ABSTRACT

THE DISSOLUTION AND MIGRATION OF MANGANESE FROM AMMONIUM PHOSPHATES

by Robert M. Weaver

In this study, the dissolution and migration of Mn in the soil, from eight different Mn-phosphate fertilizers, was investigated. The eight fertilizers consisted of $MnSO_4$ or MnO coated onto or incorporated into ammonium orthophosphate (AOP) or ammonium polyphosphate (APP) fertilizer granules. The fertilizer granules were prepared from AOP, APP and a radioisotope of Mn--Mn^{54}.

Dissolution studies were conducted by controlled leaching with H_2O and by incubation in soil. Migration studies were carried out by allowing fertilizer granules to incubate in the center of a soil core for periods of one-half, one, two, four and six weeks. The movement of Mn was determined by removing a two cm. horizontal slice from the center of the soil core. This slice was sectioned into radial segments of one, two, three, and four cm. The exchangeable and easily-reducible Mn^{54} of each radial segment was determined. Studies were also conducted to determine the influence of AOP and APP fertilizers upon the soil exchangeable and easily-reducible Mn.

Both AOP and APP fertilizers were found to cause the soil exchangeable Mn to increase. This effect was limited to a one cm. distance from the granule site and was most pronounced after the fertilizers had been in contact with the soil for one week.

The two methods of dissolution gave close agreement in the relative amount of Mn released from the eight fertilizers. The actual amount of Mn released depended upon the particular combination of the phosphate compound, the Mn compound and the method by which the Mn was added to the fertilizer granule. Combinations of Mn and P that released the greatest amount of Mn upon leaching were: $MnSO_4$-AOP and MnO-APP. Coating versus incorporating the Mn carrier caused the H_2O-soluble Mn to be released more readily upon leaching and caused an increase in the H_2O-soluble Mn content with the $MnSO_4$-AOP and the $MnSO_4$-APP fertilizers, a slight increase with the MnO-APP fertilizers and a decrease with the MnO-AOP fertilizers.

The distance that Mn moved from the eight different fertilizer materials was constant over a six week period. The amount of Mn that moved through the soil was directly related to the extent of Mn dissolution from the fertilizer. The relative distribution of Mn throughout the soil surrounding the granules was essentially identical for all eight fertilizers.

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INTRODUCTION

The use of manganese (Mn) as a fertilizer to correct soil deficiencies has increased greatly in the past two decades. An example of this increase may be seen in the figures released by the Laboratory Division of the Michigan Department of Agriculture. In 1943, Michigan fertilizer companies sold 31.27 tons of Mn-bearing fertilizers. By 1965, this figure had increased to 2,459 tons of Mn-bearing materials--nearly 80 times the amount utilized in 1943. As with other micronutrients, this increased use of Mn as a fertilizer is due to several factors. First, there is a greater awareness on the part of the soil scientist and other workers in this area in regards to the occurrence and correction of Mn deficiencies. Second, increased crop yields have placed a heavier demand on the supply of available Mn present in soils. A third factor contributing to the greater use of Mn fertilizers is the trend towards the use of high analysis fertilizers prepared from relatively pure compounds which contain little Mn as impurities.

Accompanying this increased use of Mn fertilizers, are investigations by research workers in regards to more economical and effective carriers of Mn and improved methods of application. One such new technique that has been developed and tested on a limited scale, is the incorporation of Mn compounds into mixed fertilizers. This procedure may take several forms depending upon the Mn compound used, the material into which it is incorporated and the stage of manufacture at which the Mn is incorporated. In particular, the Testing and Development Branch of the Tennessee Valley Authority has developed a procedure whereby various Mn compounds are incorporated into or coated onto ammonium orthophosphate (AOP) or ammonium polyphosphate (APP) fertilizer granules. The incorporated materials are prepared by adding the Mn carrier prior to ammoniation of the phosphate materials, while the coated materials are prepared by adding the Mn materials after ammoniation.

In addition to any possible economic advantages that may result from manufacture or application, these manganese-phosphate fertilizers developed by TVA may offer several advantages in supplying Mn in the soil. Several researchers have noted that the application of fertilizers in close proximity with phosphate fertilizers increases markedly the effectiveness of the Mn fertilizers. This favorable effect has been attributed to the pH decrease that accompanies the hydrolysis of many phosphate fertilizers in the soil and to the formation of Mn phosphate complexes that slowly release available Mn.

In the case of the inclusion of Mn compounds into APP materials a third factor may be operating which causes the Mn to be available in greater amounts. APP has been found to have a sequestering or chelating property which causes added micronutrients to be retained in a soluble form. Investigations upon the incorporation of ZnO into APP indicate that such a combined material will release five times more Zn than if the ZnO had been incorporated into AOP.

Experiments with the manganese-phosphate fertilizers developed by TVA have been largely limited to water-solubility laboratory tests and field tests in which effectiveness is measured in terms of crop yield and plant up-take of manganese. Water-solubility tests have indicated that MnO when added to APP yields a greater amount of water-soluble Mn than if the MnO is added to AOP. The case for $MnSO_4$ is reversed with the $MnSO_4$ yielding a slightly greater amount of water-soluble Mn when present in AOP than when present in APP. In the case of field trials in which $MnSO_4$ and MnO incorporated into or coated onto ammoniated superphosphate were compared it was found that generally $MnSO_4$ was a superior source of Mn over MnO. Furthermore, the $MnSO_4$ appeared to be more effective as a source of Mn when incorporated before ammoniation, while MnO appeared to be more effective when coated onto the fertilizer granule.

Little, if any work has been conducted to study the actual behavior in the soil of manganese-phosphate fertilizers. It is the purpose of this study to investigate the behavior of manganese-phosphate fertilizers in the soil. This will be carried out by observing the migration and dissolution of Mn from the fertilizer granule in the soil and how the migration and dissolution are influenced by the nature of the phosphate carrier, the manganese carrier and whether the manganese source is incorporated into or coated onto the phosphate fertilizer granule. Such a study may be of benefit for several reasons. First, in evaluating the effectiveness of the manganese-phosphate fertilizers developed by TVA, the results should have greater agronomic significance than various solubility tests in as much as the behavior of the fertilizer will be observed in the soil-the medium in which the fertilizer is actually used. Second, the results of this study may be of aid in explaining the results of past, present or future field trials with this particular fertilizer. Third, the results of this study may provide additional knowledge of the interaction of Mn and P in the soil.

LITERATURE REVIEW

The Forms of Manganese in the Soil

Manganese is considered to exist in the soil in several different forms and valence states. First, there is the divalent manganous ion, Mn^{+2}, which is the principal form taken up by plants. The Mn^{+2} ion may exist in the soil solution as water-soluble Mn or on the exchange complex of the soil as exchangeable or extractable Mn. Divalent Mn is also thought to exist in a chelate complex with certain fractions of soil organic matter (4, 8, 36, 37, 39). Second, there has been found to exist in the soil a class of hydrated, colloidal, "active" or "easily-reducible" Mn oxides. These oxides may involve mixtures of valences from 2 to 4, but some researchers consider them to be trivalent (16, 61). Third, there is Mn^{+4} which exists as the very inert oxide, MnO_2 (54, 61).

The Mn^{+2} in a soil is thought to be in equilibrium with precipitates of higher oxides or hydroxides of manganese. Leeper (54) in 1935, suggested that the equilibrium could be represented as follows:

$$Mn^{+2} \rightleftharpoons \text{colloidal hydrated } MnO_2 \rightleftharpoons \text{inert } MnO_2$$

Dion and Mann (16), in 1936, proposed a Mn cycle based upon the oxidation-reduction equilibrium between divalent and tetravalent Mn and the existence of a trivalent oxide--$Mn_2O_3 \cdot xH_2O$. The tri- and tetravalent forms are favored by high pH and oxidizing conditions. Highly stable MnO_2 is the form most likely to occur in soils at pH values greater than 8.0. Trivalent Mn is presumably favored by pH values near neutrality, while the Mn^{+2} is found in acid soils. Under slightly acid conditions, the trivalent oxide is thought to dismutate to yield divalent and tetravalent Mn.

Fujimoto and Sherman (23) in 1948, were unable to correlate the Mn cycle as proposed by Dion and Mann (16) in 1936, with the behavior of Mn in Hawaiian soils. They proposed a Mn cycle based upon dehydration-hydration reactions in addition to oxidation-reduction reactions. When free MnO, MnO_2, and water are present in the soil, addition and hydration of the oxides will take place with the formation of a complex, hydrated manganese oxide--$(MnO)_x(MnO_2)_y(H_2O)_z$. This form of oxide is considered to be stable when moisture is present and the temperature is low. If the soil becomes dry and soil temperature rises, this form of oxide is thought to break into its component parts--free MnO and MnO_2. The component parts can then come under the influence of either oxidation-reduction or dehydration-hydration processes or the MnO may be absorbed by the plant.

Factors that Influence the Behavior and Availability of Manganese in the Soil

Essentially there are three factors that control the chemistry of Mn in soils and its availability to plants--moisture, pH, and organic matter.

It has been observed that air-drying of a soil increased its exchangeable Mn content (6, 11, 22, 23, 31, 44, 80, 104, 112). This increase has been attributed to reduction of Mn oxides by a small fraction of the soil organic matter, to dehydration of a hydrated Mn oxide and to microbial activity (6, 22, 23, 114).

In contrast to drying, moistening of a soil has been found to decrease the exchangeable manganese content of a soil (11, 22, 23, 31, 46, 89). Fujimoto and Sherman (23) attributed the decrease of exchangeable manganese upon moistening to hydration of Mn oxides. However, results by Sanchez and Kamprath (89), indicates that more may be involved than a simple hydration process. They found that the reduction of exchangeable Mn as a result of moistening, was most pronounced on a high organic matter soil which had been limed. The effect of organic matter may be due to the formation of chelates with Mn^{+2} or to the enhancement of oxidation of Mn^{+2}. Water-logging a soil has been found to bring about an increase in water-soluble and exchangeable Mn (12, 29, 30, 69, 80, 86, 90). It is held that the increase in available manganese upon water-logging a soil is due to the reduction of higher oxides of Mn. Presumably this reduction is a biological one in which microorganisms utilize the Mn oxides as a source of O_2 under condition of reduced O_2 tension in the soil (55).

Soil reaction or pH has long been known to be an important factor influencing the availability of Mn in the soil. In most instances a Mn deficiency has been associated with an alkaline soil reaction and it has often been noted that the liming of a soil to a neutral or alkaline pH reduces available Mn and induces Mn deficiency (1, 11, 14, 22, 24, 27, 29, 43, 60, 65, 72, 80, 89, 92, 93, 96, 105, 112).

The addition of sulfur to a soil or other materials which decrease soil pH have been found to increase available Mn (12, 17, 20, 24, 82, 87, 91).

In some cases, it has been noted that the addition of CaO, $Ca(OH)_2$ or other basic materials that increase the soil pH to an extremely alkaline level cause an increase in available Mn (28, 45, 54, 63, 81).

The influence of pH on Mn in soils may be due to its effect on both chemical and biological oxidation-reduction processes. It has been found that an increasing soil pH hastens bacterial and chemical oxidation of Mn^{+2} (85).

Yarilova (113) found that the oxidation potential for the conversion of Mn^{+2} was a linear function of pH from pH 3.2 to pH 8.0.

Gerretsen (25) utilizing soil agar plaques, demonstrated that oxidation of Mn^{+2} to MnO_2 by soil microorganisms was most intense in a pH range of 6.3 to 7.8. Leeper and Swaby (56) found that soil microorganisms can oxidize Mn^{+2} at all pH values above 5.5; this oxidation is most rapid in well-aereated soils in the pH range of 6.0 to 7.5. Leeper and Swaby (56) also observed that at pH values above 8.0, biological oxidation of Mn did not occur. The absence of microbial formation of MnO_2 on very alkaline soil agar plaques was due to the removal of Mn^{+2} from solution as $MnCO_3$. It may very well be that this precipitation of Mn^{+2} by carbonate may be the reason that Mn deficiencies have seldom been reported on soils with a pH above 8.0 (53) and that addition of CaO or $Ca(OH)_2$ has been beneficial in alleviating a Mn deficiency in some cases (28, 45, 63, 81).

The increased availability of manganese that results when soil pH is decreased is generally attributed to the reduction of higher oxides of Mn. Mulder and Gerretsen (74) stated that a pH decrease favors reduction of MnO_2 in as much as the oxides themselves are stronger oxidizing agents under acid conditions and are more susceptible to reduction by hydroxy acids.

It is considered possible that bacterial reduction of MnO_2 can occur, but this is favored more by a low O_2 tension in the soil rather than a low pH (55).

One instance in which microbial activity is thought to enhance Mn availability is when S is added to the soil. The favorable effect of S applications in correcting a Mn deficiency is well known. It was originally thought that this beneficial effect of S was due to the decrease in pH that results when S is added to a soil. However, it was observed in some instances, that an application of S promoted an increase in Mn^{+2} that could not be attributed entirely to the decrease in soil reaction brought about by the S (10, 102, 104). Tisdale and Bertramson (101) suggested that the increase in available Mn in soils accompanying the oxidation of elemental S is due primarily to the reducing effect of S and not to the solvent action produced by the accompanying increase in acidity. Starkey (97) stated that the heterotrophic organisms involved in the oxidation of sulfur may utilize MnO_2 as a hydrogen (H) acceptor and this may well explain the efficiency of S in releasing Mn^{+2}. Recently Page (77) conducted a study which indicated that the influence of soil pH upon Mn availability is not necessarily due to the enhancement of the formation or reduction of MnO_2 as earlier suggested by various researchers (23, 54, 74, 77, 90). Page suggested that Mn becomes unavailable through the formation of complexes with the soil organic matter and that the capacity for complex formation is controlled by pH.

The organic matter content of a soil influences Mn behavior in two ways. First, its presence may enhance chemical or biological reduction of the various forms of Mn in the soil (74). Second, Mn^{+2} may form a chelate complex with certain fractions of soil organic matter (4, 8, 36, 37, 39).

It has been observed in several investigations that the rapid decomposition of organic matter with a wide C:N ratio, causes a considerable increase in the exchangeable Mn content of soil (23, 30, 41, 80). This increase is attributed to the reducing conditions produced in the soil as a result of the lowered O_2 tension and a decreased pH brought about by the rapid decomposition of the organic matter.

Retention of Mn^{+2} by soil organic matter was first suggested by Heintz and Mann (36) who noted that $\underline{N}$ NH_4OAc containing various inorganic salts extracted more Mn from an alkaline organic soil than did $\underline{N}$ NH_4OAc alone.

Hemstock and Low (37) in a study of the retention of Mn in soils stated that the results of Heintz and Mann (36) could be explained on the basis of a chelation theory. Their reasoning was based in part, on the observation that Main and Schmidt (62) had provided evidence that Mn^{+2} will form chelate complexes with alpha hydroxy and dicarboxylic acids. Hemstock and Low also pointed out that proteins, lignins, and polyuronides which are believed to constitute the major portion of soil organic matter possess the necessary functional groups for chelation as outlined by Diehl (15). Furthermore, in a study of the order of stability of chelate complexes by Mellor and Maley (68) Cu chelate was found to be more stable than the Mn chelate. For these reasons, Hemstock and Low considered that Mn^{+2} did indeed form a chelate complex with the soil organic matter and that the addition of a Cu salt to the extracting solution should release this complexed Mn. Laboratory incubation and extraction experiments substantiated their theory.

In a later paper, Heintz (35) pointed out that the use of Cu salts in an extracting solution for chelate, complexed Mn may impart a reducing property to the solution. Heintz, after Beckwith (4) used Na-EDTA to extract the complexed Mn^{+2}. Such Mn was found to constitute 10-20% of the total Mn content of alkaline, organic soils.

