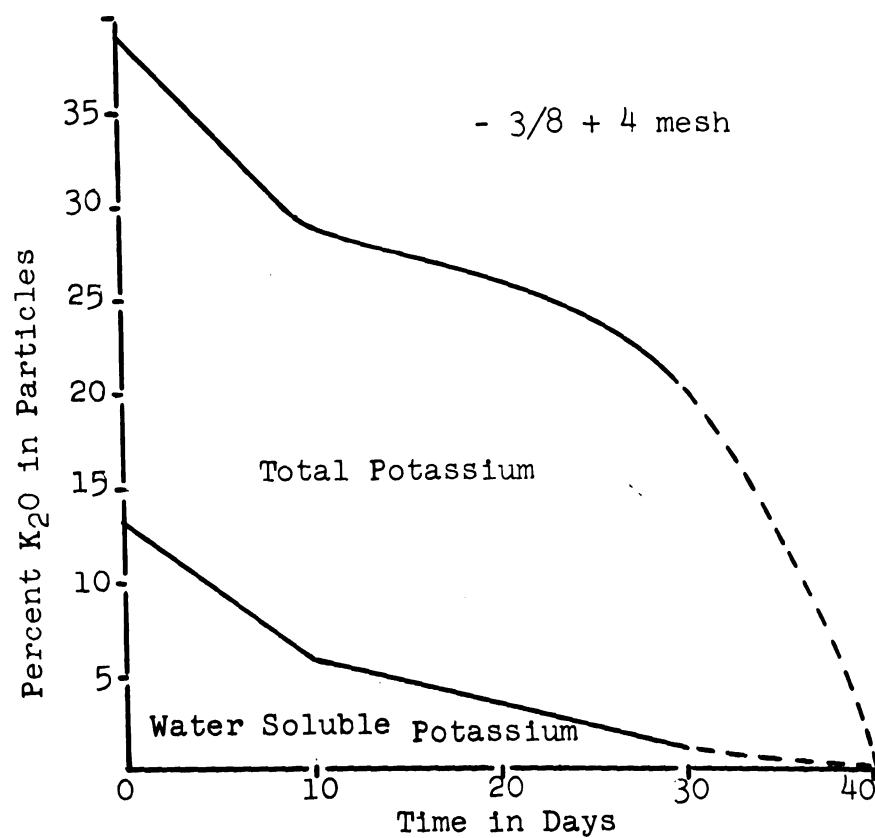


Fig. 7. Potassium remaining in potassium metaphosphate particles after exposure in the field for varying lengths of time.

leached out. Virtually no water soluble potassium was present at the end of the experiment.

Data presented in Figure 6 show that although there was no water soluble potassium present in the granules after 40 days exposure in the field, 6.6 percent total potassium was still retained in the smaller size pyrophosphate granules and 13.7 percent in the larger ones. The pattern of dissolution of potassium from the large particles of metaphosphate as given in Figure 7 is somewhat similar to that for pyrophosphate for the first 30 days exposure. However, in the 10 day period thereafter, complete dissolution and/or disintegration of these metaphosphate particles occurred. It is interesting to point out that large potassium-calcium pyrophosphate particles were recovered from a 1957 field experiment about 10 months after a surface application. At this time they contained 3.54 percent K_2O , which was probably about 50 percent of their original potassium content.

SUMMARY

Upon comparing the pyrophosphate, metaphosphate, and chloride forms of potassium in the greenhouse in 1957, it was found that the yield of beans grown on Metea sandy loam in which these various potassium fertilizers were mixed was significantly higher from pots receiving pulverized potassium metaphosphate materials. However, the potassium content of plants was not affected by the type of carrier or the particle size. When bean plants were grown on organic soil, yield and potassium uptake were not significantly influenced by the water solubility of the potash source or the particle size. The mixed application of the fertilizer resulted in significantly higher yield and potassium uptake by plants grown on this soil, indicating that to obtain maximum effectiveness of fertilizer potassium it was necessary to mix the supplemental nitrogen and phosphate fertilizer throughout the entire volume of organic soil.

Water solubility of the potassium carrier was not a factor in the yield of millet grown on Kalamazoo sandy loam in the greenhouse in 1958. Application of finer particles resulted in slightly better growth than did the use of coarser ones, and banding of the fertilizer was more effective than mixing. When the same plants were grown on Houghton

muck soil, highest yields were obtained with applications of metaphosphate. Potassium content of plants increased with increase in water solubility of the fertilizer, but neither particle size nor placement had any significant influence on uptake of potassium except in the case of the metaphosphate material. In general, it can be concluded that all the potassium sources were about equally effective in promoting the growth of plants even though potassium content of plants increased with increase in soluble potassium content of the fertilizer.

The dissolution patterns of potassium-calcium pyrophosphate and potassium metaphosphate involving continued leaching with water show that the water soluble potassium content was rapidly released from both materials. No marked difference was noted between the meta- and pyro- compounds except that the small metaphosphate particles disintegrated after continued leaching. Even after considerable leaching, only a small release of the initially non-water soluble fraction was noted in several instances.

When the fused potassium phosphates were leached with water in soil column, recovery of potassium from the soil was fairly well correlated with the original water soluble potassium contents of the fertilizer. A direct, though imperfect relationship was noted between particle size of a specific potash source and the potassium released from the fertilizer. The exchangeable and water soluble potassium

fractions, representing loss from fertilizers, were found concentrated near the surface. Demarcation between the advancing front of leaching potassium ions from fertilizer and the uniform ion concentration of the soil mass below was quite sharp.

Studies of the dissolution and migration of potassium from the metaphosphate and pyrophosphate fertilizers under conditions similar to those in the field also showed that the water soluble fraction rapidly diffuses out of both the large and small particles. However, loss from the large particles was found to be somewhat slower. After 1 to 2 days moist soil contact the release of potassium from the fertilizer source was very slow during the following 30 days period. Some water soluble potassium remained in the fertilizer particles largely as a result of equilibrium with a high concentration of soluble potassium in soil adjacent to the fertilizer source. Only very minor conversion of initially non-water soluble potassium to a soluble form is believed to have occurred.

In incubation studies, approximately three-fourths of the potassium dissolved out of the fertilizers was recovered from a volume of soil 2 x 2 x 10 centimeters in the center of which the fertilizer was banded. Lateral movement of potassium decreased rapidly with distance from the potassium source. With an increase in time of incubation there was an increase in the soluble potassium content of the lateral

adjacent volume of soil but there was very little downward movement of potassium.

When the several potash fertilizers were placed on the soil surface in the field for a period of 40 days all potassium chloride granules and potassium metaphosphate of -4+14 mesh particle size disintegrated after 20 days exposure to weather. Large and small potassium pyrophosphate particles were recoverable even after 40 days. After 10 days exposure, potassium chloride was found to contain only 50.7 percent of its original potassium. During the same period -4+14 mesh pyrophosphate and metaphosphate lost 30.7 and 95.8 per cent of the water soluble potassium, respectively, but little or no potassium from their water insoluble fractions. After 20 days exposure 70 percent of the water soluble potassium was missing from pyrophosphates of both sizes. Analysis of the large pyrophosphate particles after long exposure periods indicates the original water-insoluble potassium is released very slowly.

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