Walker and Barber (106) conducted a study to determine if the measurement of chelated Mn as well as exchangeable Mn would increase the ability to predict available Mn. Twelve Indiana soils varying in organic matter, pH, texture and parent material were treated to give two levels of Mn and acidity. Available Mn was determined by cropping the soils with German millet. It was found that chelated and exchangeable Mn were highly correlated in spite of wide variations in soil properties and that the measurement of chelated Mn did not greatly increase the ability to predict plant available Mn.

The Measurement of Available Manganese in the Soil

Much work has been expended in an effort to develop a chemical procedure that will determine accurately the plant available Mn content of a soil. So far little success has been attained in this area due to difficulties in adequately characterizing the forms of soil Mn and their response to varying soil conditions.

The total Mn content of a soil is not correlated to Mn uptake by plants (74).

Several researchers have suggested that Mn exchanged by neutral salt solutions is an index of plant available Mn present in a soil (33, 80, 100). But attempts to show a correlation between exchangeable Mn and the incidence of Mn deficiency have been disappointing, although there was a somewhat closer relationship between uptake by the plant and the estimation of exchangeable Mn than could be established between uptake and total Mn (77).

Leeper (53) suggested the use of neutral NH_4OAc containing 0.2% hydroquinone to measure the "active" Mn of a soil or the sum of the exchangeable and easily-reducible Mn. Leeper found that the active Mn exceeded 100 ppm on "healthy" soils tested and was less than 15 ppm on deficient soils. It was also noted that strongly acid soils containing less than 25 ppm active Mn were likely to become Mn deficient when limed.

Sherman and Harmer (93) also used NH_4OAc containing 0.2% hydroquinone to assess the Mn status of several mineral and organic soils. Their findings indicated that in any alkaline soil at least three ppm exchangeable Mn must be present for satisfactory crop production. In order to maintain an adequate level of exchangeable Mn, the easily-reducible fraction should be at least 100 ppm.

Sherman et al. (94) also reported successful results with the use of NH_4OAc containing hydroquinone. But, Heintz (34) was unable to distinguish soils giving "Marsh Spot" (Mn deficiency) from healthy soils with this technique. Also Jones and Leeper (48) in a study of the availability of various synthetic Mn oxides could not correlate the response of oats and peas obtained in pot experiments with the quantities of Mn in the soil as determined by the method of Leeper (53). Much better results were obtained when the reducing agent was separated from the electrolyte and $Ca(NO_3)_2$ was substituted for NH_4OAc.

Recently attention has been given to the use of phosphorous compounds and acids as extractants to estimate available soil Mn.

Hoff and Mederski (40) examined nine methods of estimating plant-available Mn, using soils from 25 fields in different parts of Ohio. The estimate of available Mn obtained by using $(NH_4)H_2PO_4$ gave the highest correlation with actual Mn uptake by soybeans.

Hammes and Berger (31) reported that 0.1 N H_3PO_4 gave a more reliable guide to uptake of Mn by oats than did $(NH_4)H_2PO_4$.

Pailoor (78) in a study of several different methods of estimating plant available Mn in Michigan soils found that 0.1 N H_3PO_4 gave the best correlation with plant uptake and yield of beans on mineral soils. However, on organic soils, NH_4OAc containing o.2% hydroquinone proved to be the more effective in estimating plant available Mn.

Manganese as a Fertilizer

The application of Mn compounds to soils or plants has long been considered a beneficial, expedite and economical means of alleviating a Mn deficiency.

Among the first researchers who found the application of Mn to soils to be of benefit were Aso (2) and Nagoaka (75) who observed that the application of $MnCl_2$ or $MnSO_4$ had a stimulating effect on rice. Gilbert et al. (27) corrected a Mn deficiency in spinach by applying eight pounds of $MnCl_2$ per acre or by spraying with $MnSO_4$ solution at the rate of 0.3 pounds per acre. Wild (111) in experiments with wheat, found that Gray Speck disease (Mn deficiency) could be controlled by the application of $MnSO_4$ at the rate of 18-24 pounds per acre applied at seeding time. Cook and Millar

(13) found that the application of 100 pounds per acre of $MnSO_4$ after Mn deficiency symptoms had appeared on white beans, resulted in normal growth. Steckel (98) found that application of 35 pounds of $MnSO_4$ per acre produced a yield increase of 12.3 bushels of soybeans grown on Mn deficient soil. Early spray application of 10 pounds of $MnSO_4$ on the same soil increased the bean yield 14 to 18 bushels per acre.

In as much as early experiments indicated that plants grown on Mn-deficient soils gave marked response to the application of Mn salts, further investigations were conducted in this area to study the effectiveness of various Mn carriers and methods of application.

Many of the investigations on types of Mn carriers were conducted in an attempt to find carriers that would act as slowly available sources of Mn. This was done because in most instances a Mn deficiency occurs as a result of soil conditions which render an otherwise adequate supply of Mn unavailable. Hence when a readily-available source of Mn is added to such a soil, the Mn may be transformed into unavailable forms. In several instances this transition has been found to be quite rapid. Wain et al. (105) treated soils in the laboratory and in the field with solutions of $MnSO_4$ and then examined at intervals the amount of exchangeable Mn. They found in an experiment with a highly calcareous soil that the exchangeable Mn down to a depth of 12 inches fell to its original level seven days after treatment. Wallace and Ogelive (107) reported that $MnSO_4$ and $MnCl_2$ used as fertilizers equivalent to 100 pounds of $MnSO_4$ per acre, were effective in combating Mn deficiency in Globe beets only during the early stages of growth.

Among the slowly-available Mn carriers that have been developed and utilized to cure a Mn deficiency are: Oxides (45, 20, 84), Frits (66, 84, 92), and Chelates (20, 34, 92). More recently, Ludwick (9) has produced a slowly-available source of Mn by fusing MnO and $MnCO_3$ with S. Initial field tests with this compound indicated that it tended to delay uptake of Mn by the initial crop and enhance the uptake by the succeeding crop.

However, in spite of the wide variety of Mn carriers that have been and are presently being investigated, $MnSO_4$ still remains the most widely used Mn source for curing Mn deficiencies (101).

The two most commonly used methods of applying Mn are soil or foliar applications. Another less common method of treatment that has been used with success in curing a Mn deficiency is that of soaking the seeds in a dilute Mn salt solution (18, 44).

Soil applications of Mn may be either broadcasted onto the soil surface and worked into the soil or banded in the row in the vicinity of the seed. The broadcast method has gained little popularity. This is because a greater reduction in the availability of the added Mn as a consequence of greater soil-Mn contact which results when the Mn carrier is broadcasted rather than banded.

Walsh et al. (108) found that a band application of 14 pounds of $MnSO_4$ per acre was more effective in curing a Mn deficiency of oats and wheat than a broadcast application of 56-112 pounds of $MnSO_4$ per acre.

Band applications of Mn carriers have proven quite successful, especially when banded along with fertilizers containing monocalcium phosphate.

Bertramson (5) in correcting a Mn deficiency on corn, found that 25 pounds of $MnSO_4$ mixed with 100 pounds of 0-12-12 (P as $Ca(H_2PO_2)_2$) and side-dressed one and one-half inches to the side and below the seed completely eliminated Mn deficiency symptoms. When manganese sulfate was banded alone, 100 pounds of $MnSO_4$ was required to produce the same effect. Similar increases in the efficiency of a Mn carrier when banded with $Ca(H_2PO_4)_2$ have been observed by several other researchers (22, 48, 50, 51, 98, 99, 109).

The favorable effect of banding $Ca(H_2PO_4)_2$ with Mn carriers has been attributed to the reactions that $Ca(H_2PO_4)_2$ undergoes in the soil. First it has been found that there is a sharp pH decrease in the immediate vicinity of the fertilizer band area (57). It is thought that this decrease in pH may either cause release of Mn from higher oxides or it may also prevent the fixation of the added Mn^{+2}. Second it is thought that there may be the formation of a manganous phosphate precipitate which slowly releases Mn^{+2} (51, 109).

Foliar applications of Mn may be either as a spray or as a dust. Spraying is the most common of the two types of foliar application.

In some cases foliar applications of manganese have been favored over soil applications, due to a lower cost of application, preventing soil fixation of the added Mn^{+2}, and increased effectiveness in supplying Mn^{+2} to certain crops (27, 64, 66).

In Michigan, foliar applications of Mn to treat a Mn deficiency are recommended when: (1) regular fungicidal and insecticidal sprays are practiced; (2) fertilizer is not applied in a band near the row; or (3) deficiency symptoms appear on the foliage (70).

The Dissolution and Migration of Nutrients Ions from Fertilizers in the Soil

In the past decade the dissolution and migration of nutrient ions from fertilizers in the soil has come under investigation. These studies have been conducted to determine the effectiveness of various physical forms of fertilizers, the most ideal placement of a fertilizer in the soil in order that nutrient availability to the plant is at a maximum and the behavior of a fertilizer material in response to varying soil conditions.

Various techniques have been employed to study the dissolution and migration of nutrients from fertilizers in the soil. In most cases these involve placing a sample of the fertilizer of known composition in a container of soil and allowing a desired amount of time for incubation. Dissolution of the fertilizer is determined by recovering the fertilizer source and analyzing it for the nutrient in question. Migration or movement of the nutrient is determined by sectioning the soil about the fertilizer source and analyzing the various sections for the nutrient in question. Studies of both dissolution and migration have been greatly facilitated by the adaptation of radioactive tracer techniques. This has made it possible to more accurately follow the nutrient ion as it moves from the fertilizer source (52).

Heslep and Black (38) studied one dimensional diffusion of P from solid phosphate fertilizers tagged with radioactive P^{32}. They utilized six different soil types varying in texture from a loam to a silt loam. The soils were brought to moisture levels ranging from 18 to 32% (oven-dryweight) by repeated spraying and mixing. The moist soil was packed in 28 by 105 mm. plastic tubes sealed at one end with aluminum foil. The soil was compacted to a bulk density of 1.3 g/cc. When the tubes were half full, a layer of P was added--20 mg. P_2O_5/cm^2. The unfilled portion of the tube was filled with soil in a like manner, sealed and incubated at 24°C. After the desired length of time, the soil was sliced in sections as it was pushed out one end of the tube. The activity of the various slices was measured.

Lawton and Vomocil (52) also utilized radioactive P in a study of the dissolution and migration of P from granulated superphosphate in some Michigan soils. In dissolution studies, superphosphate granules were placed in moist soil contained in a metal can which was sealed and allowed to incubate. At a predetermined time the containers were opened, the superphosphate granule recovered and analyzed for its activity. In the migration studies, the selected soil was brought to the desired moisture level by tumbling and spraying to obtain as uniform distribution as possible. The soil was then packed into paraffin lined sectioning boxes for study. The desired compaction was obtained by jarring layers of soil as the box was being filled. In cases where a high volume weight was desired, compaction was achieved by dropping a weight a uniform distance to pack each layer. During the filling and packing process, when each sectioning box was half full, the radioactive P source was positioned. After the box was filled, the top and edges of the hinged front were coated with molten paraffin. After the selected time interval, the boxes were opened, sectioned into slices, and each slice further divided with a concentric sampler.

Bouldin and Sample (7) in a study of the effect of associated salts on the availability of concentrated superphosphate, used cells to estimate the distribution of P in soils. The cells were prepared from two inch inside diameter, thick-walled aluminum tubing. Two three-sixteenth inch sections of tubing were attached with screws to the upper end of four inch sections of tubing. Cardboard spacers one-sixteenth inch thick, were placed between each section to facilitate sampling. Moist soil was packed into the cells. Soil was removed from the center of the soil surface so that a cavity the size of the fertilizer pellet was formed. A pellet was then placed in the cavity and the cells were sealed with plexiglass sheets to prevent moisture loss. After the desired incubation period, the cardboard spacers were removed and two three-sixteenth inch sections of the soil column were sliced off with sheet tin using the three-sixteenth inch rings as guide. Three additional three-sixteenth inch sections of soil columns were obtained by pushing the soil core out of the tube three-sixteenths of an inch and slicing off the protruding soil. The soil sections were then sampled concentrically about the pellet residue using short sections of cork borers.

Sample and Taylor (88) suggested a much simpler method to estimate the rate and extent of movement of P from fertilizers. The fertilizer material to be studied was spot-placed on a moist soil surface by removing a small core of soil which was replaced by the fertilizer. After the fertilizer and the moist soil had reacted the desired time, a disk of smooth filter paper impregnated with a solution of ammonium molybdate in HCl was placed on the soil surface over the site of application and smoothed gently with a small spatula to ensure good contact. Contact of added fertilizer with paper was avoided by cutting a small hole in the paper to match the application site. After one minute, the paper was removed and sprayed with $SnCl_2$. The extent of the resulting blue color was used to determine the movement of P.

Mordvet and Osborne (73) studied the dissolution and movement of boron from several different materials by using one and three dimensional systems. In the one dimensional system, soil was packed to a depth of 0.3 centimeters in a plexiglass Petri dish. One fertilizer granule of known mass and B content was placed in the center of each dish; then additional soil was added and firmly packed to a depth of 0.6 centimeters. After various periods of incubation a device consisting of concentric metal strips with radii of one, two, three and four centimeters, soldered together in the correct spatial relationship, was placed on the soil surface with the center over the fertilizer granule site and pressed through the soil. The residue of each granule was removed and the soil between each ring was analyzed for B.

In the three dimensional systems, gallon cans were used as the containers for the soil. Each can was cut in half horizontally. The bottom half was lined with plastic and packed with soil. One gram of the B fertilizer was placed on the soil surface. The top half of the can was then fastened in place with rubber tape and filled with soil. After incubation, the tape was removed and the soil was sectioned into two parts through the granule site. The granule residue was removed and the soil was sampled hemispherically using steel wire rings to delineate the hemispheres and a plastic spoon to scoop out the soil.

There is limited literature concerning factors influencing dissolution and migration of nutrient ions from fertilizers. This is in part due to the limited amount of research in this particular area and also due to the fact that most investigations on this particular topic, with the exception of one (49), have been primarily concerned with the actual movement and dissolution of the fertilizer rather than the influencing factors.

Dissolution of a nutrient ion from the fertilizer source into the immediate soil solution is largely dependent upon the chemical nature of the fertilizer source and the surrounding soil moisture status.

Mortevedt and Osborne (73) found that increasing the soil moisture content from 12 to 22% (0.5 to 0.2 atmospheres) caused the dissolution of B fertilizers to increase.

Lawton and Vomocil (52) found that at field capacity moisture contents, 50 to 80% of the water-soluble P moved from the granule into the soil in a one day period.

The rate and extent of the movement of the nutrient ion after it has left the fertilizer source and entered the soil solution has been found to be influenced by the concentration of the nutrient ion in the fertilizer source, the associated salts in the fertilizer source, and numerous soil properties such as moisture content, bulk density, texture, kind and amount of clay, organic matter content, pH, kind and amount of cations on the exchange complex, soluble salts and temperature (79).

In most cases where it has been studied, increasing the concentration of the nutrient ion the fertilizer source has been found to have little effect other than to increase the zone of influence or extent of migration in the soil (38, 73). However, Lawton and Vomocil (52) found that the use of larger sources of granulated superphosphate caused an appreciable difference in the distribution of fertilizer P. It was found that concentration gradients within the zone of influence were proportional to granule size. This would result from the occurrence of a dissolution rate which is greater than the migration rate.

In a study of the effect of associated salts on the availability of concentrated superphosphate, Bouldin and Brown (7) found that the distribution of P from a fertilizer granule was a linear function of the distance from the center of the granule residue. The constants in the linear equations were found to depend upon the composition of the granule in regards to various K and NH_4 salts.

Of all of the soil properties influencing the movement of a nutrient ion through the soil, soil moisture is probably the most important (52). It has been observed in several cases that increasing soil moisture causes an increase in the rate and extent of movement of the nutrient ion. The effect of increasing soil moisture content is thought to be due to a greater dissolution rate which would cause a larger concentration gradient and also to an increased diffusion of the nutrient ion through thicker water films.

Soil compaction has been found to influence the migration rate of a nutrient ion from a fertilizer source. Lawton and Vomocil (52) attributed the increase in migration rate of P from fertilizer granules as a result of increased soil compaction in part to a more rapid dissolution, but also to a greater continuity of water films around the soil particles, since after 24 hours dissolution rates were similar from granules in compacted and normal soils. The observation that an increase in bulk density increases the movement of an ion in the soil has also been noted by Phillips and Brown (79) in self-diffusion studies of Rb^{86} and Sr^{89}.

The influence of soil texture upon the migration of nutrient ions will in part depend upon the nature of the ion in question. In the case of P, Heslep and Black (38) could find no difference in the extent of diffusion in either coarse or fine textured soils. However, Lawton and Vomocil (52) found that both the migration rate and the maximum movement of fertilizer P were greater in a sand than in a loam.

MATERIALS AND METHODS

This investigation was designed to study the dissolution and migration of Mn from eight different manganese-phosphate fertilizers. The eight fertilizers consisted of $MnSO_4$ or MnO coated onto or incorporated into APP or AOP fertilizer granules. Samples of these fertilizers were supplied by the Tennessee Valley Authority.

The AOP used in this study had a grade of 12-52-0 and consisted primarily of monoammonium orthophosphate $NH_4(H_2PO_4)$. It was produced by neutralizing wet-process H_3PO_4 with NH_3 in a series of tanks where the heat of reaction evaporates a part of the water introduced with the acid. The neutralization by NH_3 results in a slurry composition which flows to a pug mill or bunger in which it is granulated by mixing with recycled fines. The granules are then dried and screened to provide a product fraction and a finer recycle fraction (9).

The APP used in this study had a grade of 16-60-0. It was produced in much the same manner as AOP except that the NH_3 was used to neutralize superphosphoric acid rather than H_3PO_4. Superphosphoric acid was developed by TVA as a fertilizer intermediate. It is a mixture containing at 33% P concentration (76% P_2O_5 by weight) about 50% of its P as

H_3PO_4, about 42% as $H_4P_2O_7$ and the remainder as higher polymeric acids. It is produced by burning P followed by limited hydration of the resulting P_2O_5 or by concentrating wet-process H_3PO_4 (73). The $H_4P_2O_7$ content of superphosphoric acid may be responsible for its sequestering properties (95).

Mn compounds were incorporated into AOP or APP by adding the Mn prior to ammoniation. The coated granules were prepared by adding the Mn compounds as a fine powder to the granules after ammoniation. A binder of 3% diesel oil was used to assure that the Mn compounds would adhere evenly and firmly to the granules. It was found that this binder was necessary if the Mn carrier was to remain on the granule over extended periods of storage.

Laboratory Preparation of Fertilizers

Preliminary analysis of the total Mn content of the fertilizer granules furnished by TVA indicated that the Mn content varied widely from granule to granule. Such a variation makes dissolution and migration studies of individual fertilizer granules much less valid since the exact composition of the fertilizer source used in the study cannot be known to any degree of accuracy. Hence it was decided to prepare fertilizer granules similar to those produced by TVA utilizing AOP, APP, and Mn^{54}. The inclusion of Mn^{54} in the fertilizer granules would make it relatively easy to accurately determine the Mn content of each individual granule used in the dissolution and migration studies. Also it would be possible to determine, in the soil, any Mn that originated from the fertilizer.

The goal in preparation of the fertilizers was to produce 40 mg. granules containing 2% Mn and an Mn^{54} content of 100,000 counts per minute.

Since the preparation of the fertilizer materials involved melting both the AOP and APP, preliminary analyses were performed to determine if the melting would seriously alter the NH_4 content of the phosphate fertilizers. It was also desired to determine if the melting process would cause extensive hydrolysis of the pyrophosphate portion of the APP materials.

The NH_4 content of melted and unmelted APP and AOP was determined by dissolving approximately 50 mg. of the fertilizer in 50 ml. of 0.1 N HCl. This solution was made basic with 25 ml. of 40% NaOH and a micro-Kjedahl apparatus was used to distill the NH_3 into 50 ml. of 4% H_3BO_3 containing two drops methyl red-bromcresol green mixed indicator. The resulting ammonium borate salt was titrated with 0.1051 N HCl to determine the amount of NH_4 present in the fertilizer.

The influence of melting upon the hydrolysis of the pyrophosphate portion of the APP fertilizer was determined by analyzing the materials for their ortho-and pyrophosphate content. Orthophosphate was determined by dissolving 50 mg. of the fertilizer in 50 ml. 0.1 N HCl. The solution was then analyzed for orthophosphate by the Vanadomolybdophosphoric yellow color method as described by Jackson (42).

The pyrophosphate content of melted and unmelted APP was determined by dissolving 50 mg. of the fertilizer in 50 ml. of 0.1 N HCl. To this solution was added five ml. 10% $MnCl_2$ and the pH adjusted to 4.1 with 0.5 N NaOH and a precipitate of manganese pyrophosphate was obtained. Eight ml. of acetone was added with stirring and the precipitate was allowed to stand for 12 hours after which the precipitate was collected by centrifugation. The precipitate was dissolved in 50 ml. 7.5 N HNO_3 and the pyrophosphate converted to orthophosphate by gently heating the solution for 15 minutes (47). The orthophosphate was then analyzed by the Vanadomolybdophosphoric yellow color method as described by Jackson (42).

Melting reduced the NH_4 and pyrophosphate content of the APP materials (see Table 1). But it was felt that the loss of NH_4 or pyrophosphate was not extensive enough to over ride the advantages that would result from using granules containing Mn^{54} for this study.

All values in Table 1 represent the mean of three determinations.

Table 1. Influence of melting upon the composition of ammonium polyphosphate and ammonium orthophosphate

Fertilizer	NH_4 (%)	P_2O_7* (%)	PO_4* (%)
AOP - Original	15.30	.....	49.48
AOP - Melted	12.38	.....	49.48
APP - Original	18.78	31.78	27.15
APP - Melted	16.69	27.15	33.38

*Expressed as percent P_2O_5.

One millicurie of Mn^{54} as the chloride salt was used in preparing the radioactive $MnSO_4$ and MnO. A stock solution was prepared which had an activity of 7.5 X 10^5 counts per minute per ml. as measured on a Nuclear Chicago scalar-analyzer. All subsequent measurements of activity in this study were made with this instrument.

The $Mn^{54}SO_4$ was prepared by adding 35 ml. of the stock solution to each of two 250 ml. beakers and two 100 ml. widemouth glass bottles. Non radioactive $MnSO_4 \cdot H_2O$ (0.6153 g.) was also added to each of the two beakers and two bottles. The containers were then placed on a hot plate and the solutions evaporated to dryness.

Radioactive MnO was prepared by adding 268 ml. of the Mn^{54} stock solution to a 500 ml. Erlenmeyer flask along with 5.7354 g. nonradioactive $MnCl_2 \cdot 4H_2O$. The Mn present in the resulting solution was precipitated as $MnCO_3$ by the addition of 20 ml. 0.2F Na_2CO_3 solution. The $MnCO_3$ was collected on a Buchner funnel and immediately transferred to a combustion boat which was inserted into an electric furnace. The $MnCO_3$ was roasted to MnO at a temperature of 150-250°C under a continuous stream of N_2. Completion of the roasting, which was indicated by a darkening of color and freedom from effervescence when tested with dilute HCl, was found to require at least 24 hours.

The incorporated Mn fertilizers were prepared by adding 10 g. of either APP or AOP to 250 ml. beakers containing either $Mn^{54}SO_4$ or $Mn^{54}O$. The materials were then melted over a Meker type burner, while stirring continuously to ensure an even distribution of the Mn materials. When the melting was complete the molten materials were poured on to pyrex plates and allowed to cool. In the case of the APP materials, it was found necessary to continue stirring after heating had been completed--otherwise the material would not crystalize. After solidification, the material was transferred to a mortar and crushed into fragments with a pestle, and screened to size by use of No. 5 and 10 mesh seives.

The coated materials were prepared by adding 5 g. of either APP or AOP granules to 100 ml. glass bottles containing either $Mn^{54}SO_4$ or $Mn^{54}O$. The phosphate granules introduced to the glass bottles had been treated in the same manner as the incorporated granules in regards to melting, crushing, grinding and screening. A small quantity of water was sprayed into each bottle and the contents were mixed with a glass stirring rod. The bottles were then placed in a drying oven to complete the coating process.

Migration Studies

The soil in which the movement of Mn was observed, was a Hodunk sandy loam secured from the soils farm at Michigan State University. The pH of this soil was 5.8; its exchangeable and easily-reducible Mn content were 16 ppm and 68 ppm, respectively.

In preparation for the migration studies, the soil was ground and screened through a two millimeter mesh seive and then brought to a moisture content of 14% (oven dry weight basis) by repeated spraying and mixing. When the required amount of water had been added, the soil was placed in a plastic bag and allowed to equilibrate in a constant temperature room (20^oC) for one to two days. Samples were then taken to check the moisture content.

The containers used in this study were cylindrical ice cream cartons 8.58 by 8.58 cm. A two cm. horizontal slice was cut from the center of each carton. This slice was then fastened on to the bottom portion of the carton with masking tape. The bottom portions of the cartons with the attached two cm. slice were filled with moist soil by adding approximately a one cm. layer of soil, tapping the carton on the lab bench several times and then placing a two kilogram weight on the soil surface. This method of packing yielded a carton of soil with a bulk density of 1.40 g./cc. on an oven dry weight basis. When the bottom portion of the carton was completely filled with soil, a cardboard disc with a seven mm. opening in the center was placed on the soil surface. The cardboard disc was marked at two places on its circumference and matching marks were made on the side of the carton so that an identical alignment could be made at a later date. A core of soil seven mm. in diameter and one cm. in depth was removed from the center of the carton by pushing a cork borer through the opening in the center of the cardboard disc. A fertilizer granule of known mass and activity[1] was then placed in the opening, the core of the soil was replaced, the top half of the carton was attached to the bottom half with masking tape and filled with moist soil in an identical manner as the bottom half. The cartons were then weighed, sealed in a plastic bag and then placed in a constant temperature room (20°C) to incubate for three days, one, two, four and six weeks.[2]

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[1] The granules used in the migration studies had a mean weight of 50.8 mg. and a mean activity of 119,168 counts/minute.

[2] Each time interval and type of fertilizer was replicated four times.

Upon completion of the desired time interval, the cartons were weighed to check for moisture loss and then sampled to determine Mn movement by removing the tape securing the top portion and slicing off the top portion of the soil core with a piece of light gauge sheet metal. The original cardboard disc was placed on the soil surface and aligned with the marks on the side of the carton that had been made when the granule was placed in carton of soil. A core of soil, 1.0 cm. in diameter and two cm. in depth and containing the fertilizer granule was removed with a cork borer. This core of soil was placed in a two ml. plastic beaker and its activity determined.[3] The remainder of the soil core was sampled by placing a set of concentric rings composed of metal strips, two centimeters in depth and soldered in positions of radii of one, two, three, and four cm. over the center of the soil core. The rings were then pushed through the soil. The tape attaching the two cm. slice to the bottom portion of the carton was removed and the two centimeter soil slice was removed with a piece of light gauge sheet metal. The soil was then removed from each ring and mixed in a plastic bag. Samples of soil were taken from the plastic bags and the amount of exchangeable and easily-reducible Mn due to the fertilizer were determined.

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[3] The counting efficiency was determined by comparison with granules of known activity that were placed in moist soil and counted.

Exchangeable Mn was determined by weighing five g. of soil (air dry basis) from each ring and placing it in a 125 ml. Erlenmeyer flask along with 50 ml. 1.0 N NH_4OAc, pH 7.0. The flasks were allowed to stand for six hours, being shaken mechanically every other hour. The extracts were filtered through Whatman # 2 filter paper into 100 ml. beakers (94). The beakers were placed on a hot plate and the filtrates evaporated to approximately 10 to 15 ml. The filtrates were then added to 25 ml. volumetric flasks and made to volume with distilled water. A two ml. portion was counted to determine the activity of Mn^{54}.[4]

Easily-reducible Mn was determined by returning the filter paper and soil to the original flask used in the exchangeable Mn determination. Fifty ml. of 1.0 N NH_4OAc containing 0.2 percent hydroquinone, pH 7.0 was added to each flask. The flasks were shaken for 30 minutes on a mechanical shaker and then for 30 minutes every other hour over a six hour period (94). The samples were treated in the same manner as the exchangeable Mn in regards to filtration, evaporation and counting activity.

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[4] The mean of three one minute counts minus the background activity was taken as the activity of Mn^{54} in the sample.

Dissolution Studies

The dissolution studies of the fertilizer granules were conducted by controlled leaching. The procedure used involved leaching granules of known mass and activity[5] at a constant rate. This was accomplished by seating a Whatman # 40 filter paper into a short-stemmed glass funnel. The funnel was supported in position by a screw clamp attached to a ring stand. The flow of water into the funnel was controlled by adjusting the stop cock of a 250 ml. separatory funnel positioned immediately above the glass funnel. The flow of water out of the funnel was regulated by means of a screw clamp attached to a section of plastic tubing connected to the glass funnel. The flow of water through the glass funnel was adjusted to 10 ml. in five minutes with a constant volume of approximately five ml. remaining in the funnel. A stop watch and an appropriate graduated receiver were used to achieve the desired flow rate. When all adjustments had been made, a fertilizer granule of known mass and activity was placed in the glass funnel. Ten ml. portions of the leachate were collected until measurement of activity indicated that no Mn^{54} was being given off or until a total of 25 ten ml. portions had been collected. Two ml. samples were used to determine the Mn^{54} content of each 10 ml. fraction.

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[5] The fertilizer granules used in the dissolution studies had a mean weight of 52.9 mg. and a mean activity of 103,675 counts/minute.

The results obtained by the leaching procedure may be open to question in regards to their agronomic significance. That is, will the behavior of the granules in regards to dissolution of manganese when they are placed in the soil, be identical to the behavior that was observed during the leaching procedure.

In order to determine the relationship between dissolution by leaching and actual dissolution of manganese from the fertilizer granules in the soil, soil dissolution experiments were conducted over time intervals ranging from 4 to 24 hours. Fertilizer granules of known mass and activity were placed in petri dishes (100 X 10 mm.) containing the same type of soil at the same moisture level and packed to the same bulk density as used in the migration studies. The fertilizer granules were placed in the soil by using a cork borer to remove a plug of soil five by five mm. into which the granules were placed. The core of soil was replaced; the petri dishes were sealed in plastic bags and allowed to incubate in a constant temperature room. At the end of the desired time interval, the granules were recovered by removing them in a core of soil with the aid of a cork borer. The cork borer used in recovering the granules had a slightly larger diameter than the original one used to place the granules in the soil. This was so as not to slice through the granule. The soil was then carefully removed from around the granule by use of a spatula and small brush. The activity of Mn^{54} remaining in the granule was determined and compared with the activity of the granule prior to being placed in the soil. No great difficulty was experienced in recovering the granules that had incubated in the soil for four hours. But, the granules that had remained in the soil for eight, sixteen, and twenty-four hours had undergone disintegration to the extent that they were not recoverable.

Phosphate-Soil Incubation Studies

Blank incubation studies were conducted in order to determine the influence of APP and AOP fertilizers upon the level of exchangeable and easily-reducible Mn present in the soil used in the migration studies. Cartons of soil were prepared in the same manner as they had been in the migration studies. A 50 mg. granule of APP or AOP was placed in the center of each core. The cartons were allowed to incubate in a constant temperature room (20°C) for periods of one, two, four, and six weeks. Duplicate samples were prepared for each time interval and P fertilizer. The cartons were sampled and analyzed for exchangeable and easily-reducible Mn in the same manner as was done in the migration studies. In this case the Mn was determined on a Perkins-Elmer Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Phosphate-Soil Incubation Studies

The results of the phosphate-soil incubation studies are listed in Table 2. The concentrations of exchangeable and easily-reducible Mn in the four radial segments after one and six weeks incubation of AOP and APP fertilizers, are illustrated in Figure 1.

Considering all four radial segments there was a tendency for exchangeable Mn to decrease as the incubation period extended from one to six weeks. This is in agreement with the observations of several researchers (11, 22, 23, 31, 46, 89), who have noted that the exchangeable Mn of an air-dried soil decreases when the soil is moistened and incubated.

The presence of APP and AOP was marked by an initial increase in the level of exchangeable Mn in the moist, incubated soil over that of the soil when air-dried. This effect was largely limited to the one cm. radial segment. As the length of the incubation period increased, the level of exchangeable Mn in the one cm. radial segment decreased. However, at any one time over the six weeks incubation period, the exchangeable Mn present in the one cm. radial segment was greater than the amount present in the two, three or four cm. radial segment.

Table 2. Influence of ammonium poly- and orthophosphates on soil exchangeable and easily-reducible Mn.

		Radial Segment							
		One Centimeter		Two Centimeter		Three Centimeter		Four Centimeter	
Fertilizer	Time	Exch.	E.-Red.	Exch.	E.-Red.	Exch.	E.-Red.	Exch.	E.-Red.
	weeks	ppm Mn							
APP	1	27	64	10	79	8	79	8	82
AOP		22	64	10	77	8	79	8	80
APP	2	16	52	8	62	4	66	4	66
AOP		10	56	7	62	5	66	4	70
APP	4	13	58	6	66	3	69	2	79
AOP		8	59	4	70	5	71	2	68
APP	6	18	66	8	78	4	80	4	79
AOP		10	71	7	76	4	76	4	75

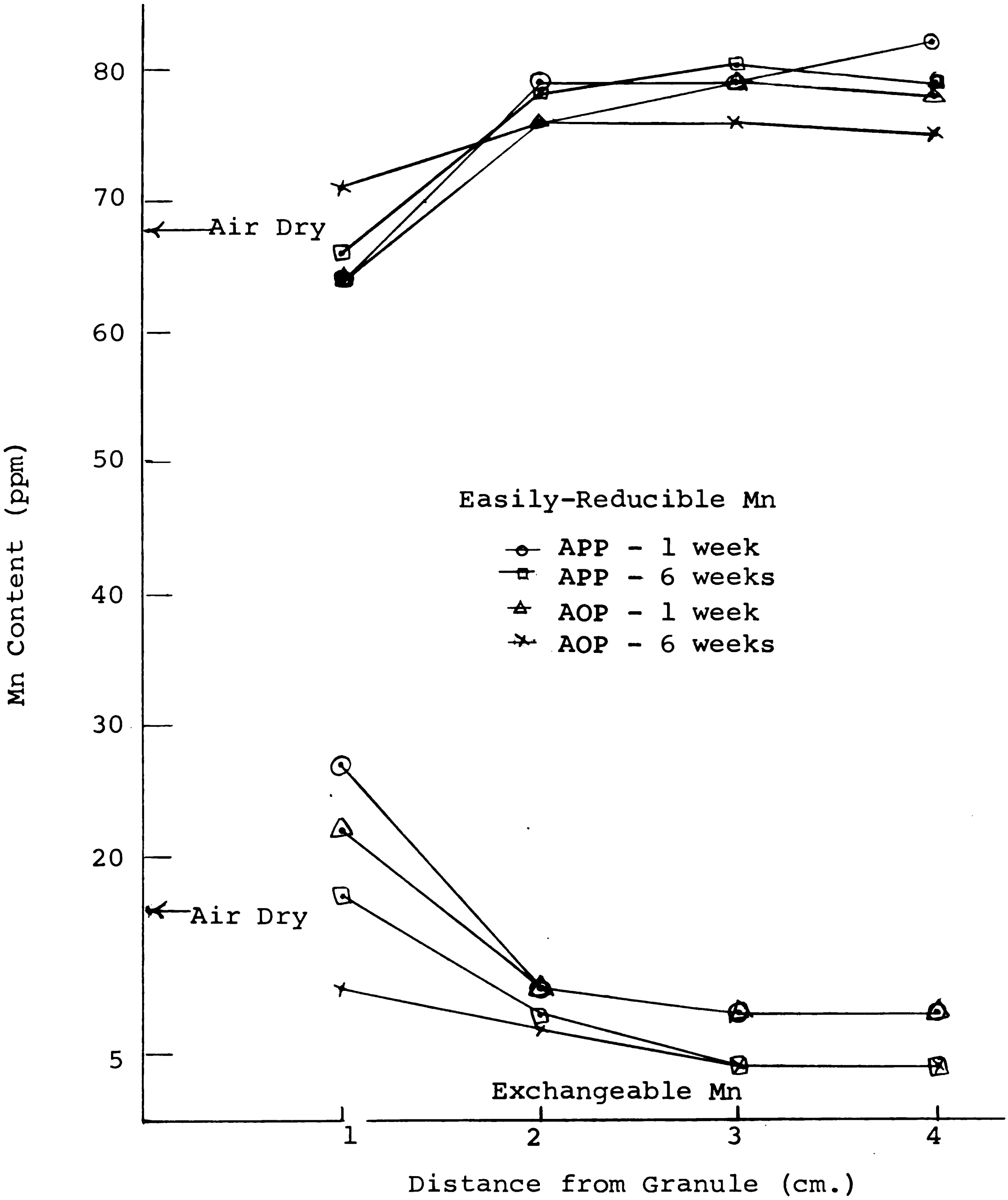

Figure 1. Influence of APP and AOP on soil exchangeable and easily-reducible Mn.

The increased level of exchangeable Mn present in the one cm. radial segment is accompanied by a decrease in the easily-reducible Mn. This would suggest that the increase in exchangeable Mn is due to the reduction of the easily-reducible Mn fraction. This reasoning follows that of several researchers (50, 51, 57) who felt that the increase in soil exchangeable Mn in the vicinity of P fertilizers occurred as a result of reduction of higher Mn oxides (valency greater than two) in response to a pH decrease brought about by the hydrolysis of the P fertilizer in the soil.

However, in this study, a factor in addition to, or other than pH appeared to cause the exchangeable Mn to increase in the vicinity of the P fertilizer. This is because the pH of an aqueous suspension of APP granules was 5.5, the pH of an aqueous suspension of AOP granules was 3.4. If the pH relationship between the two fertilizers remained the same when placed in the soil and a pH decrease was solely responsible for the increase in exchangeable Mn, then it would be expected that the AOP fertilizer would cause the greatest increase in exchangeable Mn. But in this study, the APP was found to be more effective in increasing or maintaining the level of exchangeable Mn than AOP.

It may be that the AOP fertilizer causes an increase in exchangeable Mn through a pH decrease, while APP fertilizer brings about an apparent increase in the exchangeable

Mn since its pyrophosphate portion may form soluble complexes with the trivalent Mn of the easily-reducible Mn. Such a complex might be of the type $[Mn(H_2P_2O_7)_3]^{-3}$. A complex such as the latter was found by Lingane and Karplus (58) to exist in solution between pH 4 and 7. Heintz and Mann (35) postulated that a trivalent Mn-pyrophosphate complex would exist in the soil at pH values below 7.0. Furthermore they used pyrophosphate solutions to extract easily-reducible Mn from soils with a fair amount of success.

Dissolution Studies

The results of the controlled leaching of the fertilizer granules are summarized in Table 3 and presented graphically in Figures 2 and 3. The data were interpreted by calculating the accumulated percentage of Mn^{54} originally present in the fertilizer granule that was removed by a given volume of water. Rate of release as well as total Mn^{54} released may be seen in Figures 2 and 3.

The amount of Mn removed from the various fertilizers by leaching with H_2O ranged from a high value of 51.2% for $MnSO_4$ coated on to AOP to a low of 10.6% for MnO coated onto AOP.

The leaching curves of the fertilizer granules were characterized by relative large amounts of Mn being initially released, followed by a decreasing rate of Mn release until no Mn was detectable in the leachate.

Table 3. Results of controlled leaching of fertilizers

Fertilizer*	Mn Released		H_2O Required to Effect Release
	%	Rank**	ml
APP-S-I	16.5	7	180
APP-S-C	25.0	5	220
APP-O-I	35.3	3	180
APP-O-C	36.5	2	100
AOP-S-I	34.9	4	140
AOP-S-C	51.2	1	100
AOP-O-I	22.2	6	240
AOP-O-C	10.6	8	120

*APP-Ammonium Polyphosphate; AOP-Ammonium Orthophosphate; S-Manganese Sulfate; O-Manganese Oxide; C-coated; and I-Incorporated.

**Ranked in order of % Mn released.

The amount of leaching required to remove all of the H_2O-soluble Mn varied from 100 ml. for $MnSO_4$ coated onto AOP to 240 ml. of H_2O for MnO incorporated into AOP.

The three fertilizer granules which released the greatest amount of Mn upon leaching with H_2O, also exhibited a very rapid release of Mn. The granules consisting of $MnSO_4$ coated onto AOP released 51.2% of their Mn content in response to leaching; of this amount 84% was released during the first 20 ml. of leaching. The APP coated with MnO, which yielded 36.5% of its Mn upon leaching, released 76% of this amount during the first 20 ml of leaching. The APP

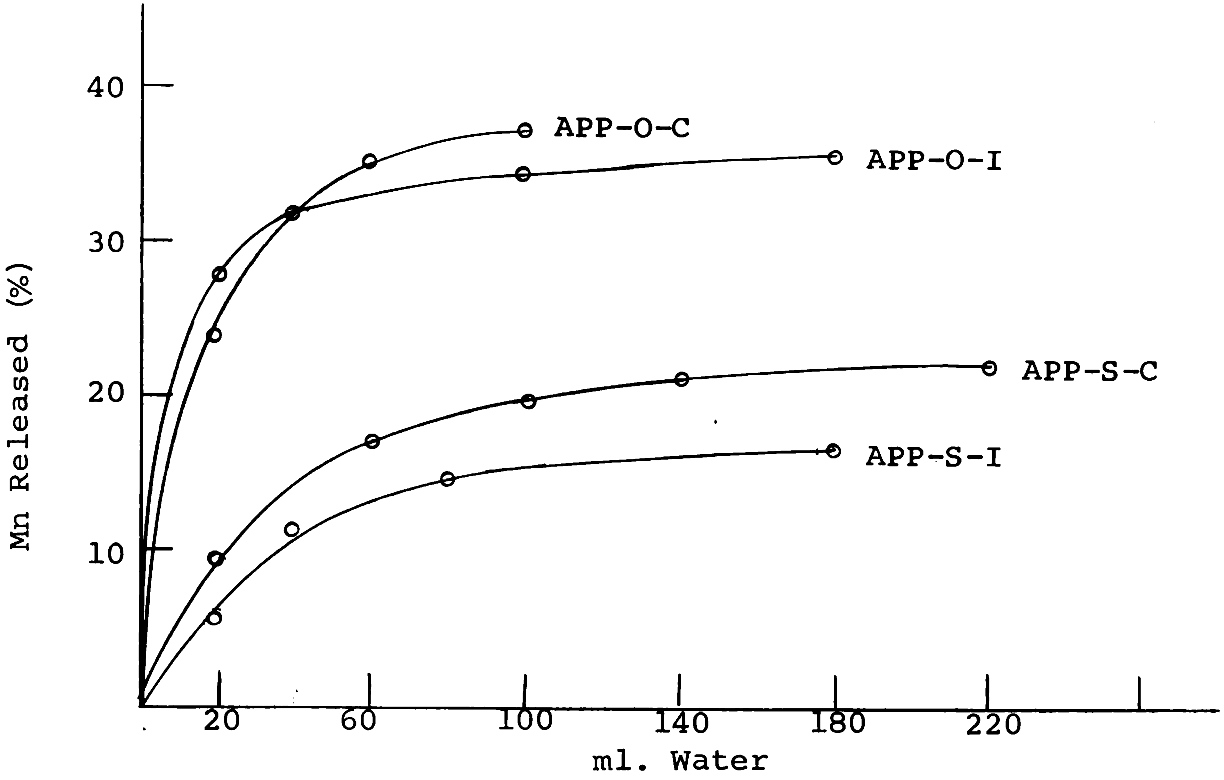

Figure 2. Accumulated percentage of Mn^{54} released from APP.

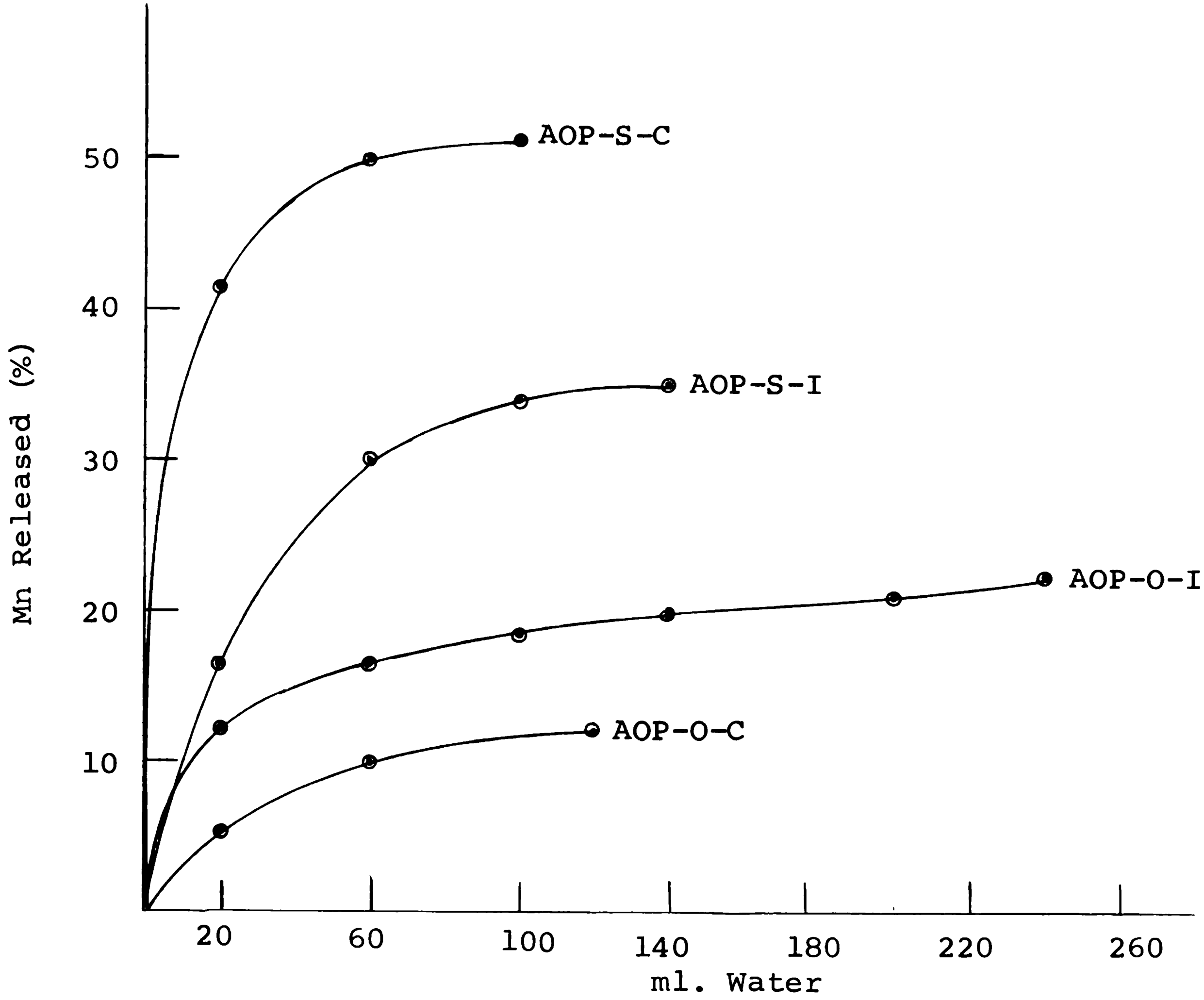

Figure 3. Accumulated percentage of Mn^{54} released from AOP.

incorporated MnO fertilizer, which released 35.3% of its Mn, released 68% of this amount in the first 20 ml. of leaching. The rapid initial release of Mn for these three materials is reflected in the initial steep slopes of their respective leaching curves.

With the particular fertilizer granules investigated in this study, there are essentially three characteristics or properties of the fertilizer granules which might influence the amount of Mn that the granules would release upon leaching. These properties are the type of phosphate compound, the type of Mn carrier and the method by which the Mn is added to the fertilizer granule.

From the order of H_2O-Mn content of the fertilizer granules listed in Table 3, it appears that the amount of H_2O-soluble Mn present in any one type of fertilizer is more influenced by the particular combination of phosphate compound, Mn carrier and the method of addition of Mn, rather than being singularly influenced by any one of these three factors. For example, the suitability of adding Mn compounds to APP in comparison to the adding of Mn compounds to AOP appears to depend upon the nature of the Mn compound added to the APP. The combination of MnO and APP seems to be more effective in releasing Mn than the combination of MnO and AOP. But on the other hand, the combination of $MnSO_4$ and AOP released more Mn than the combination of $MnSO_4$ and APP.

Previous investigations[1] have also indicated that combinations of MnO and APP release a greater amount of H_2O-soluble Mn than a combination of MnO and AOP. Likewise, it was observed that $MnSO_4$-AOP is superior to $MnSO_4$-APP in H_2O-soluble Mn content. The explanation that was given for the superiority of MnO-APP over MnO-AOP was that the sequestering properties of the APP held the MnO in a more soluble form.

If the sequestering or chelating property of APP is responsible for the greater release of Mn when MnO is added, then it would seem that the same action would occur when $MnSO_4$ is added--that is the APP-$MnSO_4$ fertilizer would release more Mn than the AOP-$MnSO_4$ fertilizer. However, in this study and others,[2] $MnSO_4$ in combination with APP has been found to yield less H_2O-soluble Mn than $MnSO_4$ in combination with AOP. There could be two possible explanations for this behavior of $MnSO_4$-APP. Since $MnSO_4$ is readily soluble in H_2O while MnO is only sparingly soluble in H_2O, but soluble in dilute acids; $MnSO_4$ may undergo chelation by APP more readily than MnO and in the process form a more stable chelate complex which releases Mn slowly. Or perhaps $MnSO_4$, due to its greater solubility, forms a precipitate with the

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[1] Personal Communication. Fundamental Research Branch, Tennessee Valley Authority. Wilson Dam, Tennessee.

[2] Ibid.

pyrophosphate fraction of the APP. Such a manganous pyrophosphate ($MnH_2P_2O_7$) precipitate does form in the test tube in the moderately acid pH range. Whatever the reason for the reduced solubility of $MnSO_4$ in combination with APP it appears that the greater the contact of $MnSO_4$ with the APP, the greater is the reduction in the amount of H_2O-soluble Mn. In this study when $MnSO_4$ was coated onto APP granules, one and a half times as much Mn was released upon leaching as was when the $MnSO_4$ was incorporated into the APP.

The greater content of H_2O-soluble Mn, indicated by the results in this study, present in a $MnSO_4$-AOP fertilizer over that of a MnO-AOP combination is probably due to the greater solubility of the $MnSO_4$.

All of the Mn-P combinations used in this study with the exception of the $MnSO_4$-APP compounds gave up their H_2O soluble Mn at a faster rate when the Mn compounds were coated onto, rather than incorporated into the granule. This was evident from the lesser amount of leaching required to remove the H_2O-soluble Mn from the coated materials. From physical considerations this is not surprising.

The $MnSO_4$-APP coated materials may have required a larger amount of leaching to remove their H_2O-soluble Mn than the incorporated counterpart, because of the procedure that was used to coat the $MnSO_4$ on to the granules. The granules were coated by spraying H_2O into a glass bottle containing appropriate amounts of $Mn^{54}SO_4$ and APP granules.

Both of these materials are H_2O-soluble, at least moreso than their counterparts--MnO and AOP. Hence in this case a more intimate association of the Mn and P compound may have occurred--moreso than would be desired when coating APP with $MnSO_4$.

Coating of the manganese compound onto the fertilizer granules in this study substantially increased the amount of Mn released upon leaching in two cases, slightly increased the amount of Mn released in another case and in one particular case appeared to substantially decrease the amount of H_2O soluble Mn that was released.

Both APP-$MnSO_4$ and AOP-$MnSO_4$ fertilizers gave up a much larger amount of Mn upon leaching when the $MnSO_4$ was coated onto the granule then when it was incorporated. In the case of the APP, coating probably resulted in a greater release of Mn in that contact of the APP with the $MnSO_4$ which may act so as to reduce the availability of Mn, is decreased. The benefits of coating $MnSO_4$ onto AOP may be the same as that with the APP materials--that is, there is less opportunity for the constituents of the granule to react with the Mn in such a way as to render it less soluble. However, if this is indeed the case with the coating of $MnSO_4$ onto AOP granules, then such combinations that may occur must be weaker than those formed by the APP and $MnSO_4$ as both the incorporated and coated AOP-$MnSO_4$ fertilizers yielded twice as much Mn upon leaching as their respective counterparts of AOP and $MnSO_4$.

In the case where coating decreased the amount of Mn released--the AOP-MnO fertilizer in comparison to the incorporation of the MnO, it may be that incorporation enhanced the solubility of the MnO. As mentioned earlier, MnO is sparingly soluble in H_2O, but soluble in dilute acids. AOP was found to yield an acid reaction when dissolved in water. Hence during the leaching process, the combination of H_2O, the accompanying acid reaction of the orthophosphates and the greater contact of the MnO with the AOP fertilizer as a result of incorporation, may have brought about an increased solubility of MnO.

The results of the soil-dissolution studies for each of the eight types of fertilizers are listed below along with the corresponding results obtained by leaching the fertilizers.

Table 4. Comparison of soil and leaching dissolution studies

Fertilizer	Soil Mn Released	Leaching Mn Released
	%	%
APP-S-I	14.1	16.5
APP-S-C	23.0	25.0
APP-O-I	44.4	35.3
APP-O-C	49.4	36.5
AOP-S-I	59.2	34.9
AOP-S-C	77.4	51.2
AOP-O-I	27.2	22.2
AOP-O-C	13.4	10.6

A comparison of the amount of Mn released by each of the fertilizers indicates a relatively greater release from MnO-APP and $MnSO_4$-AOP or MnO-AOP when dissolution is measured by incubation in the soil rather than by leaching. In the case of MnO-AOP or $MnSO_4$-AOP incorporated materials, this increase was great enough to cause a change in the order of the amount of Mn released by the fertilizers as determined by leaching. However, the relationships between the type of phosphate compound, Mn compound and method of addition of Mn in regards to the release of Mn remained essentially the same for both methods.

Migration Studies

The migration studies were evaluated by four determinations for each particular type of fertilizer granule: (1) the concentration of total fertilizer Mn that had moved beyond 0.5 cm. from the granule site, (2) concentration of total Mn per radial segment as a function of time, (3) the mean movement of Mn, and (4) concentration of Mn as a function of distance at a given time. Also a migration study was conducted in which $Mn^{54}Cl_2$ solution replaced a Mn^{54}-fertilizer granule as the source of Mn.

The total concentration of Mn used in the evaluation of the migration studies was taken as the sum of the exchangeable and easily-reducible Mn. Combining of the two fractions of soil Mn might be questionable in an exacting study of the mobility of Mn in the soil because undoubtedly the two fractions differ in their mobility. But in this study the primary interest is the dissolution and migration of plant available or potentially available Mn from the fertilizer materials.

Movement of Mn did not extend beyond a one cm. radius about the granule site in one-half week. At the end of one week, the fertilizer Mn was present in a two cm. radius about the granule site. By the end of two weeks, the fertilizer Mn had extended its presence to a radius of three cm. about the granule site and at the end of four weeks, the fertilizer Mn reached the maximum distance analyzed--four cm. from the granule site.

While Mn^{54} was detectable in the four centimeter radial segment, the quantity present was too small for meaningful, quantitative interpretations.

Quantitatively, the results of the migration studies indicated that the fertilizers varied with respect to the amount of Mn that moved from the granule and into the soil.

A measurement that indicated a direct relationship between the amount of Mn that moved in the soil and the magnitude of dissolution of Mn from the fertilizer granule, was the determination of the activity of Mn^{54} remaining in the soil core that was removed in order to recover the granule used in the migration study. The measurement of the activity of Mn^{54} present in this core of soil and its comparison with the activity of Mn^{54} prior to incubation in the soil, gave an indication of the amount of Mn that had moved into the soil at least to the extent of 0.5 cm. from the granule site.

The per cent of the Mn content of the fertilizer materials that had apparently moved into the soil at least beyond 0.5 cm. after six weeks is listed in Table 5. The corresponding soil-dissolution values are also listed in order that the relationship between the amount of Mn that moved and the extent of dissolution can be easily discerned.

Table 5. Apparent and actual movement of Mn beyond 0.5 cm. from the fertilizer granule after six weeks

Fertilizer	Apparent* Movement	Actual Movement	Soil Dissolution Mn^{54} Released
	%	c./m.	%
AOP-S-C	67.3	24,572	77.4
AOP-S-I	59.2	19,204	59.2
APP-O-C	45.0	14,826	49.4
APP-O-I	39.4	12,377	44.4
AOP-O-I	33.0	10,326	27.2
APP-S-C	30.2	8,949	23.0
APP-S-I	23.0	6,974	14.1
AOP-O-C	20.2	7,519	13.4

*Apparent Movement--from measurement of activity of Mn^{54} in the 0.5 cm. soil core.

The amount of fertilizer Mn found in the radial slice of soil analyzed also substantiated the relationship between the extent of dissolution and the amount of Mn present in the soil beyond 0.5 cm. The sum of the exchangeable and easily-reducible Mn^{54} present in the soil slice at the end of six weeks are listed in Table 5. The values are expressed on the basis of the values that would result if a granule with activity of Mn^{54} of exactly 100,000 counts had been used in each case.

A third indication of the relationship between the dissolution and the amount of Mn^{54} that moved from the fertilizer was observed when the amount of Mn^{54} present in the one and two cm. radial segment was plotted as a function of time. It can be seen from Figures 4, 5, 6, and 7 that for the most part the amount of Mn^{54} present in either the one or two radial segment is directly related to the relative dissolution of Mn^{54} from the fertilizer in question. That is, the relative order of the amount of Mn^{54} present in any one of the first two radial segments over the six weeks period is identical to the relative order of dissolution of Mn^{54} from the fertilizers. This relationship may also be seen in Tables 6 and 7 in which the total Mn^{54} found in each of the four radial segments is listed.

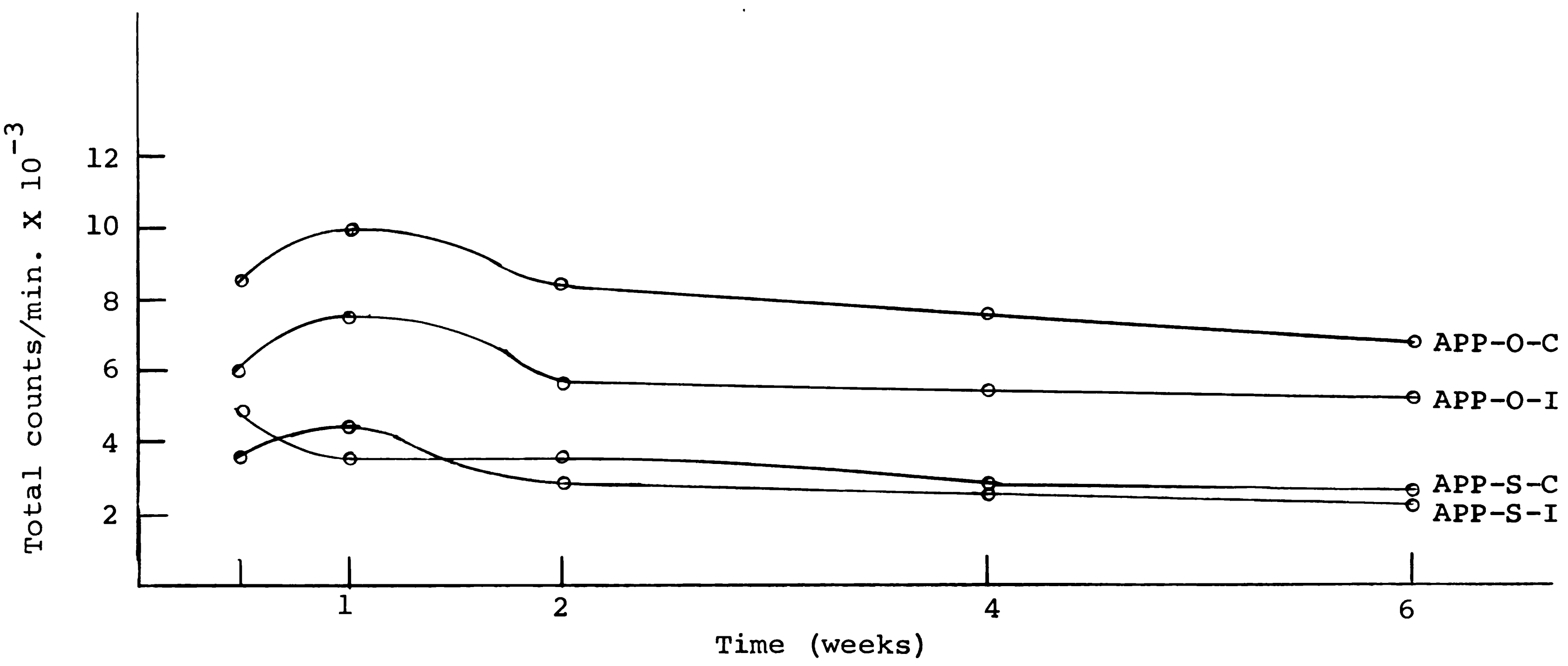

Figure 4. Concentration of Mn^{54} in one cm. radial segment - APP.

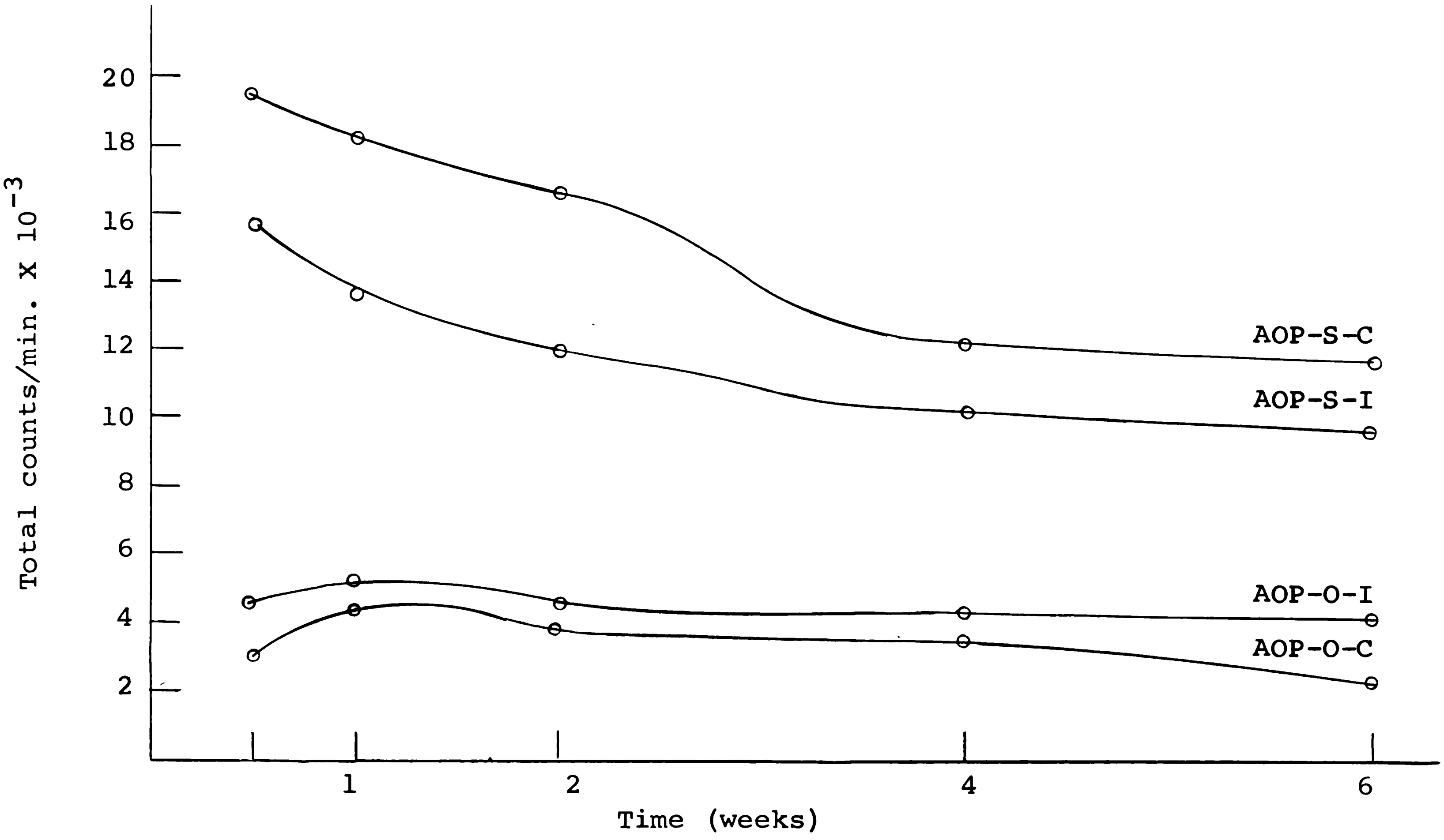

Figure 5. Concentration of Mn^{54} in one cm. radial segment - AOP.

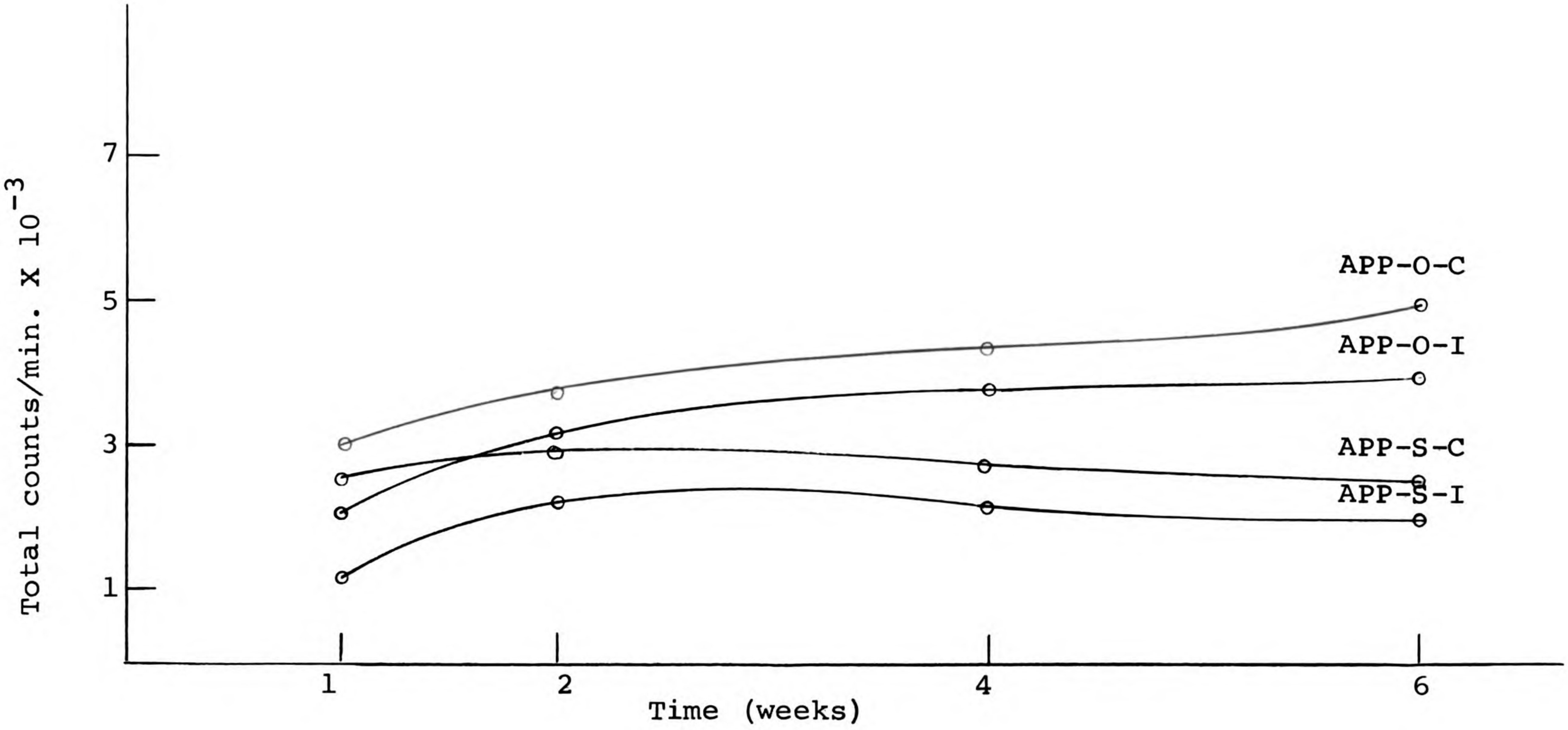

Figure 6. Concentration of Mn^{54} in two cm. radial segments - APP.

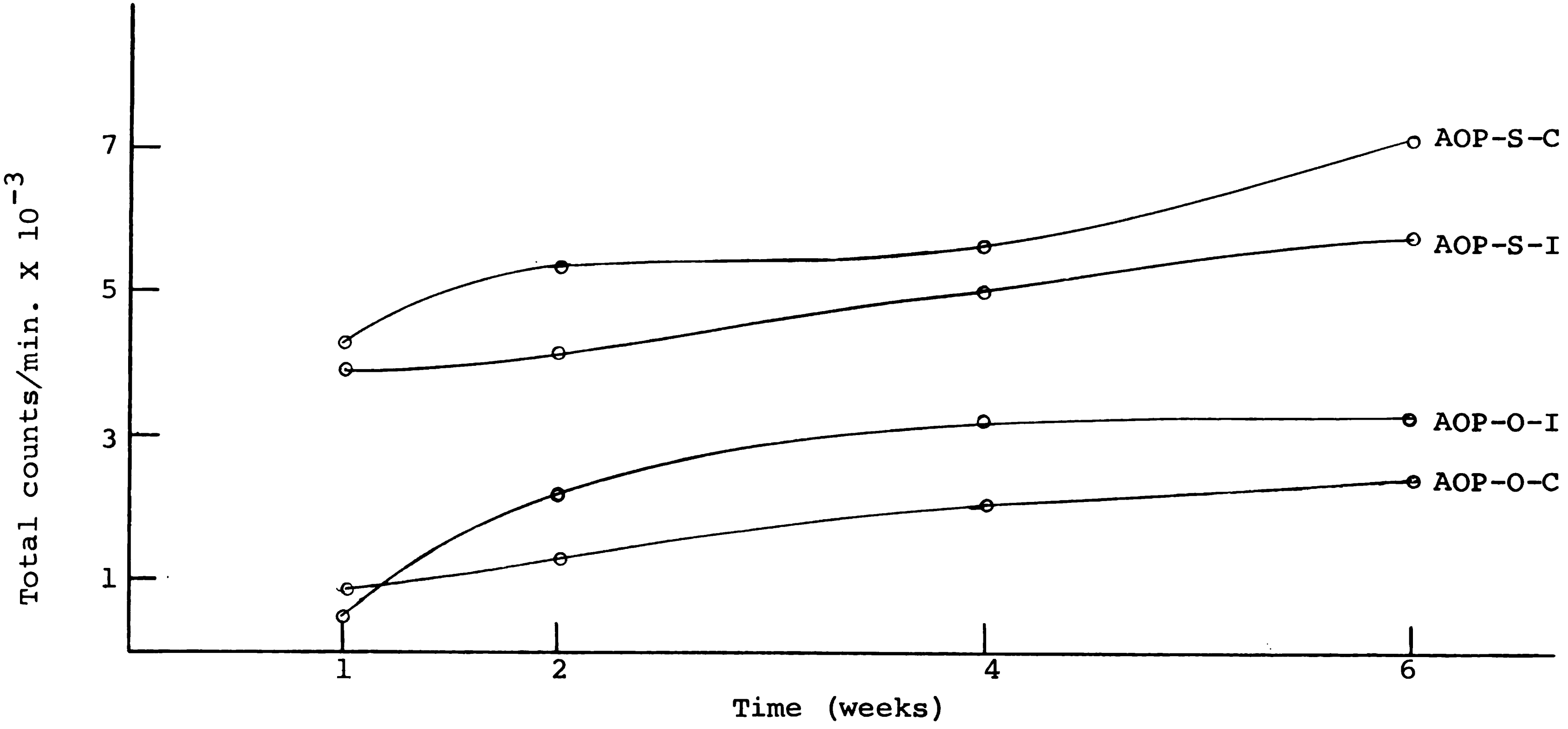

Figure 7. Concentration of Mn^{54} in two cm. radial segments - AOP.

Table 6. Total Mn^{54} in each radial segment as a function of time--APP fertilizers

Fertilizer	Time	One Centimeter	Two Centimeters	Three Centimeters	Four Centimeters
	weeks	counts/min.	counts/min.	counts/min.	counts/min.
APP-S-I	1/2	3,759			
	1	4,329	1,310		
	2	3,211	2,253	927	
	4	2,519	2,587	1,357	Detectable
	6	2,201	2,836	1,937	Detectable
APP-S-C	1/2	5,263			
	1	3,728	2,646		
	2	3,704	2,970	1,220	
	4	3,069	3,061	1,931	Detectable
	6	2,642	3,259	3,048	Detectable
APP-O-I	1/2	6,015			
	1	7,725	2,047		
	2	5,840	3,108	984	
	4	5,475	3,821	2,082	Detectable
	6	5,328	4,032	3,017	Detectable
APP-O-C	1/2	8,647			
	1	9,962	3,041		
	2	8,543	3,649	2,173	
	4	7,647	4,427	2,627	Detectable
	6	6,275	5,000	3,551	Detectable

Table 7. Total Mn^{54} in each radial segment as a function of time--AOP fertilizers

Fertilizer	Time	One Centimeter	Two Centimeters	Three Centimeters	Four Centimeters
	weeks	counts/min.	counts/min.	counts/min.	counts/min.
AOP-S-I	1/2	15,789			
	1	13,784	3,919		
	2	12,088	4,233	2,169	
	4	10,392	5,090	3,393	Detectable
	6	9,773	5,807	3,624	Detectable
AOP-S-C	1/2	19,549			
	1	15,952	6,612		
	2	13,089	8,362	1,925	
	4	12,306	8,442	3,104	Detectable
	6	11,900	8,556	4,116	Detectable
AOP-O-I	1/2	4,511			
	1	4,965	486		
	2	4,687	2,054	537	
	4	4,478	3,500	1,796	Detectable
	6	4,476	3,266	2,494	Detectable
AOP-O-C	1/2	3,383			
	1	4,486	838		
	2	3,407	1,421	817	
	4	2,819	2,064	1,027	Detectable
	6	2,253	2,491	1,448	Detectable

From the previous three observations there is substantial evidence for the existence of a direct relationship between the amount of Mn^{54} that moved into the soil for at least a distance of 0.5 cm. from the granule site and the magnitude of dissolution of Mn from the fertilizer granule. Hence it would appear that the movement of Mn was in response to a concentration gradient. That is, the greater the magnitude of dissolution, the greater the concentration gradient of Mn in the granule vicinity which results in a greater mass movement of Mn away from the granule vicinity and throughout the soil.

The relative distribution of Mn^{54} throughout the soil slice was determined by calculation of the mean movement of Mn^{54} from each of the fertilizer materials and by plotting the concentration of Mn^{54} per g. soil as a function of distance at the end of six weeks. The latter may be seen in Figures 8 and 9.

The calculation of the mean movement allowed a comparison of the movement of Mn^{54} from the eight fertilizers which differed in dissolution of Mn. The term "mean movement" was originally used by Bates and Tisdale (3) and was modified by Mordvedt and Osborne (73) to:

$$\text{Mean Movement} = \sum \frac{\text{\% Recovery of Mn/radial segment X Distance (cm.)}}{100}$$

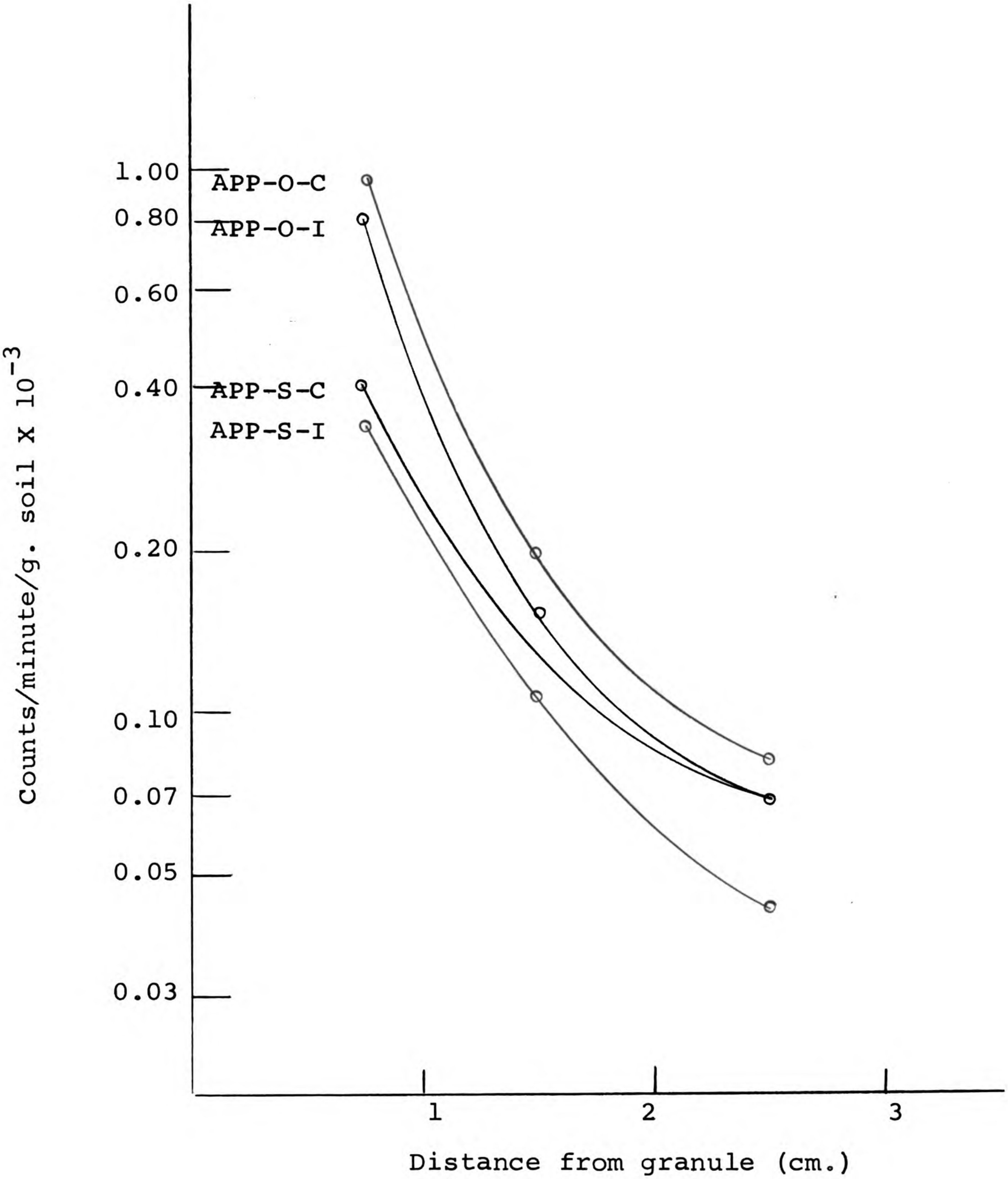

Figure 8. Mn^{54} concentration in the soil around APP granules at six weeks.

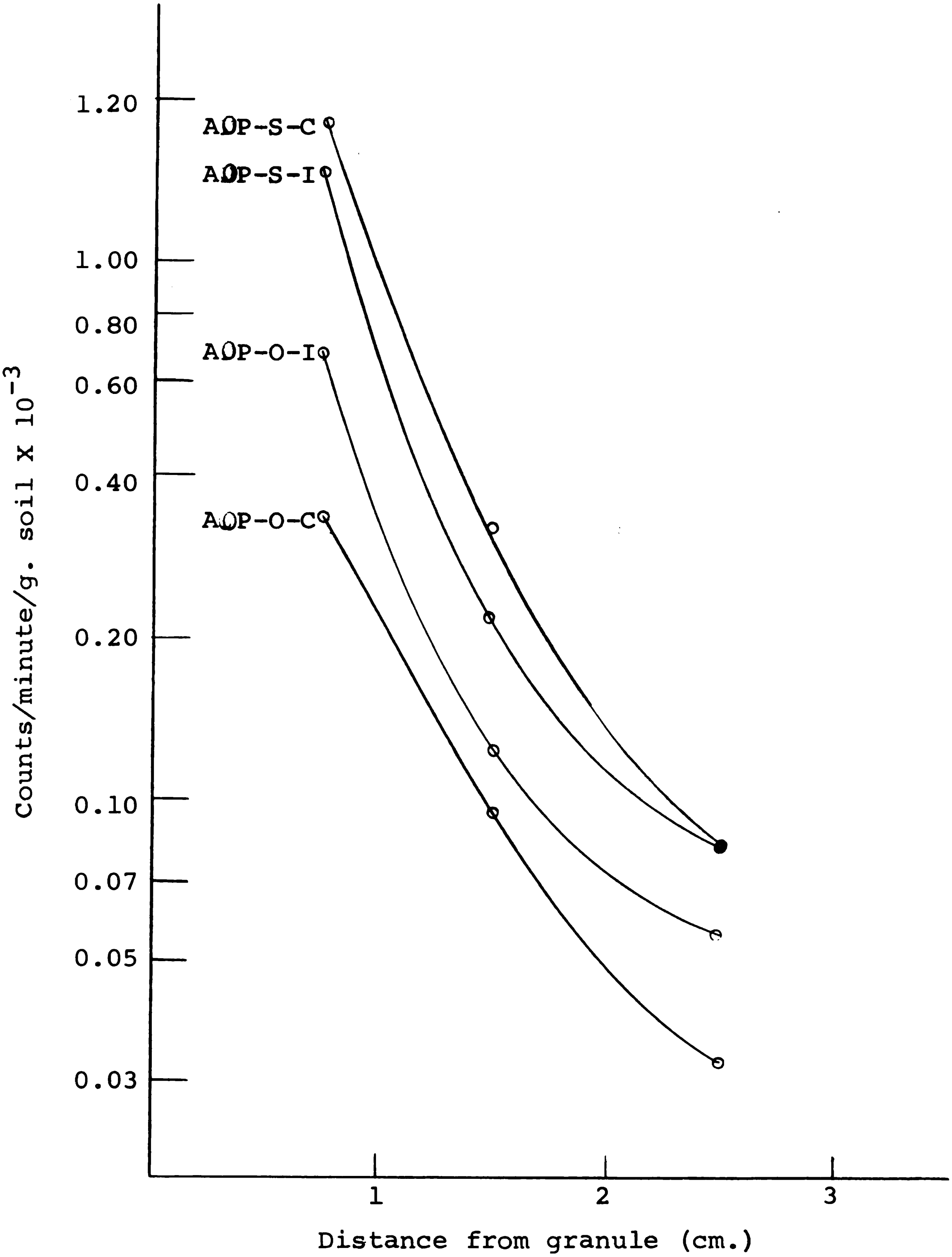

Figure 9. Mn^{54} concentration in the soil around AOP granules at six weeks.

This definition assumes that all of the Mn^{54} in any one radial segment of soil surrounding the granule site can be described as the mid-point of that segment.

The mean movement values for the fertilizer materials at the end of six weeks are listed below in Table 8. Figures 10 and 11 give the mean movement of Mn^{54} from the fertilizer materials as a function of time.

Table 8. Mean movement of Mn^{54} from fertilizer granules at six weeks

Fertilizer	Mean Movement Mn^{54} cm.
APP-S-I	1.54
APP-S-C	1.62
APP-O-I	1.42
APP-O-C	1.45
AOP-S-I	1.31
AOP-S-C	1.31
AOP-O-I	1.40
AOP-O-C	1.46

Upon examining Figures 10 and 11, it appears that there is little if any consistent significant difference among the eight fertilizers with respect to the mean movement of Mn^{54}.

To determine if any of the three fertilizer characteristics would influence the mean movement of Mn^{54}, the mean movement values for coated versus incorporated Mn fertilizers, the APP versus the AOP and the $MnSO_4$ versus the

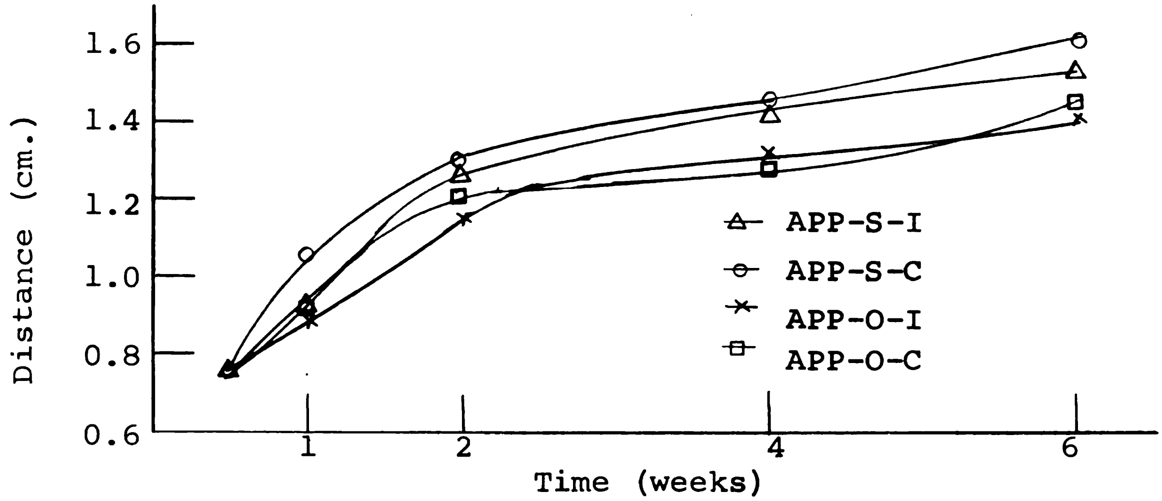

Figure 10. Mean movement of Mn^{54} from Mn-APP fertilizers.

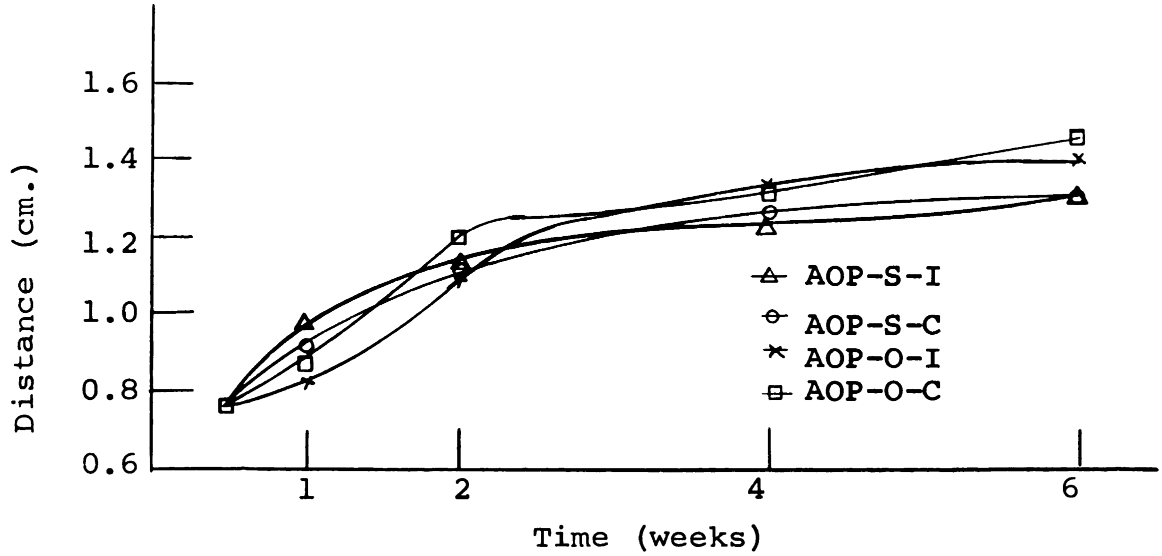

Figure 11. Mean movement of Mn^{54} from Mn-AOP fertilizers.

MnO fertilizers were calculated and plotted in Figures 12, 13, and 14. The method of addition of Mn to the fertilizer and the type of Mn compound added in this study appear to have no significant influence on the mean movement of Mn. However, in Figure 14 it is seen that the mean movement of Mn from the APP fertilizers is consistently greater than from the AOP fertilizers. This could be due to the APP fertilizers having a greater proportion of Mn^{54} in the soil surrounding them as exchangeable Mn--a more mobile form than easily-reducible Mn. That the APP fertilizers would be characterized by a higher proportion of exchangeable Mn^{54} follows from the results of the phosphate-soil incubation studies, in which it was found that the APP fertilizers either increased or maintained the soil exchangeable Mn at a higher level than did the AOP fertilizers.

The results of the migration study in which $Mn^{54}Cl_2$ solution was used as the source of Mn rather than a fertilizer granule are listed in Table 9. The amount of Mn^{54} and the distance that Mn^{54} moved through the soil are both greater than that observed for the fertilizer granules. This undoubtedly is a consequence of the greater availability of Mn. It is also observed from Table 9 that the movement of Mn through the soil is largely due to the exchangeable Mn fraction. This is evident in that the outer-most radial segment which contains Mn^{54} at the end of one-half, one or two weeks has a greater proportion of exchangeable Mn than

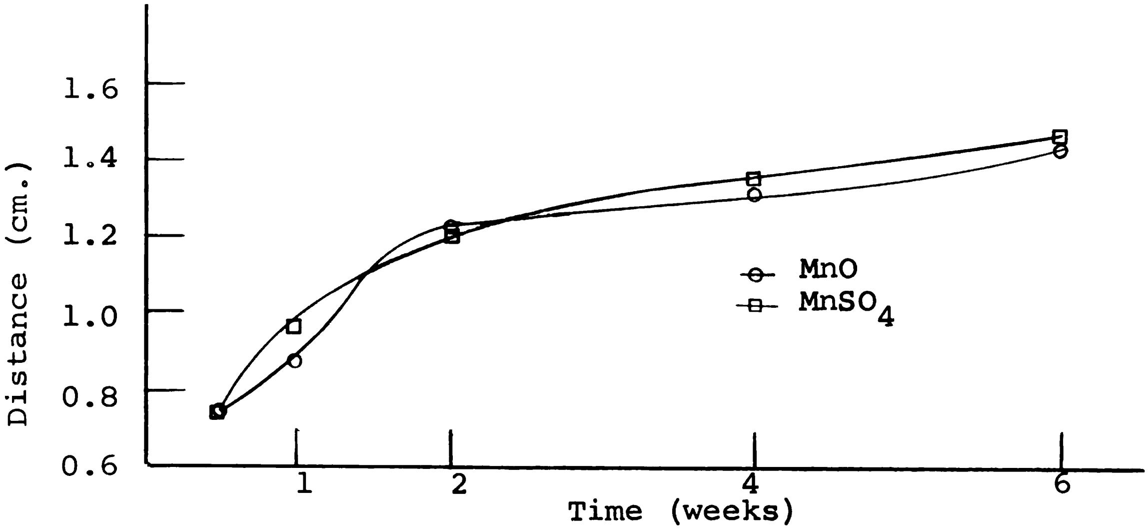

Figure 12. Mean movement of Mn^{54} from MnO versus $MnSO_4$ fertilizers.

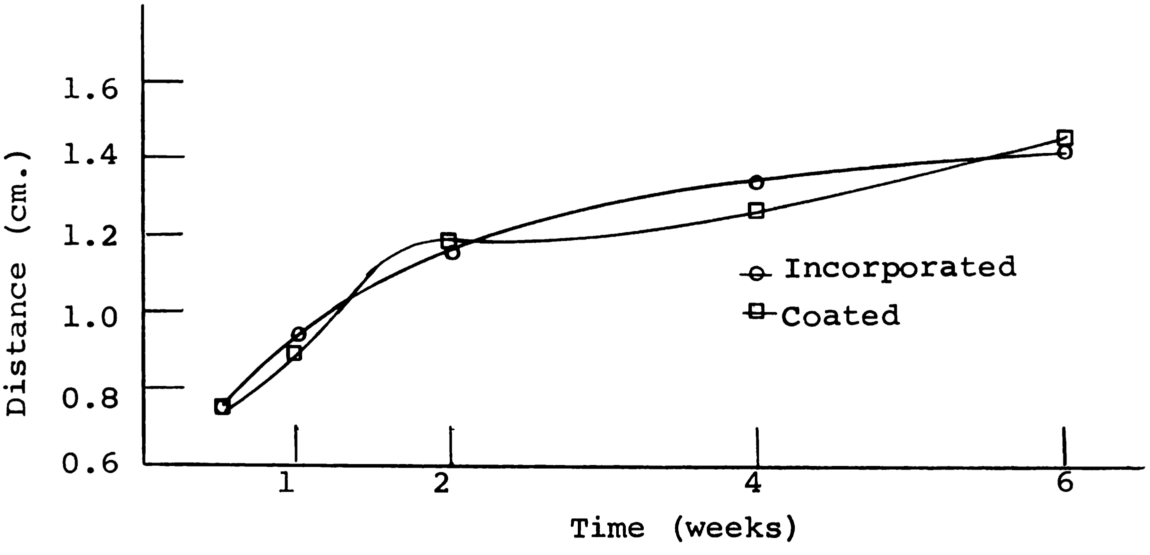

Figure 13. Mean movement of Mn^{54} from coated versus incorporated fertilizers.

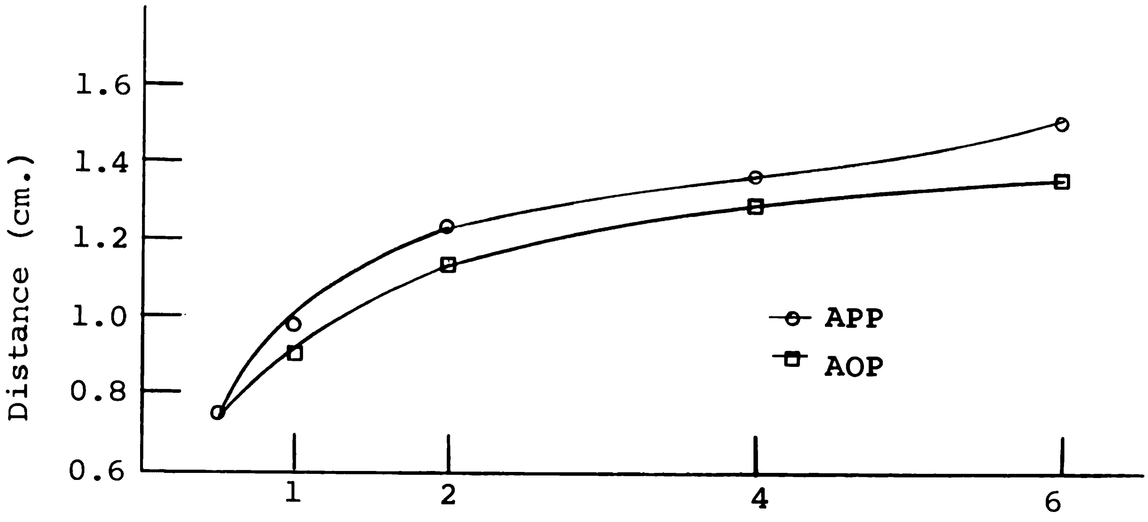

Figure 14. Mean movement of Mn^{54} from APP versus AOP fertilizers.

Table 9. Summary of Mn soil migration utilizing $Mn^{54}Cl_2$ solution*

			Radial Segment							
			1 Centimeter		2 Centimeters		3 Centimeters		4 Centimeters	
Time	Apparent** Movement	Actual Movement	Exch.	E.-Red.	Exch.	E.-Red.	Exch.	E.-Red.	Exch.	E.-Red.
weeks	%	counts/min	counts/min.		counts/min.		counts/min.		counts/min.	
1/2	83.8	35,574	15,500	16,603	2,532	939	.....	.....	.....	.....
1	86.0	35,829	4,476	23,611	4,003	780	2,959	.....	.....	.....
2	86.6	37,434	1,693	25,331	1,328	5,800	.....	3,550	Detectable	

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*Based on 100,000 counts/minute original soil source.

**Determined from activity remaining in 0.5 cm. soil core.

the prior radial segments. Table 9 indicates a rapid decrease in the level of exchangeable Mn as time progresses and a corresponding increase in the level of easily-reducible Mn. In the one cm. radial segment the easily-reducible Mn^{54} constitutes 51.6% of the total Mn^{54} present after one-half week incubation. After two weeks, the level of easily-reducible Mn had increased to 93.7%. This pronounced increase in the proportion of Mn^{54} present as the easily-reducible form is not necessarily observed when a fertilizer granule was used as the source of Mn.

The per cent easily-reducible Mn^{54} present in the one cm. radial segment for each of the eight fertilizers as a function of time is illustrated in Figures 15 and 16. The per cent of easily-reducible Mn^{54} varied with time ranging from a low of 15.9% for the coated $MnSO_4$-AOP four weeks to a high of 62.9% for the incorporated MnO AOP at one week. It is difficult to account for the variation that occurred in the relative level of easily-reducible Mn^{54} especially the sharp decrease that took place between two and four weeks. This decrease may be due to the influence of the phosphate content of the fertilizers. However, if this was the case, then it seems that the reduction should have taken place sooner, as the phosphate-soil incubation studies indicated that the maximum decrease of easily-reducible Mn occurred after one week. But a direct comparison can not

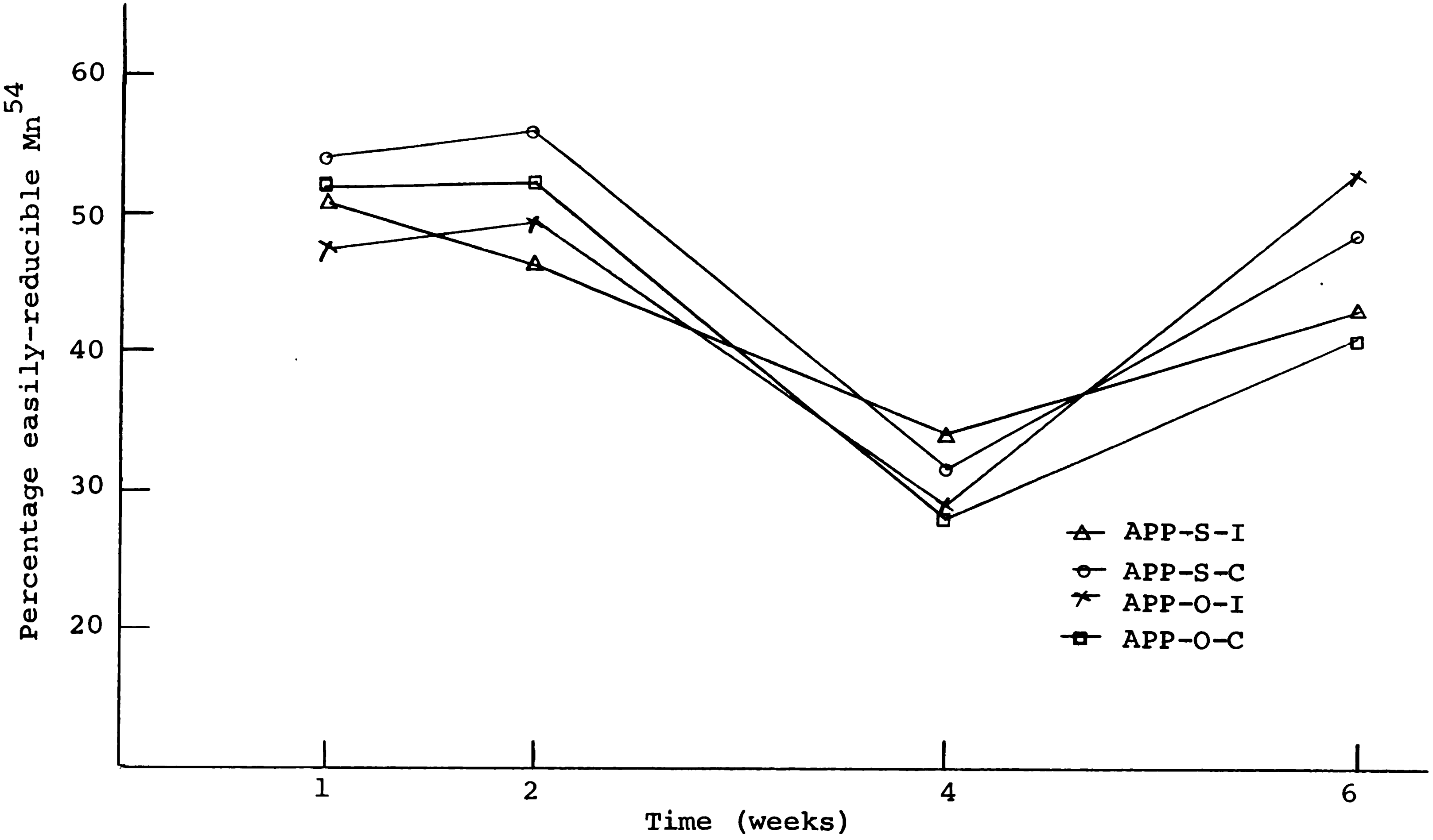

Figure 15. Percentage of Mn^{54} present in one cm. as easily-reducible Mn-APP.

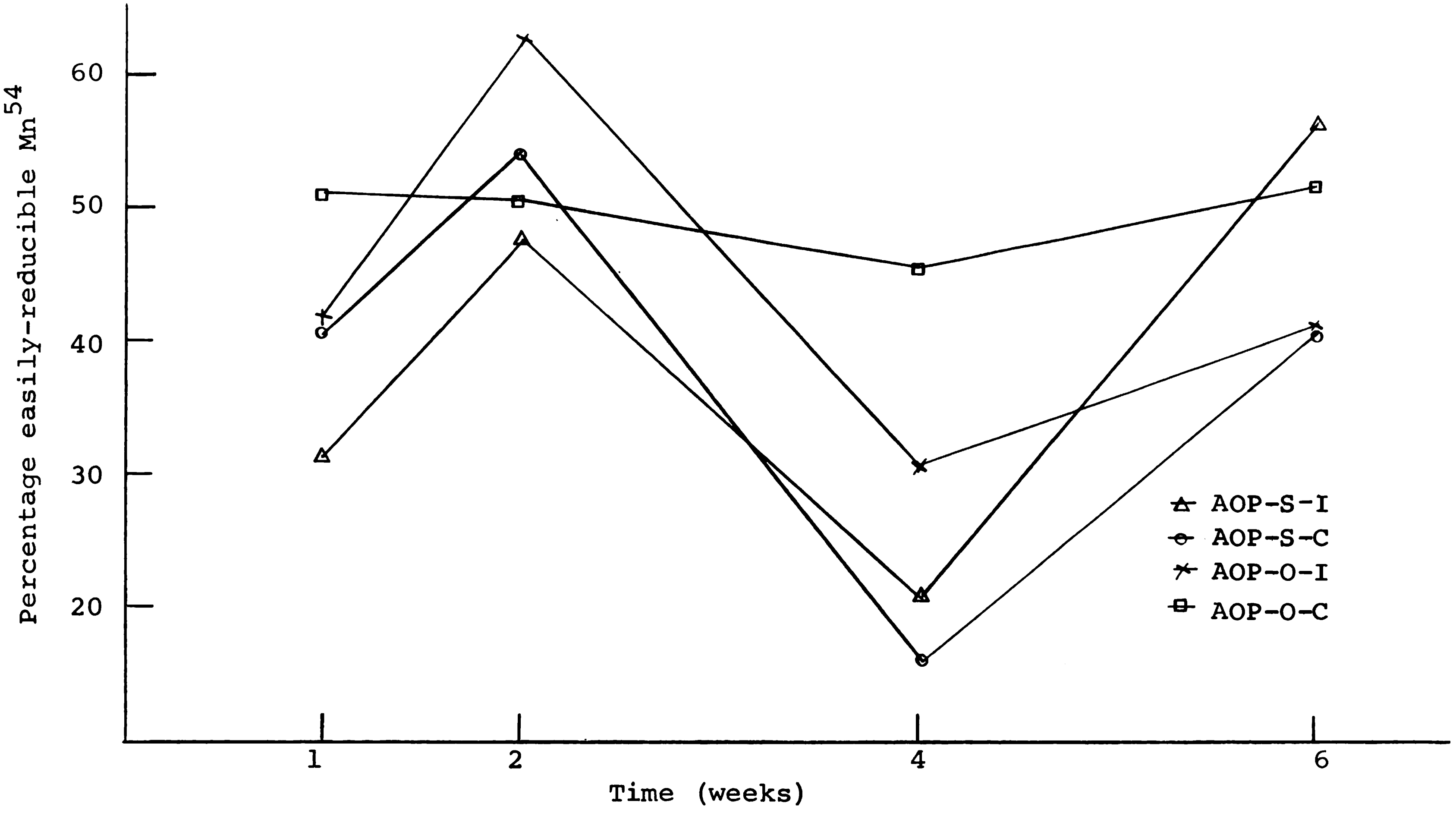

Figure 16. Percentage of Mn^{54} present in one cm. as easily-reducible Mn-AOP.

necessarily be made between the granule migration studies and the phosphate-soil incubation studies. In the migration studies the entire one cm. radial segment was not analyzed for easily-reducible Mn^{54}--only the portion between 0.5 and one cm. Hence it would be expected that any influence of the phosphate portion of the fertilizer granule would not be observed as soon in the migration studies as in the phosphate-soil incubation studies. However, the lower per cent of easily-reducible Mn that occurs when a Mn-phosphate granule is incubated in the soil rather than $Mn^{54}Cl_2$ solution indicates that the phosphate portion of the fertilizer will decrease the level of easily-reducible Mn and correspondingly increase the level of exchangeable Mn regardless of the exact time that the maximum effect will be observed.

SUMMARY AND CONCLUSIONS

Both the AOP and the APP fertilizer caused the soil exchangeable Mn to increase. APP was slightly more active in this respect than AOP. In this study the increase was limited to a one cm. distance from the granule site and was most pronounced after the fertilizers had been in contact with the soil for one week. From a consideration of the action of AOP and APP on soil exchangeable Mn it would seem that combinations of AOP and APP with Mn compounds would be effective Mn fertilizers.

The two methods of dissolution--controlled leaching and incubation in the soil gave close agreement in the relative amount of Mn released from the eight fertilizers and with the amount of fertilizer Mn found in the soil. Hence the measurement of the H_2O-soluble Mn content of these fertilizers may indeed have agronomic significance.

The amounts of Mn released from the eight fertilizers depended upon the particular combination of phosphate compound, Mn compound and method by which the Mn compound was added to the fertilizer granule. The relative order of the extent of dissolution of Mn in the soil was:

Coated-$MnSO_4$-AOP>Inc.-$MnSO_4$-AOP>Coated-MnO-APP>Inc.-MnO-APP>Inc.-MnO-AOP>Coated-$MnSO_4$-APP>Inc.-$MnSO_4$-APP>Coated-MnO-AOP. Coating the Mn compound on to the fertilizer granule caused the H_2O-soluble Mn to be released more rapidly than when the Mn was incorporated into the granule.

The exchangeable fraction of Mn in comparison to the easily-reducible fraction was largely responsible for the movement of Mn in the soil. The amount of Mn which moved from the fertilizer and throughout the soil was directly related to the extent of Mn dissolution from the fertilizer. The relative distribution of fertilizer Mn throughout the soil appeared to be independent of the dissolution of Mn from the fertilizers and was essentially identical for all eight fertilizers. One possible exception could be the Mn-APP fertilizers which yielded a slightly higher mean movement of Mn throughout the six weeks period than the corresponding Mn-AOP fertilizers.

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